

Ion enrichment in aerosols dispersed from bursting bubbles in aqueous salt solutions

By SHERMAN J. GLASS, JR¹ and MICHAEL J. MATTESON², *School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA*

(Manuscript received September 18, 1972; revised version January 15, 1973)

ABSTRACT

It is well known that a large part of the soluble salts found in soils, rivers, and lakes comes from rainwater. These salts are believed to originate as ocean spray carried into the atmosphere from the surface of the seas. Here, tiny bubbles come to the surface and fracture, sending upward aerosols which contain these salts. Studies have been shown that the ratio of the ions present within these aerosols are considerably different from those found in the oceans. The purpose of this investigation was to examine the bubble-bursting process in an effort to determine what is influencing the change in ion ratio. This was done by simulating the bubble-bursting mechanism in very simple salt solutions of concentrations similar to those found in the ocean. Variables examined were concentration, ion character, particle size, and pH. It was found that definite trends in enrichments of one ion species with respect to another in the aerosol phase are related to the ratios of ions in the bulk solution. Also affecting enrichment is the pH of the bulk solution. Enrichments varied with aerosol droplet size in a periodic fashion, with peaks around 1.0 and 6.0 μm . The results further point to the fact that the ionic double layer is a major factor in the enrichment process in that it influences the ionic equilibria in the thin film of a bubble.

Introduction

It is uncommon for one to observe a large area of the ocean's surface engaged in a foaming or bubble-bursting process. However, at any one time, about three to four percent of the world's oceans, on the average, is engaged in this process. In this whitecap area, approximately one hundred thousand bubbles break in a square meter each second and send aerosol droplets upward (Blanchard, 1963, 1972). This bubble-bursting process is of great meteorological importance for at this air-sea interface a unique exchange of matter and energy takes place.

The first investigator to suggest the ocean as a source of particles for the atmosphere was Aitken who in 1881 proposed that a significant number of air-borne particles might originate at

the surface of the sea and also be the source of nuclei for cloud formations. Following Aitken's theory, many investigators examined the oceans for such a process and Jacobs in 1937 suggested the bubble-bursting mechanism as the source. However, not until 1948 and Woodcock's experiences with a "red tide" off the coast of Florida did the bubble-bursting mechanism re-emerge as a prominent theory for the source of atmospheric nuclei. This theory was then confirmed by the work of Aliventi & Lovera (1950), Boyce (1951), and Facy (1951).

After the bubble-bursting mechanism was fairly well accepted as responsible for the atmospheric nuclei, an enormous amount of work was initiated to determine exactly what the mechanism of the bubble-burst involved. Blanchard (1963, 1967) and his associates utilized high speed photographic equipment to arrive at the actual process. They determined that a bubble rises to the surface forming a thin shell or film, which quickly ruptures sending upward film drops of the micron and submicron size range. After the film rupture, the bubble collapse

¹ Supported by Training Grant No. AP-00086-02, Office of Air Programs, Environmental Protection Agency.

² Person to whom correspondence should be addressed.

ses, producing a jet, which in turn, breaks up into jet drops. MacIntyre (1972) has discussed the mechanics of this process in considerable detail.

Continued studies by Blanchard (1963, 1967) and his associates uncovered a phenomenon of charge separation caused by the bubble-bursting process. It is suspected that this phenomenon is the source of a large fraction of the charged particles found in the atmosphere.

In addition to the charge separation aspect of the bubble-bursting mechanism, this phenomenon is also considered the origin of large amounts of sea salt found in the atmosphere. An estimate of between two and ten billion tons of sea-salt per year is believed transferred from the ocean to the atmosphere by this process (Blanchard, 1963; Eriksson, 1959). Recently, attention has been drawn to the various ionic species involved in this mass transfer. The major reason for this concern has grown out of studies showing that the ratios of the ions present in the atmosphere in the form of clouds and in rainwater are considerably different from the ratios of the same ions in seawater. Several investigators, MacIntyre (1970), Wilkness & Bressan (1971, 1972), Judson (1953) and Bloch et al. (1966, 1972) have shown that during the process by which aerosol droplets are injected into the atmosphere, an ion fractionation takes place such that certain ions are enriched relative to others while going from the bulk phase to the disperse phase.

