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CHEMICAL FRACTIONATION AT THE AIR/SEA INTERFACE

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INTRODUCTION

The ocean is one of the major natural sources of atmospheric particulate matter, or aerosols. However, there is considerable evidence that the chemical composition of atmospheric particles over the ocean is often significantly different from that of bulk seawater. It has often been suggested that the relative difference in chemical composition of the atmospheric particles and seawater may be due to chemical and physical processes occurring during the production of these particles at the air sea interface. The occurrence, or nonoccurrence, of this selective chemical fractionation or enrichment has been the subject of considerable research and controversy in the field of atmospheric chemistry during the past several decades. Unfortunately, inadequate analytical techniques and poorly designed field and laboratory studies have in many cases led to the postulation of novel but unlikely theories to explain inaccurate data. The primary intent of this review is to evaluate the data for common trace substances present in marine aerosols in an attempt to ascertain whether their source may be the ocean or some other natural or anthropogenic process.

Atmospheric Sea Salt Particles and the Marine Aerosol

It has been estimated that the ocean produces between 10^{15} and 10^{16} g yr of atmospheric sea salt particles with radii less than approximately 20 μm (Eriksson 1959, 1960, Blanchard 1963). Estimates of the total annual production of atmospheric particles from all natural sources, incorporating the lower value of 10^{15} g yr from the sea, suggest that the ocean may contribute 30–75% of the total production (Hidy & Brock 1970, Robinson & Robbins 1971, Peterson & Junge 1971). Eriksson (1959, 1960) estimated that approximately 90% of the atmospheric sea salt particles are removed over the ocean, with 10% being deposited on land as the cyclic salts subsequently carried by streams and groundwater. This would result in from 10^{14} to 10^{15} g yr of continental cyclic salts, according to these two production estimates. Livingstone (1963) calculated that the annual global input of cyclic salt Na from river runoff into the ocean is approximately 10^{14} g yr, which is equivalent to a total salt content of approximately 3×10^{14} g yr. Atmospheric sea

salt apparently plays a significant role in atmospheric and terrestrial geochemical cycles. Significant enrichment of trace substances on these particles, compared to the source seawater, may be an important factor in the overall geochemical cycles of these substances.

Most of the sea salt particles with atmospheric residence times longer than a few minutes are believed to be produced by bubbles breaking at the sea surface. Blanchard & Woodcock (1957) investigated various mechanisms for bubble production in the ocean, for example, breaking waves or raindrops and snowflakes striking the water surface. They suggested that, except under local conditions, breaking waves, or whitecaps, are by far the most important source of bubbles. Boyce (1951) showed that relatively few salt particles were produced by the mechanical disintegration of the water in a breaking wave, but that a considerably greater number of particles were produced a few seconds later when the air bubbles resulting from wave action burst at the sea surface. Using high speed photography, Kientzler et al (1954) showed that a bubble at a seawater surface forms a jet, which ejects two to five droplets into the air. Blanchard (1963) found that the diameter of these jet droplets was approximately 10% of the diameter of the bubbles from which they were formed. Mason (1957) and Blanchard (1963) also found that a significant but variable number of smaller droplets, called film droplets, were also produced by the shattering bubble film cap.

Relatively little is known of bubble size and number distribution on the open sea. Blanchard & Woodcock (1957) measured the distribution of bubbles between about 75 μm and 750 μm diameter in waves breaking on a beach. They pointed out that

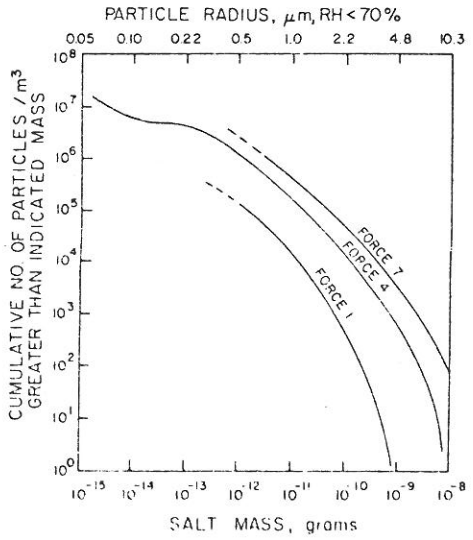

Figure 1 Atmospheric sea salt particle distribution several hundred meters above the ocean surface near Hawaii at various wind forces. After Woodcock (1953, 1972).

their methods were biased against the millimeter-sized bubbles, which they indicated were present, but in low abundance. Medwin (1970) investigated the bubble distribution in the ocean under relatively light wind conditions, but there has unfortunately been no work on the complete bubble distribution at various wind speeds in open ocean areas. Blanchard (1963) estimated that on a global basis, 3 4% of the ocean surface is covered by whitecaps at any time, resulting in an overall oceanic production rate of approximately 0.1 jet droplets cm^{-2} sec^{-1} and 0.07 film droplets cm^{-2} sec^{-1}. These figures are based on individual bubbles bursting at the sea surface, using the bubble distribution of Blanchard & Woodcock (1957). Little information is available on the production of atmospheric particles by the bursting of bubble clusters or foams, although this may be an important source for these particles.

Woodcock (1953) made numerous measurements of the size and number distribution of atmospheric sea salt particles with salt masses between 10^{-8} g and 10^{-12} g. Figure 1 illustrates a typical particle distribution several hundred meters above the ocean surface near Hawaii for force 1, 4, and 7 winds. Woodcock (1972) extended his earlier work down to particles with a salt mass of 10^{-15} g, and these results are also shown in Figure 1 for force 4 winds. Woodcock found that the number of particles and their mass median diameter increased with increasing wind speed and with decreasing altitude above the sea. He attributes the discontinuity in the distribution shown in Figure 1 for force 4 winds to a zone of transition from a bubble jet to a bubble film source for the droplets in this size range.

Junge (1972) summarized our understanding of the distribution of atmospheric particles in marine air and pointed out that, in addition to sea salt particles, a number of other components can be distinguished in the undisturbed marine aerosol. These include large, apparently organic particles with radii greater than 20 μm; mineral dust particles; particles with radii less than 0.03 μm, possibly the result of trace gas reactions or the reactions of small ion clusters (Vohra et al 1970, Mohnen 1970); and the so-called tropospheric background aerosol. The latter is a rather homogeneous aerosol uniformly distributed within the troposphere over the ocean (and continents) at about 200–400 particles per cm^3 of air, with a maximum in the range of $\sim$0.1 μm radius. Sulfate is a likely major component of the background aerosol. Perhaps the most important point made by Junge (1972) is that the marine aerosol is composed of many substances that have sources other than the sea. This has often been ignored in field and laboratory studies of chemical fractionation of atmospheric sea salt particles. Distinguishing between chemical substances present on sea salt particles injected into the marine atmosphere during the bubble-breaking process and those present on other components of the marine aerosol is very difficult, but is necessary in order to properly assess the presence and importance of chemical fractionation processes. We shall return to this question a number of times during our discussion.

Standardized Chemical Fractionation Notation

The Working Symposium on Sea-to-Air Chemistry, held at Fort Lauderdale, Florida, January 30–February 4, 1972, recommended a standardized nomenclature to

quantitatively describe apparent chemical fractionation at the air/sea interface (Duce et al 1972a). This nomenclature, used throughout this paper, is as follows:

$$\text{Fractionation: } F_{Na}(X) = \frac{(X/Na)_{atm}}{(X/Na)_{sea}} \quad (1)$$

$$\text{Enrichment: } E_{Na}(X) = \frac{(X/Na)_{atm}}{(X/Na)_{sea}} - 1, \quad (2)$$

where $(X/Na)_{atm}$ is the mass ratio of substance X to sodium in any atmospheric sample, e.g. rain, particles, etc, and $(X/Na)_{sea}$ is the ratio of substance X to sodium in bulk (subsurface) seawater.

Occasionally Na is not measured in field and laboratory studies and such elements as Cl or Mg are used as seawater reference elements. They then replace Na in the notation above. Sodium is preferred as a reference element over chlorine, primarily because a vapor phase of Cl is present in marine air and because the exchange of Cl between the vapor and particle phases may confuse the interpretation of enrichments based on Cl. It might be noted that fractionation, F, is the same as the term enrichment factor, EF, used a number of papers in the literature. A value for $E_{Na}(X)$ equal to 0 indicates no enrichment, positive or negative; whereas values of $F_{Na}(X)$ equal to one indicate no enrichment for substance X.

The calculation of a positive enrichment for any substance according to Equation 2 does not indicate that this increased concentration is caused by some process occurring during sea salt particle production at the air/sea interface. Enrichment as defined above gives no information as to the source of the substance of interest. This relationship simply points out whether or not the substance is present in a relative abundance similar to that in bulk seawater. Several investigators have attempted to distinguish between the apparent enrichment of some substance due to the addition of that substance to the sample from a non-sea salt source and a true enrichment due to either physical or chemical processes occurring during particle production at the sea surface. One approach (Lazrus et al 1970, G. L. Hoffman & Duce 1972) is to calculate simple linear regression equations to describe the relationship between Na and the substance of interest. For any substance X, the slope of the regression line should represent the X/Na ratio associated with the sea salt component of X, while the intercept of the regression line represents the quantity of the non-sea salt component. For example, consider Figure 2, which is a plot of 110 samples collected in Hawaii and analyzed for Ca and Na by G. L. Hoffman & Duce (1972). The mean total Ca/Na ratio for these samples was 0.045 ± 0.011. With a seawater Ca/Na ratio of 0.0381, this results in an apparent enrichment – i.e. a value for $E_{Na}(Ca)$ – of 0.20 ± 0.20. However, from the slope of the regression equation and the standard deviation of this slope (0.037 ± 0.001), the calculated value for $E_{Na}(Ca)$ becomes -0.03 ± 0.03. The intercept, 0.021, suggests that 0.021 $\mu g\ m^{-3}$ of Ca has some source other than that associated with the Na. It must be pointed out that this approach assumes that the nonmarine intercept is constant in time and space, which is quite unlikely. In addition, it assumes that the sea salt Na overwhelms any Na contribution from other sources. Therefore, this approach must be used with caution, but it is at least a first step in differentiating between a sea salt and non-sea salt source for various substances.

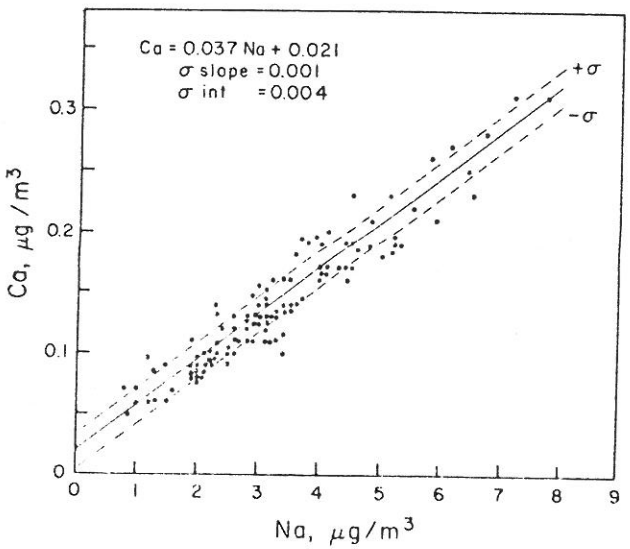

Figure 2 Atmospheric Na vs Ca concentrations observed from a 20 m high tower on the coast of windward Oahu, Hawaii. After G. Hoffman & Duce (1972).

Sampling location is a critical factor in any field studies of chemical fractionation at the air/sea interface. Atmospheric samples collected near the continental margins obviously have a high probability of containing significant quantities of particulate matter of nonmarine origin. Midocean sampling sites are less disturbed. Atmospheric sampling from ships is easily subject to contamination from the ship itself unless great care is taken. Aircraft can often provide suitable sampling platforms, as can midocean islands. Even here, however, care must be taken to avoid collection of local surf-produced particles, which can be chemically quite different from the bubble-produced particles formed on the open sea (Duce & Woodcock 1971). Finally, samples collected even a few km inland from the coast, on either islands or continents, will almost certainly be contaminated with significant quantities of land-produced aerosols – natural, anthropogenic, or both. These precautions appear obvious to most people working in the field today, but it is surprising and discouraging to realize how many past investigations (some very recent) have produced data that were rather useless in evaluating the significance of chemical fractionation because one or more of these factors was ignored.

BUBBLES AND THE SEA SURFACE MICROLAYER

When bubbles break at the surface of the ocean they skim off a very thin layer of the air–sea interface to produce the atmospheric film and jet droplets. MacIntyre (1968,

1972) investigated this microtome effect for jet droplets using a combination of experimental and theoretical approaches. Figure 3*a* presents a simulated time sequence of what occurs after the collapse of a dyed bubble (MacIntyre 1972). This sequence illustrates the flow of surface material down the interior of the bubble cavity, transported by an irrotational single capillary ripple, and concentration of this material into the top of the jet before the first jet droplet breaks off. Subsequent jet droplets are composed of material that was present in consecutively deeper concentric shells in the bubble cavity, as shown in Figure 3*b* (MacIntyre 1972). MacIntyre calculated that the material present in the top jet droplet was originally spread over the interior of the bubble surface at a thickness equal to approximately 0.05% of the bubble diameter, and he assumes this relationship is valid for all bubble sizes. Thus the top jet droplet from a 100 μm diameter bubble is composed of material from a surface layer only 0.05 μm thick. The second jet droplet is produced from the next 0.05 μm layer, etc. With a bubble size distribution in the sea ranging from $\sim$50 μm to perhaps 1500 μm diameter, the top jet droplets produced from these bubbles strip off approximately the top 0.025-0.75 μm of the air/water interface. Iribarne & Mason (1967) reached a similar conclusion in their studies of charge transfer during bubble bursting. The chemical composition of this extremely thin stripped surface layer is determined both by the composition of the ocean surface layer before the bubble arrives at the surface (the surface microlayer) and the composition of the bubble skin itself.

It is interesting to note that when the bubble cap or film shatters to produce film droplets, it is probably no thinner than 2 μm, since these bubble caps show no visible interference patterns which become apparent for thinner films (MacIntyre 1972). As MacIntyre (1974a) points out, this suggests that the jet droplets, which are generally larger than the film droplets, may be sampling, or may be composed of, a much thinner layer of the water surface than the smaller film droplets. The smaller jet droplets are apparently composed of material from a thinner layer of the surface

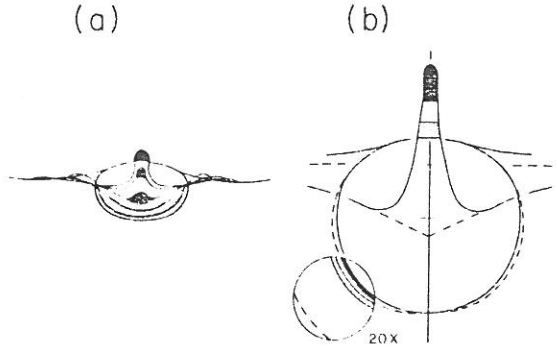

Figure 3a Simulated time sequence of jet droplet formation after the collapse of a dyed bubble. From MacIntyre (1972), with permission of the author. *b* Source of material present in the first three jet droplets produced from a bursting bubble. From MacIntyre (1972), with permission of the author.

than the larger jet droplets. Unfortunately, although we now have a rather good qualitative picture of these processes occurring in the upper few hundred micrometers of the ocean surface, the detailed hydrodynamics remain largely unknown. MacIntyre (1974a) presents an excellent review of our present understanding of these processes.

Since the breaking bubbles produce atmospheric sea salt particles from such a thin layer of the ocean surface, our attention should turn briefly to the chemical composition of the thinnest surface layer of the oceans, the surface microlayer. The surface microlayer thickness is operationally defined by the type of microlayer collector used. The term microlayer itself implies no particular thickness, chemical composition, or concentration, but simply refers physically to the thin surface layer being sampled. A variety of systems have been used to sample the marine surface microlayer. These systems include, among others, the use of plastic or metal screens (Garrett 1965), to collect the top 100-300 μm of the water surface; glass plates (Harvey & Burzell 1972) for the top 30-60 μm; rotating drum collectors mounted on rafts (Harvey 1966) for the top 50-60 μm; germanium prisms (Baier 1972) to sample organic layers as thin as monomolecular for subsequent analysis by internal reflection infrared spectroscopy; and the bursting bubble itself (Fasching et al 1974) to generate atmospheric sea salt particles from bursting bubbles produced in a closed system at sea. Hatcher & Parker (1974) have compared the collection characteristics of several of these collectors.

Because the various collectors sample different thicknesses of the ocean surface, the principles by which they collect surface material often differ, and the sea state conditions under which they can be used vary widely, comparison of studies using different types of collectors has been difficult. However, the chemical composition of the surface microlayer is evidently significantly different from that of water 10–20 cm or more below the surface. Among the substances significantly concentrated in the surface microlayer are a wide variety of organic substances, including fatty acids and alcohols (Garrett 1967, Duce et al 1972b, Wade & Quinn 1975, Miget et al 1974, Marty & Saliot 1974); hydrocarbons (Garrett 1967, Baier 1972, Baier et al 1974, Ledet & Laseter 1974, Morris 1974); glycoproteins and proteoglycans (Baier et al 1974); chlorinated hydrocarbons such as PCB (Seba & Corcoran 1969, Duce et al 1972b, Bidleman & Olney 1974); particulate and dissolved organic carbon, nitrogen, and phosphate (Williams 1967, Nishizawa & Nakajima 1971); and trace metals (Duce et al 1972b, Piotrowicz et al 1972, Szekielda et al 1972, Barker & Zeitlin 1972, G. Hoffman et al 1974). Numerous marine organisms have also been found concentrated in the surface microlayer (Sieburth 1971, Harvey 1966, Parker & Barsom 1970, Tsiban 1971, Marumo et al 1971, Bezdek & Carlucci 1972). Thus the potential certainly exists for atmospheric sea salt particles produced from this thin layer of the ocean to have a chemical composition significantly different from that of subsurface water.