MacIntyre (1970) has observed that, in general, ions of higher ionic potential, or charge/mass ratio are enriched relative to those of lower potential. For example, sulfate is enriched with respect to chloride and potassium with respect to sodium in going from the bulk to the disperse phase. Wilkness & Bressan (1971, 1972) confirm MacIntyre's hypothesis by showing experimentally a decrease in F^-/Cl^- in aerosols produced in the laboratory. Judson et al. (1953) show the same trend with SO_4^{2-}/Cl^- as do Bloch et al. (1966) with K^+/Na^+ , Br^-/Cl^- and Ca^{++}/Na^+ . However, Kobajashi (1961) and Sugawara (1965) report F^-/Cl^- ratios between ten and a thousand times higher in natural aerosols than those found in sea water. These latter findings suggest perhaps a more complex mechanism than that proposed by MacIntyre for ionic enrichment found in atmospheric aerosols. Woodcock et al. (1971), for example, found that particles of sea salt of different size in the marine air of Hawaii

exhibit different ratios of iodine to chlorine. Barker & Zeitlin (1972) report enrichments in aerosol samples of most metals relative to sodium, especially the alkali and alkaline earth metals. They show the greatest enrichments on the smaller, Aitkin size, aerosols, and then another peak for the giant aerosol size range. The work of Hoffman & Duce (1972), in which low enrichments of Mg^{++} and K^+ relative to Na^+ were detected in the bulk to aerosol phase transport, appears to contradict the results of others who report relative enrichments of 100 percent and greater.

The purpose of this investigation was to examine the bubble-bursting mechanism in an effort to determine what is influencing the change in ion ratio. This has been done by stimulating the bubble-bursting process in very simple salt solutions. Aerosols produced by this process were collected by impaction and filtration devices. Analysis was made by conventional atomic absorption spectroscopy techniques. Ions studied were Na^+ , Mg^{++} , Li^+ , and K^+ . Variables examined were ion concentration, solution pH and aerosol particle size.

Apparatus and procedure

All of the solutions used for analysis of the bubble-bursting mechanism were prepared using distilled, deionized water and reagent grade chemicals. In each case sodium chloride was three percent of the solution by weight. The other ion to be studied, magnesium, potassium, or lithium, was added in ratios as desired. The anion was in the chloride form. The ratios ranged from approximately 1/120 to 1/2 of ion studied to sodium ion. Standard procedures utilizing a Mettler balance and volumetric glassware were followed in preparing these solutions.

Once a solution was prepared with the ratio of ions desired, it was placed in a 250 milliliter boiling flask. A gas dispersion tube was immersed into the flask. In an attempt to keep the bubble characteristics the same for all samples, the level of fluid within the boiling flask was kept constant as well as the depth of the gas dispersion tube. Also, the gas flow rate was held steady at 1.5 liters per minute for all runs. It was found that these conditions produced bubbles between 0.2 mm and 3.0 mm in diameter. A few bubbles larger than 3.0 mm were

formed by attachment to the walls of the vessel. Although the actual distribution of bubble size was not measured, it is believed that the bubble characteristics were constant for each run due to the precautions previously discussed.

Since there appears to be a relationship between ion enrichment and aerosol size range, we devised a collection arrangement whereby different aerosol size ranges could be captured and analyzed. This was done by using an impaction device in series with a filter. Here, the entire flow of aerosol was sent through a tube fitted with a 1.0 mm orifice. At a specified distance from the orifice was a glass plate. For a constant rate of gas flow, aerosols of a specific diameter or greater have a momentum great enough to be thrown from the gas stream to the glass plate. Aerosols of a smaller mass stay in the gas stream and are carried on to a filter for collection. The impaction process is capable of discriminating between two distinct particle size ranges within certain limits. The size range fractionation can be estimated from the collection efficiencies of particles in a gas stream flowing perpendicular to a flat plate, which is a function of the Stokes Number of the particles (Fuchs, 1964).

$$\text{Stk} = \frac{2r^2 U_0 \rho}{9\mu R} \quad (1)$$

where

r = limiting radius of fraction collected

U_0 = air stream velocity in orifice

ρ = particle density

μ = viscosity of air

R = radius of curvature of air flow streamline (separation distance of orifice to plate)

For air at room temperature at a flow rate of 1.5 l/min through a 1 mm orifice, and assuming $\rho \approx 1.00$ g/cc, equation (1) becomes, after rearranging,

$$r = 7.08 R^{\frac{1}{2}} \sqrt{0.5 \text{Stk}} \text{ in } \mu\text{m when } R \text{ is in cm} \quad (2)$$

Fuchs (1964, p. 153) presents experimental results from several investigators showing that, for impingement instruments, virtually 100 percent efficiency (total capture) is achieved when $\sqrt{0.5 \text{Stk}} = 0.8$, and zero efficiency (total passage) when $\sqrt{0.5 \text{Stk}} = 0.3$. From these empirical data we then set for cutoff radii

$$r_{100\%} = 5.65 R^{\frac{1}{2}}$$

$$r_{0\%} = 2.12 R^{\frac{1}{2}}$$

This then represents, for a given impinger setting, R , the lower limit of the particle sizes, $r_{100\%}$, which are totally captured in the impinger, and the upper limit of particle sizes, $r_{0\%}$, which are totally collected on the filter.