The air/sea interface and air sea exchange processes in general can also be significantly modified by human activities, particularly in nearshore areas. Oil spills and man-made sea slicks can affect certain physical characteristics of the air sea interface. These slicks cause damping of capillary waves and retardation of evaporation, as well as changes in gas exchange rates and the number and size

distribution of the atmospheric sea salt particles produced from these waters (Blanchard 1963, Garrett 1972). High concentrations of such potentially harmful substances as pesticides, petroleum hydrocarbons, and heavy metals have been observed in the microlayer. Bacteria can be transported to the water surface by rising bubbles and then ejected into the atmosphere (Blanchard & Syzdek 1972). The potential health hazard from this type of exchange was pointed out by Adams & Spendlove (1970), who measured coliform bacteria on aerosols downwind from a sewage treatment plant. Other pollutants concentrated in the surface layers of the water may be similarly injected very efficiently into the atmosphere.

The surface of the ocean is generally quite turbulent, and it is difficult to imagine the surface microlayer as anything but dynamic. MacIntyre (1974a) points out that swells and ripples on the ocean surface do not destroy the enriched surface layer but only change its thickness. However, as winds increase and waves break there will be a constant mixing of surface material into subsurface water and transport of surface material back upward. G. Hoffman et al (1974) have calculated that the average lifetime of particulate iron in the top 100–300 μm of the ocean surface under 5–8 m/sec winds is only a few seconds before it is mixed back into subsurface waters. Even with this short surface residence time, however, particulate iron was always significantly enriched in the top 100–300 μm compared to water 20 cm below the surface.

What causes substances to be enriched at the air/sea interface? Some solid substances are present simply because of density differences and some lipoids, such as hydrocarbons, are present because they are practically insoluble in seawater, but most of the material enriched at the surface is either surface active or associated in some way with surface-active material. Surface-active substances are characterized by a molecular structure containing both hydrophobic and hydrophilic portions, hence their affinity for an air water interface. The chemical composition of these surfactants concentrated at the ocean surface has been the subject of some controversy. Garrett (1967), investigating chloroform soluble surfactants in the surface microlayer, suggested the surfactants are largely lipid material, such as fatty esters, free fatty acids, and fatty alcohols. Baier et al (1974), on the other hand, report that the major organic components of the marine surface microlayer are glycoproteins and proteoglycans. According to the latter investigators, their technique of internal-reflection infrared spectroscopy is capable of nondestructively determining petroleum, lipids, proteins, and polysaccharides, and they conclude that lipids constitute only a small fraction of the organic matter in the microlayer.

Although many of the enriched substances in the surface microlayer are not surface-active themselves, they may be associated with surfactants and thus be transported to the surface with the surface-active agent. Examples include mineral particles and marine organisms such as bacteria or plankton covered with a surface-active coating, and trace metals complexed with functional groups in proteinaceous surfactants. Most likely, under breaking wave conditions, the primary mechanisms of transport of surfactants and their associated substances to the ocean surface is by bubbles. Considerable evidence indicates that bubbles are quite effective in transporting this material in seawater (reviewed in subsequent sections). Thus the chemical composition of the ocean surface microlayer, the surface of bubbles rising through the water, and the jet and film droplets are closely interrelated and interdependent, although the overall geochemical importance of these interrelationships is not well understood in many cases.

A number of other mechanisms that would cause higher concentrations of various ionic species at the air/sea interface compared to subsurface water have been suggested. MacIntyre (1974a) has reviewed these mechanisms in detail: (*a*) Gibbs surface adsorption, where inorganic ions that lower the surface free energy are concentrated and those that raise the surface free energy are depleted at the surface (Bloch & Luecke 1968); (*b*) the Ludwig-Soret effect, where ions migrate to different regions of a thermal gradient field (Komabayasi 1962); (*c*) alteration of the surface water structure, where ions that disrupt this structure because of their size and/or charge are rejected from the air/water interface whereas those that alter the structure least are preferred (Horne & Courant 1970); and (*d*) electrical double-layer effects, where size and charge of ions may be related to the degree of attraction to or repulsion from the surface double layer (Glass & Matteson 1973). Although these processes can probably cause increased concentration of certain ions at an air water interface, MacIntyre (1974a) points out that these processes probably only affect ionic concentrations to a depth of a few molecular layers. Their geochemical importance in causing the large enrichments often measured experimentally in the surface microlayer and atmospheric sea salt particles, which represent layers hundreds to thousands of times thicker, may therefore be marginal.

EXPERIMENTAL DATA

Marine Organisms and Organic Carbon

If significant chemical fractionation of trace substances occurs during the production of atmospheric sea salt particles at the air/sea interface, it very likely results from the association of these substances with organic matter, living or dead, in the ocean. Our attention should focus first on what is known about the ocean atmosphere exchange of organic material. The atmospheric transport of organisms has been investigated since the 1850s, primarily because of interest in the spread of disease. A number of studies report the presence of marine organisms in the atmosphere. Zobell & Mathews (1936) found that the type of bacteria in air over coastal locations was a function of wind direction. Marine forms dominated during onshore wind conditions. Woodcock (1948) suggested that the red tide toxin, produced by the dinoflagellate *Gymnodinium breve*, was transferred from the Gulf of Mexico to the atmosphere as a component of sea spray droplets produced during the bursting of air bubbles in the water. The presence of this material, apparently associated with the atmospheric particles, resulted in human respiratory irritation along the Florida coast and inland during red tide blooms. Stevenson & Collier (1962) identified three species of diatoms and four flagellates in the atmosphere, all in the nannoplankton size range (< 5 μm), and Maynard (1968) found several species of dinoflagellates in shipboard atmospheric samples and several diatoms in atmospheric samples from higher altitudes. Aubert (1974) identified terrestrial bacteria in coastal locations of the Mediterranean sea and marine bacteria over open ocean areas. The metabolic and

physiological characteristics of the bacteria differed depending on whether the samples were collected over the Mediterranean Sea or the Atlantic Ocean.

Carlucci & Williams (1965) investigated the transport of bacteria to the seawater surface in a laboratory foam column. They found that the presence of particulates enhanced the transport of bacteria and the efficiency of bubble transport varied from species to species. Also using a laboratory foam column, Wallace et al (1972) demonstrated that rising bubbles are capable of transporting a substantial portion of the particulate matter found in surface seawater samples to the air/sea interface. These authors suggested that phytoplankton in stationary and post-stationary phases of growth are apparently more subject to flotation than cells in the log phase of growth. In a subsequent study, Wallace & Duce (1975) found that 30–59% of the particulate organic carbon (POC) could be scavenged from samples of surface water from Narragansett Bay by rising bubbles in the foam column.

Sutcliffe et al (1963) reported that *Phaeodactylum tricornutum* were enriched in droplets produced by bursting bubbles in the laboratory by over an order of magnitude compared to bulk seawater. In subsequent studies, Blanchard & Syzdek (1970, 1972) showed that the freshwater bacterium *Serratia marcescens* could be concentrated on jet droplets by up to a factor of 10^4 relative to the water from which the droplets were produced. The magnitude of this concentration factor was a function of jet droplet (and thus bubble) size, bacteria concentration in the bulk solution, and bubble age, i.e. the length of time available for the bubble to scavenge bacteria. Increasing bubble age, up to about 20 sec, resulted in significantly higher concentrations of bacteria on the jet droplets, but the bubble surface apparently became saturated after this time, as no further concentration was observed. Blanchard & Syzdek (1974) calculated that the bubble collection efficiency (i.e. the number of bacteria scavenged by a bubble rising through the water divided by the number of bacteria present in the volume of water swept out by the rising bubble) for transporting these bacteria to the surface was ~0.12%. The efficiency of the transfer of these bacteria from the water surface to the jet droplets was estimated by Blanchard & Syzdek (1974) to vary between 14% and 85%, depending on the age of the bubbles.

Bezdek & Carlucci (1972) found that the concentration factors for the marine bacterium *Serratia marinorubra* on laboratory-produced jet droplets varied as a function of droplet size, with the greatest concentration factor generally found on intermediate size droplets. Concentration factors using naturally occurring bacteria in seawater ranged from 33 to 250 and appeared to depend on the type of bacteria. Carlucci & Bezdek (1972) suggest that the scavenging of bacteria by bubbles is not the critical step in jet droplet enrichment of these organisms but that the bacteria are enriched in the sea surface microlayer before the bubbles arrive. Thus they believe the bacteria found on the jet droplets are largely from the microlayer.

There have been relatively few studies of organic carbon (OC) in the marine atmosphere considering the potential importance of organic carbon to chemical fractionation in general. In addition, different fractions or classes of organic material were measured in these investigations, making intercomparison of the results very difficult. Lodge et al (1960) reported a mean concentration of 1.6 $\mu g\ m^{-3}$ of benzene-soluble organic material in samples collected over the Pacific Ocean. The benzene-

extractable organic material/salt mass ratio of 0.29 was equivalent to an enrichment of over 1000. Blanchard (1964) reported the presence of surface-active organic material on sea salt particles collected on thin platinum wires on the coast of Hawaii Island. In a later study, Blanchard (1968) estimated that the surface-active organic material/salt mass ratio varied from 0.3 to 0.7 on these particles. In a study from a coastal tower on Oahu, Hawaii, Barger & Garrett (1970) found the chloroform extractable organic (lipoid) material in atmospheric particles collected on glass fiber filters, as measured by weighing the material remaining after the chloroform was evaporated, ranged from 0.7 $\mu g/m^3$ to 6.3 $\mu g/m^3$, with a lipoid/salt mass ratio of 0.07 to 0.14. They found that the lipoid content increased with increasing salt content. E. Hoffman & Duce (1974) determined the total organic carbon content of sea salt particles collected on glass fiber filters from a coastal tower in Bermuda, using the wet oxidation analytical technique of Menzel & Vaccaro (1964). The total organic carbon content varied from 0.15 $\mu g/m^3$ to 0.47 $\mu g/m^3$ and the organic carbon/salt mass ratio varied from 0.01 to 0.19, equivalent to E_{Na}(OC) values of ~300 to 6000. In contrast to the study of Barger & Garrett (1970), E. Hoffman & Duce found that the organic carbon concentration was relatively constant, resulting in an inverse relationship between the organic carbon/salt ratio and the salt content. This inverse relationship has also been confirmed by R. Chesselet (personal communication) for samples collected from ships over the north Atlantic Ocean.

The inverse relationship between the organic carbon/salt ratio and sea salt concentration in the atmosphere may be explained if the organic carbon is present primarily on the smaller particles with longer atmospheric residence times and thus more uniform spacial and temporal concentration patterns. Indeed, Barker & Zeitlin (1972) showed qualitatively that the relative concentration of organic carbon increases with decreasing particle size. The source for the proposed small particle carbon may be the ocean or it may be gas phase reactions of natural or anthropogenic hydrocarbons or adsorption of these substances on other particles present in the atmosphere (Goetz & Klejnot 1972, Hoppel & Dinger 1973, Lovelock & Penkett 1974). About 50% of the background aerosol is volatile at 320°C (Twomey 1971). Although Twomey (1971) and Rosen (1971) attributed the volatility to loss of $(NH_4)_2SO_4$ or H_2SO_4, several authors (Blanchard 1971, Pueschel et al 1973) have suggested the volatile substances could be organic compounds. Clearly the determination of the significance of non-sea salt components of organic carbon in the marine atmosphere is critical before we can assess the importance of chemical fractionation of organic carbon at the air-sea interface. We can, however, estimate a maximum input of organic carbon from the ocean to the atmosphere on sea salt particles. If we assume the mean organic carbon/salt ratio of 0.05 observed in Bermuda by E. Hoffman & Duce (1974) is a reasonable estimate for the marine atmosphere as a whole and represents the organic carbon/salt ratio on sea salt particles and if we use the atmospheric sea salt production estimates of 10^{15} g/yr (Eriksson 1959, 1960) to 10^{16} g/yr (Blanchard 1963), the organic carbon transport from ocean to atmosphere ranges from 5×10^{13} g/yr to 5×10^{14} g/yr. This is from 0.25% to 2.5% of the estimated total organic carbon productivity of the oceans, which is 2×10^{16} g/yr (Ryther 1969). In the same range is Rasmussen & Went's (1965) estimate of the

natural atmospheric production of hydrocarbons from terrestrial vegetation: 4.4×10^{14} g/yr.

There have been several laboratory investigations of the transport of organic material from the ocean to the atmosphere. Bezdek & Carlucci (1974) studied the transport of insoluble monomolecular films to the atmosphere by bursting bubbles. They found that ^{14}C stearic acid was incorporated into the jet droplets and that the smaller droplets were more enriched in this material than larger droplets.

E. Hoffman & Duce (1976) investigated several factors in the laboratory that influence the quantity and enrichment of organic material transported into the atmosphere by bursting bubbles. E_{x_a} (OC) was found to be a function of bubble path length and the particular seawater used as a source. Water from Narragansett Bay, which is relatively shallow and characterized by a high dissolved and particulate organic carbon content, a high suspended load, and a large phytoplankton population, produced sea salt particles with OC/Na ratios averaging 0.098 ± 0.053. Water from the Sargasso Sea, which is characterized by lower levels of organic carbon, a lower suspended load, and a low phytoplankton population, produced sea salt particles with OC/Na ratios of 0.008 ± 0.005. The difference between the organic carbon concentration of these two bodies of water is one cause of the marked differences in the aerosol OC/Na ratios. However, when the OC/Na ratios of the aerosols are divided by the OC/Na ratio in the different seawaters to calculate E_{x_a} (OC) values, these values are 250 ± 145 for Narragansett Bay aerosols and 73 ± 27 for Sargasso Sea aerosols. The significantly different enrichment factors for aerosols from these two different water masses suggest that not only is the quantity of organic material in the seawater important, but also the chemical form of the organic material is perhaps even more critical in determining the amount of organic carbon on the sea salt particles.

The effect of bubble age noted by Blanchard & Syzdek (1972, 1974) for bacteria was also confirmed for total organic carbon in the experiments of E. Hoffman & Duce (1976). An increase of bubble path length by a factor of three before bubble bursting increased E_{x_a} (OC) by a factor of approximately two. Generally there was no difference in E_{x_a} (OC) using either filtered or unfiltered seawater, suggesting that the dissolved or colloidal fraction of the organic material was primarily responsible for the bulk of the organic carbon in the sea salt particles produced in this investigation. Since the possible enrichment of virtually all substances during bubble breaking at the ocean surface depends on association with organic carbon, further studies of the character and source of this material are urgently needed.

Alkali and Alkaline Earth Metals

One of the most confusing and controversial questions in the air sea chemical exchange literature over the past few decades has been the presence or absence of significant chemical fractionation of the alkali alkaline earth elements Mg, Ca, K, and Sr. A number of early papers indicated that many or all of these elements were significantly fractionated in marine aerosols compared to seawater (e.g. see Sugawara et al 1949, Koyama & Sugawara 1953, Oddie 1960, Komabayasi 1962). Enrichments of greater than ten were not uncommon. Most of these earlier field studies were

conducted in areas with potentially significant contributions from nonmarine sources to the marine aerosol. Indeed, the data in several of the Japanese papers above show that the enrichment of these elements increased as the sampling sites were moved progressively further inland. However, relatively little consideration was given at the time to the possibility that the high enrichments observed for these elements might be due to non-sea salt particles in the samples collected.

In more recent field studies involving these elements in marine aerosols, awareness of the importance of the atmospheric sampling site has grown. Atmospheric samples have been collected at several midocean locations by a number of groups during the past few years and a different picture is beginning to emerge relative to chemical fractionation of these elements. Enrichment values obtained for Mg, Ca, K, and Sr in some of these recent studies are presented in Table 1. There is no significant enrichment of Mg or Sr reported in any of these recent studies, nor, in most cases, any enrichment of Ca or K. Where apparent enrichment has been observed it has generally been explained by the presence of crustal material in the samples. Several different approaches have been used in these papers to identify and correct for a non-sea salt component for these elements. In studies in Hawaii and over the North Atlantic, G. Hoffman & Duce (1972) and E. Hoffman et al (1974) calculated enrichments from considerations of the slope of the linear least squares regression line calculated from plots of Mg, K, Ca, and Sr vs Na, as described previously. As seen in Table 1, enrichments calculated in this manner are very close to zero, indicating that the sea salt-associated components of these elements are present on the particles in seawater composition, within a very few percent. This strongly suggests little or no chemical fractionation in the areas sampled.

In a different approach to the same problem, several workers (Tsunogai et al 1972; Wilkniss & Bressan 1972, Wada & Kokubu 1973, Buat-Menard et al 1974) have either analyzed only the water-soluble component of the samples they collected or the water-soluble and water-insoluble fraction separately. The basic assumption is that the K, Ca, Mg, and Na in the sea salt particles are water soluble but the K, Ca, etc, in other components of the marine aerosol, particularly mineral dust, are not. However, Tsunogai et al (1972) found significant enrichment of K and Ca in the water-soluble fraction, which was attributed to a water-soluble component of land-derived Ca and K. Wada & Kokubu (1973) also believed that the contribution of water-soluble Ca and K from land sources had to be evaluated before drawing conclusions about the chemical composition of sea salt particles. These conclusions are not surprising. Far from land, it is unlikely that atmospheric sea salt and mineral dust particles exist as discrete particle populations. Coagulation processes, such as cloud and raindrop formation and evaporation, etc, will destroy these discrete distributions relatively quickly. The extent and rate of leaching of the various alkali alkaline earth metals from the dust particles in the saline droplets has not been measured, but at the expected pH of 5–6 in these particles, it may be rather significant.