This technique provides a rough estimate of the two size ranges fractionated in the impingement process and, by varying R , we can test several ranges of particle sizes. It is, however, not an exact separation of particle sizes, since in the size range

$$2.12 R^{\frac{1}{2}} < r < 5.65 R^{\frac{1}{2}}$$

some of the particles will be deposited in the impinger and some in the filter. We allowed some overlap in the tests to show this effect (Fig. 5). Each time the orifice was positioned within the impaction tube, it was done with the aid of a five power optical microscope to enhance the accuracy of the placement.

The aerosol escaping collection by the impinger was collected on a silver membrane filter with pore sizes of 0.22 microns. This filter was grounded to prevent buildup of static charge which could possibly influence the collection process.

It was found that when bubbling dry air at 1.5 liters per minute, it took six to eight hours to build up enough aerosol deposit in the impinger and on the filter to allow for accurate analysis of the ion components.

At the end of each run, the silver membrane filter was removed from the filter holder and placed in 50 ml of distilled water to soak for twenty-four hours. The impinger tube and impinger probe were washed with distilled water and these washings were collected and diluted to 100 ml. The bulk solution was collected and diluted a thousand to one for analysis.

A Perkin-Elmer Atomic Absorption Spectrophotometer, Model 303, was used for analysis of the samples. Attached to the spectrophotometer was a digital concentration readout device capable of giving direct readings of concentration when concentration is linear in relation to absorbance. For the ions examined, sodium, lithium, magnesium, and potassium, this relation was found to be true.

For each of the samples to be run, a set of standards of concentrations similar to those of the samples were made up and used to calibrate the concentration readout device. Once the spectrophotometer and concentration indicator

were calibrated, it was a simple matter to determine the concentration of ions within each of the samples.

In each case, one ion was compared to sodium for change in ion concentration ratios. These data were reported for both the impinger and filter as percent sodium enrichment, E . Equation 3 shows the form of E in comparison to potassium ion.

$$E = \frac{(C_{Na^+}/C_{K^+})_{\text{sample}} - (C_{Na^+}/C_{K^+})_{\text{Bulk}}}{(C_{Na^+}/C_{K^+})_{\text{Bulk}}} \times 100 \% \quad (3)$$

pH Studies

In an attempt to determine if pH had an effect on the enrichment process due to the bubble bursting mechanism, a solution of magnesium chloride and sodium chloride was prepared with a mole ratio of magnesium ion to sodium ion of 0.074, the solution having a pH of 9.3. The solution was divided into four equal parts and the pH of each was adjusted using concentrated hydrochloric acid. The resulting pH values were 9.3, 6.1, 3.4, and 1.7. This procedure was used to ensure magnesium-to-sodium ratios that were equal in all solutions. The change in chloride concentration was not felt to be significant.

Each of these solutions was bubbled with nitrogen rather than compressed air in order to avoid pH changes due to absorbed CO_2 . Analytical procedures for the pH studies were identical to others using the atomic absorption spectrophotometer.

Results

Enrichment versus concentration

Three different ions were examined as to their enrichment in comparison to the sodium ion. These were lithium, potassium, and magnesium. In each case a number of concentration ratios were examined. These ranged from as low as 1/100 to 1/2 in comparison to the sodium in the bulk. The sodium was held constant in all solutions at 3% sodium chloride by weight.

The results of these examinations are presented in Figs. 1, 2, and 3. In each case except one the greater enrichment was found in the sample collected by the filter (Fig. 1, $\text{K}^+/\text{Na}^+ = 0.18$). In that set of tests where the impinger shows

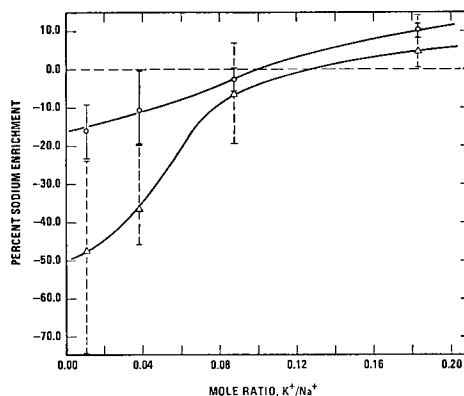


Fig. 1. Enrichment of the sodium ion in aerosols dispersed from KCl-NaCl solutions. Aerosol collected with filter: average (Δ), range (---). Aerosol collected with impinger: average ($\circ$), range (—). Negative sodium enrichments correspond to an increase in the K^+/Na^+ molar ratio in the aerosol phase. Na^+ bulk concentration constant for all molar ratios: 0.513 molar.

more enrichment on the average than the filter, the results from the filter overlap those from the impinger, pointing to a possibility of greater enrichment.

In the set of samples where lithium is compared to sodium, a fifth set of samples was run with an ion ratio, Li^+/Na^+ , of 0.01. However, in the impinger as well as the filter no lithium

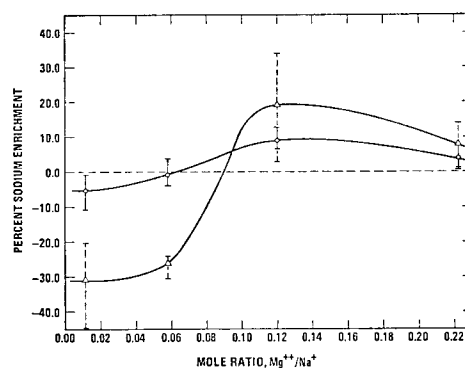


Fig. 2. Enrichment of the sodium ion in aerosols dispersed from $\text{MgCl}_2\text{-NaCl}$ solutions. Aerosol collected with filter: average (Δ), range (---). Aerosol collected with impinger: average ($\circ$), range (—). Negative sodium enrichments correspond to an increase in the $\text{Mg}^{++}/\text{Na}^+$ molar ratio in the aerosol phase. Na^+ bulk concentration constant for all molar ratios: 0.513 molar.

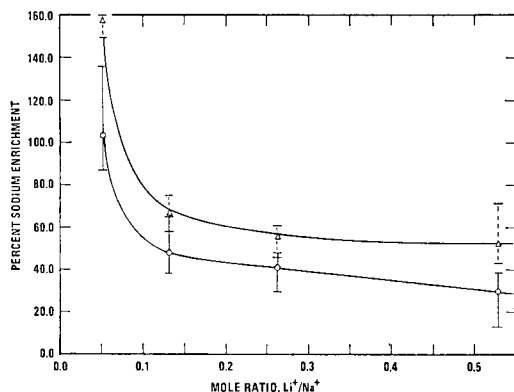


Fig. 3. Enrichment of the sodium ion in aerosols dispersed from LiCl-NaCl solutions. Aerosol collected with filter: average (Δ), range (---). Aerosol collected with impinger: average ($\circ$), range (—). Na^+ bulk concentration constant for all molar ratios: 0.513 molar.

could be found. This pointed to a total enrichment of sodium at that concentration ratio.

Both Mg^{++} and K^+ enriched compared to Na^+ at lower bulk ratios and this enrichment gradually decreased as the ratio of concentration in the bulk increased until the sodium became enriched as shown in Figs. 1 and 2. Lithium, however, allowed great sodium enrichment at low concentration ratios which decreased as the concentration ratio of lithium to sodium increased as shown in Fig. 3.

Enrichment versus pH

All aqueous solutions for bubble bursting examination were prepared with distilled, deionized water of a pH 7.0. Since compressed, dry air was used for all runs except those specifically designed to study pH, the pH dropped slightly because of the carbon dioxide present. Bulk solutions were found to have a pH of 6.4 ± 0.3 after eight hours of run time which indicates only one hydrogen dissociated from the carbonic acid molecule, thus leaving the bicarbonate ion in solution.