For samples collected over the North Atlantic, Buat-Menard et al (1974) found that E_{x_a}(Mg) in the water-soluble fraction of the aerosol was generally near zero and that E_{x_a}(Ca), which ranged from zero to ten, was related to the quantity of the water-insoluble fraction (see the section on sulfate). Although some of the high K enrich-

Table 1 Some representative values for alkali and alkaline earth enrichments in marine aerosols

Location	No. of samples	$E_{Na}(Mg)$	$E_{Na}(Ca)$	$E_{Na}(K)$	$E_{Na}(Sr)$	Remarks	Reference
Norwegian Sea cruise	6	—	—	3.4 ± 2.1	—	total aerosol analyzed	Chesselet et al (1972b)
Antarctica	5	0.06 ± 0.06	0.33 ± 0.08	0.35 ± 0.11	—	total aerosol analyzed	Chesselet et al (1972b)
Windward coast of Oahu	119[a]	−0.02 ± 0.01	−0.03 ± 0.03	0.05 ± 0.08	−0.11 ± 0.04	total aerosol analyzed, samples contain < 50 ng m^{-3} Fe	G. Hoffman & Duce (1972)
North and South Pacific cruises	25	0.13 ± 0.15	1.7 ± 0.9	1.0 ± 0.7	—	water-soluble aerosol only	Tsunogai et al (1972)
Atlantic, Caribbean, and Pacific cruises	9	—	—	0.26 ± 0.18	—	water-soluble aerosol only	Wilkniss & Bressan (1972)
Mid-Pacific cruise	18	−0.02 ± 0.05	0.46 ± 0.83	0.17 + 0.46	—	water-soluble aerosol only	Wada & Kokubu (1973)
Caribbean to West Africa cruise	19	−0.34 ± 0.18	1.3 ± 1.7	0.15 ± 0.20	—	water-soluble aerosol only	Buat-Menard et al (1974)
West Africa, Gulf of Guinea coastal cruise	17	0.00 ± 0.07	2.3 ± 3.3	1.2 ± 1.6	—	water-soluble aerosol only	Buat-Menard et al (1974)
North Atlantic cruises	5-8[a]	0.02 ± 0.05	−0.03 ± 0.09	−0.03 ± 0.04	−0.15 ± 0.21	total aerosol analyzed, samples contain < 10 ng m^{-3} Fe	E. Hoffman et al (1974)
North Atlantic cruises	36-38[a]	0.07 ± 0.02	0.22 ± 0.04	−0.03 ± 0.03	−0.16 ± 0.08	total aerosol analyzed, samples contain < 250 ng m^{-3} Fe	E. Hoffman et al (1974)

[a] Enrichments based on regression line slope and standard deviation of the slope
[b] 56 samples for K
[c] 36 samples for K

ments also appeared related to the amount of water-insoluble material in their samples, the largest values for $E_{Na}(K)$ were found in samples collected over the more biologically productive areas off the West African coast, especially over the upwelling region in the Gulf of Guinea. Buat-Menard et al (1974) speculated that the K enrichment in this area was due to true chemical fractionation at the air sea interface resulting from the association of K with high concentrations of surface-active material in these biologically rich waters.

The effect of dust on $F_{Na}(K)$ for particles collected during onshore wind conditions in Bermuda is shown in Figure 4 (Hoffman 1975). Note that $F_{Na}(K)$ is used in this figure rather $E_{Na}(K)$, because it is impossible to plot zero and negative values on log-log plots. Using atmospheric Fe as an indicator of dust, this figure clearly shows the dependence of $F_{Na}(K)$ on the Fe/Na ratio. When the dust contribution is relatively insignificant (i.e. Fe/Na approaches zero), $F_{Na}(K)$ approaches one. If this data is replotted as K/Na vs Fe/Na, the slope of the resulting regression equation (excess K/Fe) is 0.326 ± 0.005. This suggests a crustal source for the excess K, since the mean K/Fe ratio in soil is ~0.36 (Vinogradov 1959). Air mass trajectories calculated for these Bermuda samples indicate that the dust collected can originate from the Sahara desert and the east coast of North America. Notice the magnitude of the effect of dust on $F_{Na}(K)$ in Figure 4. During onshore wind conditions, apparent fractionation up to ten is found, even at this coastal location over 1000 km from the nearest major land mass. This appears to be entirely the result of the additional K component present in continental dust that has been transported from 1000 to 5000 km across the ocean.

It has been suggested that the enrichment of alkali and alkaline earth metals in

Figure 4 The effect of dust, as indicated by the Fe/Na ratio, on the apparent fractionation of potassium in marine aerosols collected from a 20 m high tower on the coast of Bermuda (E. Hoffman 1975).

sea salt particles is a function of particle size, with only the smallest particles being significantly enriched. Indeed, if the smaller particles are more enriched than the larger particles, this would explain apparent enrichments of these elements in particles at high altitudes (Chesselet et al 1971) and in particles and snow collected at the South Pole (Chesselet et al 1972a). The cascade impactor data of Barker & Zeitlin (1972) from a coastal tower on Oahu, Hawaii, indicate that enrichment of K, Ca, and Mg on the small particles cannot be ruled out. However, their reported analytical uncertainties are so large that their data cannot confirm this either. Chesselet et al (1972b) also investigated the particle size distribution of K and Ca over the Norwegian Sea, but again the reported analytical uncertainties in the data make a definitive interpretation impossible. Andren & Harriss (1971) found enrichment of Ca and depletion of Mg on all the particle size ranges investigated 10 km inland in Puerto Rico and on board a ship in the Carribbean. They found the smaller particles were less enriched in Ca than the larger particles. Mineral dust may again be involved since several of their samples were collected inland, and the general area is often under the influence of the Sahara dust plume. Winkler (1975) found that the mass ratio of the elements Cl:K:Ca is significantly different from seawater on particles ≤ 0.2 μm radius over the Atlantic Ocean. Winkler is uncertain as to the cause of the relatively high K and Ca concentrations on these small particles and notes that chemical fractionation is a possibility. He points out that mineral dust and anthropogenic sources may also be significant.

A vast literature on the composition of rain in coastal locations routinely shows enrichment of the alkali alkaline earth elements relative to seawater, but it has been shown that particulate matter above two km in height is fairly uniform in composition, whether collected over continental or marine areas (Blifford & Gillette 1972, Delany et al 1973). As mentioned previously, this background aerosol has a maximum number distribution at ~ 0.1 μm radius (Junge 1963, 1972) and a rather long residence time in the atmosphere. Thus its origin relative to a continental or marine source is obscured. Since the contribution of this background aerosol becomes more and more important with increasing altitude, the use of high altitude aerosols, oceanic cloud water, or oceanic rain water (e.g. Bloch et al 1966) to indicate chemical fractionation at the air sea interface is often misleading and certainly complicates the question.

In conclusion, the often-observed apparent enrichment of the alkali and alkaline earth metals relative to Na probably results in most cases from the inclusion of non-sea salt particles, particularly continental dust, in the environmental samples. Fractionation of these elements in the environment is likely restricted to a few percent in most areas of the world ocean. The possibility that K may be fractionated at the air sea interface in biologically productive areas remains, but the global geochemical importance of this is unknown.

There have been a number of laboratory studies of the possible chemical fractionation of these elements. Several have shown significant enrichment, particularly of K and Ca, whereas others have shown little or no enrichment (e.g. see Komabayasi 1964; Bloch & Luecke 1968, 1972; Bruyevich & Korzh 1970; Glass & Matteson 1973; Morelli et al 1974; F. Hoffman 1975). Many earlier studies have been reviewed by

MacIntyre (1974a). These laboratory model studies differ from each other and from the natural environment in so many ways that it is extremely difficult to evaluate them in terms of natural processes occurring at the ocean surface, and we make no attempt to do so. Suffice it to say that there is no real reason to doubt the results in any of these studies, but on the basis of the most recent field data above, whatever mechanism or mechanisms caused the observed laboratory enrichments of these elements appears to be of limited importance in the environment.

Phosphate

In the laboratory study perhaps most responsible for the recent interest in bubble scavenging of surfactants and associated substances and their injection into the atmosphere, Baylor et al (1962) found that the inorganic dissolved phosphate in filtered seawater could be efficiently stripped from the seawater by bubbling. In their investigation, the concentration of phosphate in seawater at any time, C_t was given by

$$C_t = C_o e^{-Kt}, \tag{3}$$

where C_o = initial $PO_4^{=}$ concentration, t = time after initiation of experiment, and K = velocity or removal constant. K was a function of bubbling rate and the total surface area of the bubbles. Baylor et al (1962) believed that the phosphate removed from the water column was largely transferred into the atmosphere. The phosphate remaining in the seawater after bubbling was primarily associated with organic material and was filterable, that is, it no longer passed through a 0.45 μm pore size filter. In a subsequent study, Sutcliffe et al (1963) found that the atmospheric particles produced by laboratory bubbling of filtered seawater were indeed highly enriched in phosphate and that most of the phosphate in the aerosol was particulate rather than dissolved and was organically associated. There was considerable interest in whether collapsing bubbles could generate organic aggregates in the sea, as the implications to the marine food chain were obvious. It is now realized, however, that very small particles are necessary for the nucleation of the larger aggregates in seawater; these small particles are most likely colloidal in nature and therefore were not trapped by the 0.45 μm pore size filters used (Batoosingh et al 1969). Nevertheless, these experiments clearly showed that bubble scavenging of certain dissolved and/or colloidal organic materials and other associated substances, such as $PO_4^{=}$, significantly enrich these other substances in atmospheric particles.