In testing the effect of pH, pure nitrogen was used in order to prevent pH changes due to the presence of carbon dioxide. It was found that an enrichment of sodium over magnesium increased as the pH changed from neutral in both directions as shown in Fig. 4. Since a minima occurs in the enrichment in the pH range 6.0–7.0, it was concluded that the pH

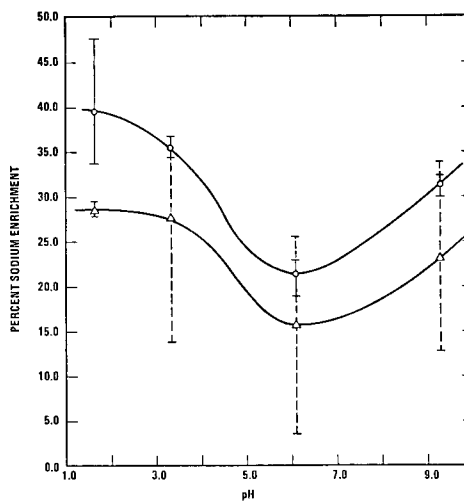


Fig. 4. Effect of pH on enrichment of the sodium ion in aerosols dispersed from a MgCl_2 -NaCl solution where $\text{Mg}^{++}/\text{Na}^+ = 0.074$, $\text{Na}^+ = 0.513$ molar. Aerosol collected with filter: average (Δ), range (---). Aerosol collected with impinger: average ($\circ$), range (—).

shift in tests with air had a negligible influence on the enrichment.

Influence of size ranges on enrichment

The influence of various particle size ranges on ion enrichment was tested collecting different size fractions of aerosols in the impinger and filter, and the enrichments are presented in Fig. 5. These runs were made with a solution of magnesium chloride and sodium chloride. Here, the magnesium-to-sodium ion ratio in the bulk phase was 0.118. The data obtained from filter

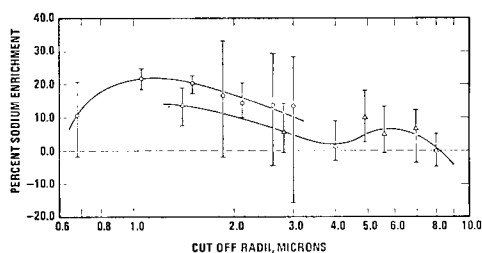


Fig. 5. Enrichment of the sodium ion in various size ranges of aerosols dispersed from a MgCl_2 -NaCl solution where $\text{Mg}^{++}/\text{Na}^+$ (molar) = 0.118, $\text{Na}^+ = 0.513$ molar. Aerosol collected with filter: average (Δ), range (---). Aerosol collected with impinger: average ($\circ$), range (—).

collections represent that particle size and smaller while the cutoff radii for the impinger collections represent that size and larger. Enrichment values from the lower sizes of particles collected by filtration appear to be greater than those from the larger particles collected by impingement. This is a consequence of the fact that the heavier, larger fraction contain those particles with almost no enrichment.

The actual enrichment for specific sizes alone would likely be much more exaggerated than the curves found experimentally for size range collections since the size range collections give integrated values and tend to dampen the extremities of enrichment for individual sizes.

Two maxima appear at about 1.0 and 6.0 μm radii, and the enrichment does not increase with decreasing particle size, but the relation seems to be some kind of harmonic.

Discussion of results

As previously discussed, MacIntyre (1970), Wilkness & Bressan (1971, 1972), and some other investigators report a trend of enrichment of salt in aerosols generated from the bursting of bubbles that follows an order of high ionic potential. For example, sulfate is enriched with respect to chloride as is potassium with respect to sodium in going from the bulk to the disperse phase. On the other hand, Kobajashi (1961) and Sugawara (1965) report opposite trends in natural aerosols for fluoride and chloride ions.

From our studies, it appears that this discrepancy can be explained. As is especially apparent with the studies conducted on magnesium and sodium, and potassium and sodium systems, the degree of enrichment observed is highly dependent on ion ratios in the bulk phase. The lithium and sodium system also reflects this trend; however, it does not change enrichments from one ion to the other as do the other two systems.

It is noteworthy that the enrichments found at bulk concentration ratios close to seawater for the magnesium and potassium system are almost exactly the same as the maritime averages presented by Junge (1963) for Western Europe. These are 36% potassium enrichment at a bulk molar ratio of 0.04 for K^+/Na^+ and 25% magnesium enrichment for a bulk molar ratio of 0.06 for $\text{Mg}^{++}/\text{Na}^+$.

A well accepted theory of water molecule

orientation is that of the electrical double layer established at the gas-liquid interface of water. As presented by Loeb (1958), at the interface a statistically significant number of the water molecules orient themselves with their oxygen atoms outward and their hydrogen atoms toward the water. The consequent polarization charge on the surface then attracts negatively charged ions which set up a negative shield over the positive field. This negative layer in turn is covered, in a looser fashion, by a diffuse layer of positive ions. Depending on the pH and ionic content of the solution these layers assume varying thicknesses and potentials.

Now as the air bubble emerges from the solution a film of liquid is compressed between the air in the bubble and the air above the solution. We are therefore presented with a special situation of two double layers, back-to-back. Since this film is extremely thin, it is likely that the ions in this region are not characteristic of the bulk solution but, rather, are those ions held by the opposing ionic double layers. This situation also occurs at the interface between two adjacent bubbles and is analogous to two colloid particles in close proximity. Langmuir (1938) has studied the latter case in detail and showed that the excess number of ions, n_{ex} , between two opposing double layers is related to the bulk value, n_0 , by the expression

$$\frac{n_{\text{ex}}}{n_0} = \exp(\psi M/kT) - \exp(-\psi M/kT) - 2 \quad (4)$$

where

ψM = midpoint potential
 k = Boltzmann constant
 T = temperature

We should now consider what may cause one anion to be enriched relative to another in this film. Concentration, or availability of ions, appears as though it would play a major role in this selection process but, perhaps, equally important are ionic mobilities or dimensions. Ionic mobility is the capability of an ion to travel in a solvent as well as its ability to attach itself to solvent molecules. Ionic mobilities in water as reported by Davies (1930) for the ions examined are (18°C) sodium, 43.4 $\text{cm}^2/\text{volt sec}$; magnesium, 45.5 $\text{cm}^2/\text{volt sec}$; lithium, 33.3 $\text{cm}^2/\text{volt sec}$; and potassium, 64.4 $\text{cm}^2/\text{volt sec}$. It seems reasonable that an ion such as potassi-

um with high ionic mobility and smaller dimension, when hydrated, might more easily be drawn to an ionic double layer than a slower and larger, hydrated ion such as sodium. It would then be this ability to "fit" in the ionic double layer that is responsible for enrichments seen at low concentration ratios of K^+/Na^+ .

In general as the second anion, X^+ is added to the fixed bulk concentration of Na^+ , the larger of the two ions enters the double layers in increasing amounts. This increases the sodium enrichment in the case of K^+ and Mg^{++} and reduces it in the case of Li^+ . It is possible that the smaller ion occupies a fixed number of sites in the double layer and that its concentration in the film is established at very low ratios of X^+/Na^+ in the bulk. Further increase of bulk concentrations of X^+ could then not add to the concentration of X^+ in the disperse phase for hydrated ionic dimensions $X^+ < Na^+$, but would increase in the disperse phase for $X^+ > Na^+$, since in the latter case it would be the Na^+ ions which have occupied a fixed number of sites. It appears that the ratio of K^+ to Na^+ in an ionic double layer might be relatively constant at bulk ratios around 0.11 and higher as seen in Fig. 1, since at this ratio the enrichment seems to have reached a maximum.

The same trend appears true of Mg^{++}/Na^+ although zero enrichment occurs at a lower Mg^{++}/Na^+ bulk ratio of 0.08 as seen in Fig. 2. As the mobilities of the two ions become more nearly equal the enrichments do not seem so great as is reflected in Figs. 1 and 2 at low ion ratios. Since lithium is very slow compared to sodium, the opposite trend is expected and is found as illustrated in Fig. 3. Here, it is felt that Li^+ is so slow as well as so highly hydrated that it has a difficult time getting into the ionic double layer and thus shows no enrichment.

Another factor which influences the ionic ratio in the disperse phase is pH. Because of their relatively small size, a change in either the number of OH^- ions or H^+ ions in the bulk would change that concentration in the double layer and it would also change the ionic characteristics of the double layer. From Fig. 4 it appears that by increasing the number of H^+ ions, and because of their greater mobility, we decrease the number of Mg^{++} ions needed to satisfy the electronic balance in the double layers. A corresponding increase in the number

of OH^- ions does not produce the opposite effect since here we are forming $Mg(OH)_2$ which is relatively insoluble.

The oscillating trend of enrichment as a function of aerosol size range (Fig. 5) was also observed by MacIntyre (1970) for a phosphate-sodium system, and by Seto & Duce (1972) working with iodine and NaCl. This would indicate that enrichment is strongly dependent on bubble film thickness. There may be a cyclic repetition of optimum ionic "fits" or compatibilities of the double layers within various film thicknesses which yield varying enrichments depending on some type of stacking arrangement with alternating layers of smaller and larger anions.