Bruyevich & Kulik (1967a) also found significant enrichment of $PO_4^{=}$ in aerosols produced by bubbling seawater in the laboratory. MacIntyre & Winchester (1969) and MacIntyre (1970) followed up these initial studies with a detailed laboratory investigation of phosphate enrichment on the atmospheric sea salt particles. Using radioactive $^{32}PO_4^{=}$ and $^{22}Na^{+}$ tracers and a variety of aqueous bubbling solutions, MacIntyre (1970) always found excess phosphate in the aerosol. $F_x(PO_4)$ ranged from 0.01 to 10 for jet droplets and as high as 1000 for what he believed were droplets from a well-drained film cap. Figure 5 shows the results of three runs using filtered seawater, distilled water, and distilled water with a negatively charged surfactant (sodium lauryl sulfate) added. The highest enrichment was observed for the intermediate size atmospheric particles, approximately 1.6 μm radius, which MacIntyre

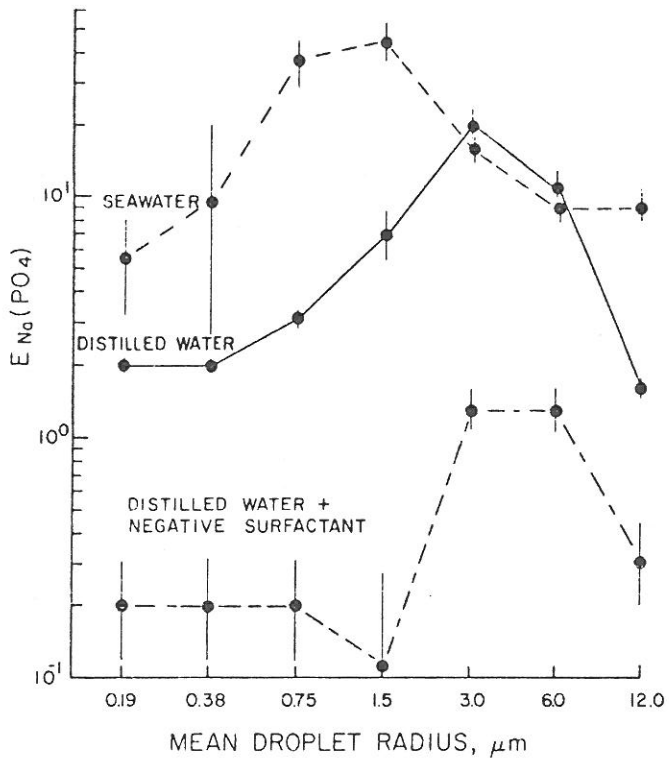

Figure 5 Enrichment of phosphate as a function of particle size for atmospheric particles produced in the laboratory by bubbles bursting in various "ocean" solutions. After MacIntyre (1970).

believed were the film droplets because they were produced from very large bubbles with a large film cap area. Similar studies with numerous smaller bubbles, which produced primarily jet droplets, showed little particle size dependence of $E_{Na}(PO_4)$. The use of seawater resulted in higher values for $E_{Na}(PO_4)$ than distilled water, probably because organic surfactants have a higher concentration in seawater. However, when the surfactant sodium lauryl sulfate was added to the distilled water, the enrichment dropped by an order of magnitude. MacIntyre (1970) pointed out that for this surfactant the surface active moiety is the lauryl sulfate anion, which should attract positive ions, rather than the negative $PO_4^{=}$ ion. Thus $PO_4^{=}$ enrichment is significantly decreased. When a positive surfactant, such as cetyltrimethylammonium bromide, was used in distilled water, values for $E_{Na}(PO_4)$ were ten or greater. MacIntyre (1970) suggested that ions with high ionic potential, i.e. large charge and small size, are preferred as counterions, or ions with a charge opposite to that of the surfactant. Thus, for example, Ca^{2+} and Mg^{2+} are preferred

over Na^+. MacIntyre (1970) suggested that this counterion mechanism plays a major role in the association of surface-active substances with inorganic ions, which in turn could result in the enrichment of the inorganic ions in atmospheric sea salt particles. Koske (1974) suggests this mechanism may be responsible for the barium enrichment that he observed on sea salt particles produced by distillation of seawater in the laboratory.

Surprisingly, we have been able to find no data on phosphate enrichment in the ambient marine aerosol. Although there is considerable data on sodium and such nutrients as phosphate, nitrate, etc. in rainfall, most of these studies were undertaken as part of general ecological and biological field programs and are not in suitable locations for collection of true marine rainfall. Perhaps most representative of marine air is the rain data of Allen et al (1967) from the small island of Signy, off the coast of Antarctica in the South Orkney Islands. As part of a nutrient balance study, these authors concluded that the primary source of phosphate on the island was precipitation and that the phosphate and other nutrients in the precipitation came from the sea. The average value for $E_{Na}(PO_4)$ in the Signy Island precipitation was 170. Allen et al (1968) undertook a similar study in England. At two stations ranging from 2 to 8 km from the sea, their data suggest $PO_4^{=}$ enrichments of over 1000. However, the air over the highly populated, agricultural, and industrialized island of Great Britain is certainly not representative of uncontaminated marine air. The general geochemical importance of the atmospheric transport of phosphate to and from marine areas remains to be determined.

Nitrogen Compounds

With the demonstration that phosphate can be efficiently transported from the sea to the atmosphere on particles from bursting bubbles, it is rather surprizing that so little research in this context has been carried out on nitrogen containing nutrients. We have found no data on organic nitrogen in marine aerosols. Two investigations in New Zealand, however, suggest the potential importance of the chemical fractionation of organic nitrogen compounds. Wilson (1959) investigated the organic nitrogen content of snows collected 1600–2600 m above sea level on remote mountains located 20–160 km from the sea. Because the samples were freshly collected from regions where no plants or animals exist, Wilson expected no contamination from these sources. He could see no insoluble inorganic matter in the samples with the naked eye and believed that no (or very little) crustal weathering products were present. He felt strongly that the source of the organic nitrogen in these samples was the ocean.

The organic nitrogen (ON) concentration in the snow ranged from 20 mg liter to 200 mg liter. A single coastal rain sample contained 200 mg liter organic nitrogen, whereas typical seawater off New Zealand contained 8 μg liter. These concentrations, combined with Na measurements made on the same samples, result in $E_{Na}(ON)$ values ranging from 4×10^1 to 1×10^6. These are extremely high enrichments and, if correct, suggest that the transport of organic nitrogen from the sea to coastal areas could be significant in the nutrient balance of some regions. The high organic

nitrogen concentration in coastal marine rain was confirmed by Dean (1963), who found 170 mg/liter in rain at Taita in coastal New Zealand. Organic nitrogen concentrations of ~25 mg liter were found by Williams (1967) in rain over the ocean off California and near Samoa. High enrichments relative to seawater were also found for NH_4^+ in the rain and snow samples of Wilson (1959), and an enrichment for total nitrogen of 2×10^4 was found in a foam sample collected on a rocky coast north of Wellington, New Zealand.

Are such high enrichments in the atmosphere possible from a marine source? As a crude attempt to answer this question, we can make the following calculation. Assuming the organic nitrogen in the atmosphere was present on sea salt particles when they were produced at the sea surface, assuming the average value of $E_{Na}(ON)$ for particles in the atmosphere near New Zealand is 2×10^5, and assuming the organic nitrogen concentration in the mixed layer of the ocean near New Zealand is ~8 μg liter, the concentration of organic nitrogen in the surface layer stripped by the bursting bubbles, i.e. the top 0.05–0.5 μm, must be ~1.6 g liter. (This concentration could be attained in this surface layer by the transport of a quantity of organic nitrogen equivalent to that present in approximately 1–10 cm of subsurface water. This is perhaps not completely unreasonable.) Williams (1967) found the concentration of both dissolved and particulate organic nitrogen ranged from 100 μg/liter to 500 μg liter in the top 150 μm of the ocean surface off Peru and off California. We assume an average concentration of 300 μg/liter in the 150 μm microlayer. The microlayer concentrations observed were 1.5–50 times concentrations present at depths of 10–30 meters. However, if this organic nitrogen in the 150 μm microlayer is actually concentrated in a much thinner layer from 0.05 μm to 0.5 μm thick, which the bursting bubble strips into jet droplets, the concentration in this thinner layer would be ~0.1–1 g/liter – close enough to the required concentration of 1.6 g/liter calculated above that we cannot dismiss the possibility that this mechanism is potentially significant in the environment. However, these calculations and any interpretation of this field data in terms of chemical fractionation must be viewed cautiously because our understanding of the interactions of such gaseous species as NO, NO_2 and NH_3 with aerosols and rain and cloud droplets is limited and because chemical reactions of these inorganic nitrogen species with organic material in these particles and droplets are possible.