Regarding the significance of these results in nature, the authors would like to make special reference to the work of Cheng (1970, 1971), who was able to photograph the supercooling of water droplets and the melting of ice pellets. Both processes yielded swarms of aerosols in the submicron range. In the supercooling of droplets, freezing began at about $-17^\circ C$, and smaller droplets were continuously ejected during the 50 second freezing period. Evidently freezing started around the outer shell and moved inward. As ice occupies more volume than the water replaced, tremendous pressures must occur in the liquid core of the droplet, eventually blowing a spray of droplets out a fracture in the ice shell. Concerning the melting of ice pellets, numerous air bubbles are released and accelerated radially to the surface of the melting pellet. Microdroplets are then generated by the bursting of these bubbles at the air-water interface. Cheng's work has been challenged by Rosinski et al. (1972), who repeated several variations of Cheng's experiment and were unable to find any production of microdroplets. However, the physical process as described above seems plausible and would account for Cheng's observations.

We mention this subject because of the accompanying ion enrichment possibilities. The implication here is that ion enrichment occurs not only at the ocean surfaces, but continually throughout the atmosphere in the repeated freezing and melting of droplets which originated at sea. The aerosols ejected from the ocean surface may be enriched in one ion with respect to another. When these aerosols grow by condensation, freeze and eject new microdroplets,

this new generation would be even more enriched. After several generations of repeated ion fractionation we may reach an aerosol very highly concentrated in one particular ion. This may be a possible source of the sodium constituent of the airglow phenomenon.

Conclusions

1. The enrichment of ions in aerosols generated from the bubble bursting process is strongly dependent on relative ion concentrations in the bulk solution. At low ion ratios in the bulk solution ($X^+/Na^+ < 0.06$ molar ratio) significant increases in the X^+/Na^+ ratio can be expected in the disperse phase when the ionic mobility of X^+ is less than that of Na^+ . Depending on the ratio of the ionic mobilities, a correspondingly large decrease in the X^+/Na^+ ratio in the disperse phase is found where the ionic mobility of X^+ is greater than that of Na^+ .

2. Enrichments of Mg^{++} and K^+ with respect to Na^+ from bulk concentrations corresponding

to seawater have been demonstrated in simple bubble bursting tests to agree with those enrichments found in rainwater reported in maritime locations in Western Europe.

3. Aerosols formed by the bubble bursting mechanism from salt solutions are more highly enriched in the smaller particle size range, however enrichment is not a simple function of size but appears to take periodic increases with decreasing size range.

4. The pH of the bulk solution changes the enrichment little when in the 6.0–7.0 range, however increasing enrichments of Na^+ with respect to Mg^{++} were found at $pH < 6.0$.

Acknowledgement

The authors are indebted to Dr Kevin C. Beck, School of Geophysical Sciences, at this Institute for his guidance in absorption spectroscopy.

REFERENCES

- Aitken, J. 1881. On dusts, fogs, and clouds. *Trans. Roy. Soc. Eidenburgh* 30, 337–368.
- Aliventi, G. & Lovera, G. 1950. Sui nuclei di condensazione di origine marittima. *Geofisica Pura e Applicata* 16, 133–135.
- Barker, D. R. & Zeitlin, H. 1972. Metal-ion concentrations in sea-surface microlayer and size-separated atmospheric aerosol samples in Hawaii. *J. Geophys. Res.* 77, 5076–5086.
- Blanchard, D. C. 1967. *From raindrops to volcanoes*, pp. 46–127. Doubleday and Company, Garden City, N. J.
- Blanchard, D. C. 1963. *Progress in Oceanography* (ed. M. Sears), pp. 71–202. Pergamon Press, New York.
- Blanchard, D. C. 1972. The borderland of bursting bubbles. *Sat. Rev.* 54, 60–63.
- Bloch, M. R., Kaplan, D., Kertes, V. & Schnerb, J. 1966. Ion separation in bursting bubbles. *Nature* 209, 396–397.
- Bloch, M. R. & Luecke, W. 1972. Geochemistry of Ocean water bubble spray. *J. Geophys. Res.* 77, 5100–5105.
- Boyce, S. G. 1951. Source of atmospheric salts. *Science* 113, 620–621.
- Cheng, R. J. 1970. Water drop freezing: Ejection of microdroplets. *Science* 170, 1395–1396.
- Cheng, R. J. 1971. Annual Report, Atmospheric Sciences Research Center, SUNY, Albany, 158, 21.
- Davies, C. W. 1930. *The conductivity of solutions*. Chapman-Hall, London.
- Eriksson, E. 1959. The yearly circulation of chloride and sulfur in nature: meteorological, geochemical, and pedological implications. Part I. *Tellus* 11, 375–403.
- Facy, L. 1951. Embruns et noyaux de condensation. *J. Scientifique Meteorologie* 3, 62–68.
- Fuchs, N. A. 1964. *The mechanics of aerosols*, pp. 151–159. Pergamon Press, Oxford.
- Hoffman, G. L. & Duce, R. A. 1972. Consideration of the chemical fractionation of alkali and alkaline earth metals in the Hawaiian marine atmosphere. *J. Geophys. Res.* 77, 5161–5170.
- Jacobs, W. C. 1937. Preliminary report on the study of atmospheric chlorides. *Mon. Weather Rev.* 65, 147–151.
- Judson, C. M., Lerew, A. A., Dixon, J. K. & Salley, D. J. 1953. Radiotracer study of sulfate ion adsorption at the air/solution interface in solutions of surface active agents. *J. Phys. Chem.* 57, 916–923.
- Junge, C. E. 1963. *Air chemistry and radioactivity*, pp. 289–365. Academic Press, New York.
- Kobajashi, S. 1961. Geochemistry of fluorine in natural waters, p. 68. Sugiyama Women's College, Nagoya.
- Langmuir, I. 1938. The role of attractive and repulsive forces in the formation of tactoids, thixotropic gels, protein crystals, and coacervates. *J. Chem. Phys.* 6, 873–885.
- Loeb, L. B. 1958. *Static electrification*, pp. 61–80. Springer, Berlin.
- MacIntyre, F. 1970. Geochemical fractionation during mass transfer from bursting bubbles. *Tellus* 22, 451–461.
- MacIntyre, F. 1972. Flow patterns in breaking bubbles. *J. Geophys. Res.* 77, 5211–5228.
- Rosinski, J., Langer, G. & Nagamoto, C. T. 1972. On the ejection of microdroplets from the surface

- of a freezing water drop. *J. Appl. Meteor.* 11, 405-406.
- Seto, F. Y. & Duce, R. A. 1972. A laboratory study of iodine enrichment on atmospheric sea-salt particles produced by bubbles. *J. Geophys. Res.* 77, 5339-5349.
- Sugawara, K. 1965. Exchange of chemical substances between air and sea. *Oceanogr. Mar. Biol. Ann. Rev.* 3, 59.
- Wilkniss, P. E. & Bressan, D. J. 1971. Chemical processes at the air-sea interface: the behavior of fluorine. *J. Geophys. Res.* 76, 736-741.
- Wilkniss, P. E. & Bressan, D. J. 1972. Fractionation of the elements F, Cl, Na, and K at the sea-air interface. *J. Geophys. Res.* 77, 5307-5315.
- Woodcock, A. H. 1948. Note concerning human respiratory irritation association with high concentrations of plankton and mass mortality of marine organisms. *J. Marine Res.* 7, 56-62.
- Woodcock, A. H., Duce, R. A. & Moyers, J. L. 1971. Salt particles and raindrops in Hawaii. *J. Atm. Sci.* 28, 1252-1257.

ОБОГАЩЕНИЕ ИОНАМИ АЭРОЗОЛЕЙ, ПОЛУЧАЕМЫХ ПРИ ВЗРЫВЕ ПУЗЫРЬКОВ В СОЛЕВЫХ РАСТВОРАХ

Хорошо известно, что большая часть растворимых солей, находимых в почве, реках и озерах происходит из дождевой воды. Предполагают, что эти соли происходят из пены океанов, переносимой в атмосферу с поверхности морей. Маленькие пузырьки подходят к поверхности и разрушаются, посылая вверх частички аэрозоля, содержащие эти соли. Исследования показали, что отношения ионов в этих аэрозолях значительно отличаются от тех, которые находят в океане. Целью данного исследования было изучение процесса взрыва пузырьков с тем, чтобы определить, что влияет на изменение отношения ионов. Это было сделано воспроизведением взрыва пузырьков в очень простых

солевых растворах с концентрациями, подобными океаническим. Переменные, которые изучались, были концентрация, характер ионов, размер частиц и pH. Было найдено, что определенные тенденции к обогащению одними видами ионов по отношению к другим в аэрозольной фазе связаны с их соотношениями в массе раствора. Величина pH раствора также способствует обогащению. Обогащение меняется с размером капель аэрозоля периодическим образом с пиками вблизи 1,0 и 6,0 *мкм*. Результаты далее указывают на факт, что двойной слой ионов является главным фактором в процессе обогащения, потому что он влияет на ионное равновесие в тонкой плёнке пузырька.