Williams (1967) discussed the general implications of enriched nitrogen transport into the atmosphere on sea salt particles to the nitrogen cycle in the sea and suggested that, if highly enriched nitrogen is a general phenomenon, this "closed system of nitrogen recycling would greatly reduce the net input of nitrogen into the sea" from continental sources. The implications to the overall nitrogen cycle are potentially significant, but this subject awaits considerable additional research.

In a different aspect of the nitrogen problem, Bloch & Luecke (1970) showed in the laboratory that inorganic NH_4^+ is enriched in the particles produced by boiling artificial salt solutions of NH_4Cl and collecting the condensate and spray produced. They explained that their NH_4^+ enrichments, which ranged up to ~1000, were due to hydrolysis of NH_4^+ in the seawater, with the subsequent enrichment of NH_4OH at the water surface due to Gibbs adsorption. As mentioned above, the question

of NH_4^+ in atmospheric aerosols is complicated by the interaction of gas phase NH_3 with the saline droplets. While NH_4^+ is apparently enriched in marine aerosols and rain relative to seawater (Junge 1957, Wilson 1959, Menzel & Spaeth 1962, Williams 1967, Tsunogai 1971), there is no strong evidence to suggest that this NH_4^+ originates on the particles produced at the sea surface.

The Halogens

CHLORINE Chlorine is the major mass component of atmospheric sea salt and is relatively easy to analyze. One might expect this element to be the most thoroughly understood relative to chemical fractionation. However, there is still considerable uncertainty regarding the marine atmospheric chemistry of chlorine. A Cl gas phase exists in marine air, and considerations of the Cl/Na ratio and Cl enrichment during particle production are complicated by the possibility of Cl gain or loss from the aerosol after its formation. Most of the data on Cl/Na ratios are from rain, with relatively little information for atmospheric particles in open ocean areas. Wilkniss & Bressan (1972) measured Cl/Na ratios on atmospheric particles in midocean and near-continent marine air. The mean value for $E_{Na}(Cl)$ from their midocean samples was -0.07 ± 0.21, although for particles >2 μm radius $E_{Na}(Cl)$ was $+0.04 \pm 0.19$. Along the east coast of the United States, they found $E_{Na}(Cl)$ values ranging from −0.99 to −0.31. They note that these negative enrichments are undoubtedly due to the simultaneous collection of continental aerosols with relatively high Na concentrations. Chesselet et al (1972a) found the mean value of $E_{Na}(Cl)$ to be -0.04 ± 0.02 on particles from several midocean locations, whereas Peirson et al (1974) found an average value of −0.09 during 1972 and 1973 at Lerwick in the Shetland Islands. On a cruise in the mid-Pacific, Wada & Kokubu (1973) found a mean value of -0.03 ± 0.03 for $E_{Na}(Cl)$, and the data of Buat-Menard et al (1974) over the North Atlantic indicate a mean of -0.12 ± 0.11.

Perhaps the most valuable data to date is that of Martens et al (1973), who investigated the variation of the Cl/Na ratio with particle size in Puerto Rico. On the

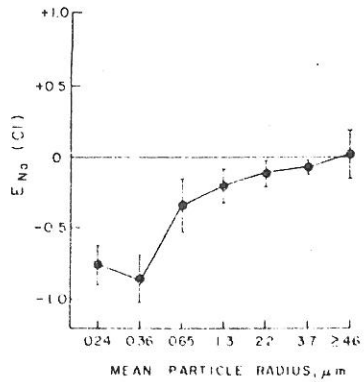

Figure 6 Enrichment of Cl as a function of particle size for atmospheric samples collected at coastal and inland sites in Puerto Rico. After Martens et al (1973).

basis of the Cl/Na ratio in the particles, corrected for any Na contribution from weathered crustal material, they calculated a 7–25% depletion of Cl relative to the expected seawater composition. The average $E_{x_a}(Cl)$ for their bulk marine aerosol was -0.12 ± 0.09. Most importantly, they found this Cl depletion was very particle-size dependent, with increasing depletion of Cl with decreasing particle size. Figure 6 presents a composite of $E_{x_a}(Cl)$ vs particle size for their four samples at coastal and inland Puerto Rico sites. Martens et al (1973) ascribe this marked decrease of $E_{x_a}(Cl)$ on the small particles to a loss of Cl to the gas phase. Based on similar studies in the San Francisco Bay area, where NO_2 was simultaneously measured, these authors conclude that HCl is released from the particles after uptake of gaseous HNO_3 (and perhaps SO_2). Assuming that the HNO_3 and SO_2 uptake is controlled by diffusion to the particle surfaces, under nonequilibrium conditions the smaller particles, with their larger surface area to volume ratio, will be most affected by the addition of these gases and subsequent loss of HCl. If chemical equilibrium is ultimately reached between the gases and the particles, there should be no difference in the Cl/Na ratios on particles of different sizes. The existence of such a difference suggests that, if this mechanism is valid, equilibrium is not attained.

The mean $E_{x_a}(Cl)$ for the six midocean studies above is -0.08 ± 0.04, equivalent to an apparent 8% loss of Cl to the gas phase, assuming no chemical fractionation of Cl relative to Na during particle production. A gaseous Cl component does exist in the marine atmosphere. Although its chemical form is still uncertain, the concentrations are generally 1–5 $\mu g/m^3$ near sea level, with the gaseous/particulate Cl ratio averaging about 0.5 (Junge 1957, Duce et al 1965, Chesselet et al 1972a, Rahn et al 1976). Thus, if this gaseous Cl is generated from the atmospheric sea salt particles, it must have an atmospheric residence time approximately six times that of particulate Cl, or ~2–3 weeks. Delany et al (1973, 1974) measured the vertical profile of Cl/Na in aerosols over continental and marine areas up to 9 km. Over the sea the ratio fluctuated around the seawater value, but over continental areas the ratio generally increased with height, which Delany and co-workers believed was caused by interaction between the continental aerosol and gaseous Cl.

There have been a number of suggestions for the reactions that may release gaseous Cl from sea salt particles. These include the uptake of SO_2 (Eriksson 1959, 1960) or HNO_3 (Robbins et al 1959) to release HCl, described previously, the reactions of Cl^- with O_3 to produce Cl_2 (Cauer 1938), the uptake and reaction of NO_2 with NaCl to produce NOCl (Schroeder & Urone 1974), and photochemical reactions in either the sea or atmospheric particles to produce the pernitrite ion, which subsequently reacts with Cl to release Cl_2 and/or NOCl (Petriconi & Papee 1972). Valach (1967) and Lazrus et al (1970) suggest that volcanoes are the major source for marine atmospheric gaseous Cl. Zafiriou (1975) has suggested that significant quantities of CH_3Cl may be generated in seawater by the reaction of CH_3I with Cl^-. Zafiriou points out that CH_3Cl should be quite stable in seawater and should exchange with the atmosphere, where it would be photostable and probably have a relatively long residence time. CH_3Cl (and CCl_4) is a major component of the light chlorocarbons present in the atmosphere in the state of Washington (Grimsrud & Rasmussen 1975) and it does not appear to have an anthropogenic source. In addition, at a coastal Bermuda site, Rahn et al (1976) have found that only about 25% of the gaseous Cl is inorganic (as measured by capture on LiOH impregnated filters), and 75% is apparently organic (as measured by capture on activated charcoal, which is quite efficient for CH_3Cl). Determination of the inorganic and organic speciation of gaseous Cl in marine air will be critical in understanding the interaction between atmospheric sea salt particles and these gaseous components.

There have been a few laboratory studies of Cl fractionation. Chesselet et al (1972b) found no deviation of the Cl/Na ratio on bubble-produced sea salt particles in the laboratory as compared to seawater. Wilkniss & Bressan (1972), in a similar study using a cascade impactor, found no deviation from the seawater ratio on the largest particles, but a slight negative enrichment on the submicron particles produced. There appears to be no strong evidence to suggest that there is any significant fractionation, either positive or negative, for Cl during particle production.

There is extensive data on the Cl/Na ratio in rain, from both coastal and inland areas. The early data was reviewed by Junge (1963). Most results show a negative enrichment for Cl, with an average $E_{x_a}(Cl)$ of approximately -0.05 to -0.10. Recent studies of rain in Hawaii at various altitudes, reported by Seto et al (1969), show no significant Cl enrichment. In studies of the Cl/Na ratio in cloud water 1000 m above sea level in Puerto Rico, Lazrus et al (1970) likewise found no statistical difference from seawater. Many past samples were collected in areas with potential for significant contributions of continental material to the rain. Owing to the presence of a gas phase, possible incorporation of continental and background aerosols from higher altitudes, and the fact that rainout and washout efficiency is a function of both particle size and particle composition, any general attempt to understand the chemistry of atmospheric particles through rain analysis is fraught with problems; this is especially true for particulate chlorine.

BROMINE There is little evidence to suggest that bromine is fractionated during sea salt particle production. However, gaseous bromine may be released from sea salt particles to a greater extent than Cl after the particles enter the atmosphere, resulting in a Br/Cl ratio on the particles that is slightly depleted relative to seawater. Duce et al (1967) and Moyers & Duce (1972a) investigated the Br/Cl ratio as a function of particle size from 20 m high towers directly on the coast of the islands of Hawaii and Oahu. Figure 7 presents the mean values for $F_{Cl}(Br)$ for 12 cascade impactor samples from Oahu. To facilitate graphical display of this data, F rather than E values are presented. Values for $F_{Cl}(Br)$ were generally less than unity for all particle sizes. The mean value for $F_{Cl}(Br)$ for the total particle population suggests that, relative to Cl, 40% more of the Br has apparently been lost to the gas phase. Moyers & Duce (1972a) measured the gaseous Br concentration in Hawaii, and it averaged approximately 50 ng m^3, or 4–10 times the particulate bromine concentration. This suggests that, if the gaseous bromine does result from sea salt particle release, the residence time of the gaseous species is several times that of particulate Br. Martens (1973) has investigated $F_{x_a}(Br)$ as a function of particle size at both coastal and inland stations in Puerto Rico. His results agree with the Hawaii data presented in Figure 7 for particles with radii > 1 μm. For particles between 0.5 μm and 1 μm, however, $F_{x_a}(Br)$ ranged

from 2 to 11 for four samples. Martens (1973) notes that the high fractionation values for Br on the smallest particles may be due to local contamination by the presence of Br associated with Pb from the combustion of tetraethyllead and ethylene bromide in gasoline. Measured Br/Pb ratios on these small particles in Puerto Rico support this suggestion.

Duce et al (1973) have measured atmospheric bromine at the geographic South Pole at 2800 m above sea level, and $F_{Cl}(Br)$ is greater than 12 for the total aerosol population sampled. Gaseous bromine was found to be approximately 20 times the particulate Br concentrations. Similar high value for $F_{Cl}(Br)$ were found by Cadle (1972) in the midlatitude, northern hemisphere stratosphere, at an altitude of approximately 10 km, and by Delany et al (1973) at altitudes from 1 km to 9 km over marine and continental areas. The latter group suggested that the high $F_{Cl}(Br)$ values at higher altitudes may result from gas phase reactions yielding NH_4Br aerosol. Cadle suggested that the high stratospheric Br/Cl ratio might result from increased Br from the combustion of ethyl fluid in gasoline. Another possibility is the uptake of natural gaseous Br on the background aerosol. In summary, it appears that there is no strong evidence for bromine fractionation at the air–sea interface and that deviations of the Br/Na or Br/Cl ratio from seawater values are probably caused by the exchange of a natural gaseous bromine phase with the sea salt particles and

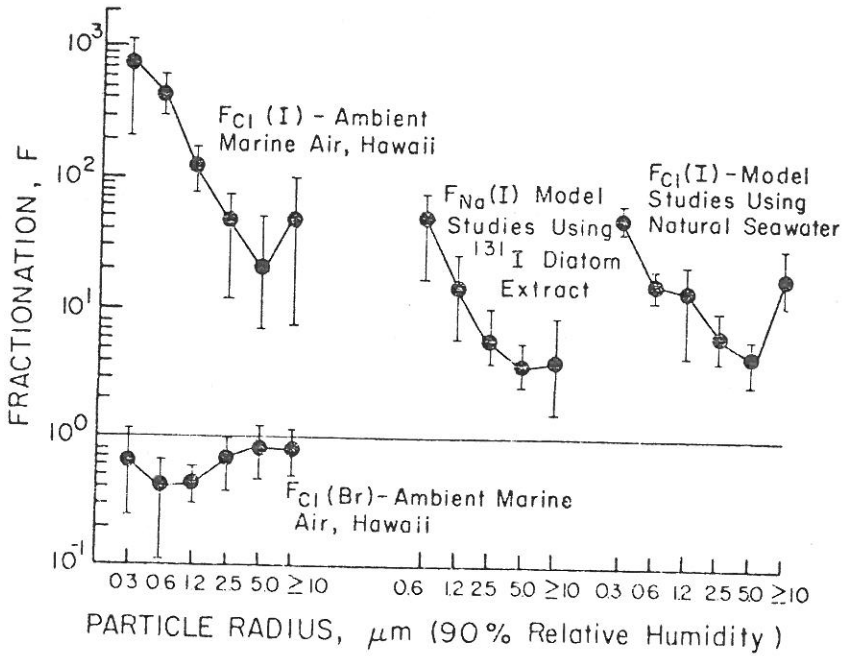

Figure 7 Fractionation of I and Br as a function of particle size for samples collected from a 20 m high tower on windward Oahu, Hawaii and from a laboratory model ocean-atmosphere system. From Moyers & Duce (1972a,b) and Seto & Duce (1972).

Table 2 Some representative values for iodine enrichment in marine aerosols

Location	Reference	E(I)	Reference
Sugashima Island, Japan, 200 m	Cl	10–100	Komabayasi (1962)
Tokyo, Japan, near sea level	Cl	2500	Miyake & Tsunogai (1963)
New Zealand coast, sea level to 35 m	Cl	35–500	Dean (1963)
Hawaii Island, sea level to 2000 m	Cl	10–200	Duce et al (1965)
Barrow, Alaska coast, 10 m (winter)	Cl	55–10,000	Duce et al (1966)
Oahu, Hawaii coast, 20 m	Cl	80–300	Moyers & Duce (1972b)
McMurdo, Antarctica coast, 50 m	Cl	750–28,000	Duce et al (1973)
South Pole, Antarctica, 2800 m	Cl	≧12,000	Duce et al (1973)
Puerto Rico, 20–450 m	Na	220	Martens (1973)

background aerosol or by the addition of Br-rich particles from the combustion of ethyl fluid.

IODINE Iodine is one element for which there is considerable evidence for chemical fractionation at the air/sea interface. A number of studies have shown that iodine enrichment in marine aerosols generally ranges from 100 to 1000. Some representative values for iodine enrichment are presented in Table 2. The sea is the accepted source for atmospheric iodine present in marine aerosols, but the mechanism for enrichment remains uncertain. It is likely that either (*a*) a gaseous form of iodine, probably I_2 or CH_3I, is released from the ocean surface and exchanges with the particles, or (*b*) surface-active organic material enriched in iodine in the sea is scavenged by rising bubbles and injected preferentially into the atmosphere. Evidence supports both mechanisms and indeed both are probably important in the environment.

In marine air, iodine is generally found on smaller particles than is Br or Cl. In studies from 20-meter-high towers on the coasts of Hawaii and Oahu, Duce et al (1967) and Moyers & Duce (1972b) found that the major mass of iodine is generally on particles with radii of 0.5–1.0 μm whereas the major mass of Cl is present on particles with radii of 1–5 μm at 90% relative humidity. This results in a general increase in the I/Cl ratio, or $F_{Cl}(I)$, with decreasing particle size, as illustrated in Figure 7. Duce et al (1967) point out that, if the high iodine enrichment is the result of gaseous uptake by the particles, the overall effect of the addition of gaseous iodine to the particle chemical composition would be inversely proportional to the particle radius. Using their experimental data, Robbins (1970) developed a mathematical diffusion model for the reaction of gaseous iodine with particle surfaces that could explain quantitatively the particle size dependence of the I/Cl ratio. His model, however, required that all the particles have the same, rather short, residence time of approximately 15 min. Moyers & Duce (1972b) suggested that the enrichment variation with particle size may be due to a rather slow interaction of the gas phase with the particles, so that the residence time of the particles becomes the controlling factor in the uptake of gaseous iodine. The smaller particles, with their longer atmospheric residence times (Esmen & Corn 1971, Junge 1972) would thus have higher iodine

enrichment. If the gas-particle interactions are inorganic in nature and involve such species as I_2, I^-, and IO_3^-, Moyers & Duce (1972b) showed that thermodynamic equilibrium would probably never be attained and the particles would continue to act as a sink for gaseous iodine as long as they remain in the atmosphere.

An obviously critical factor in this discussion is the presence of gaseous iodine over the ocean. Duce et al (1965) and Moyers & Duce (1972b) found that the general level of gaseous iodine in surface air near Hawaii ranged from 5–20 ng m^{-3}, with the gaseous species generally two to four times particulate iodine. In Antarctica, both at coastal and inland sites, the gaseous concentration was 2–3 ng m^{-3}, again two to four times particulate iodine. The chemical form of the gaseous iodine is still quite uncertain. Miyake & Tsunogai (1963) added $^{131}I^-$ to a model ocean system and found I_2 released when the system was irradiated with light at 300–500 nm. They attributed the I_2 release to:

$$2I^- + 1/2\,O_2 + H_2O \xrightarrow{h\nu} I_2 + 2OH^- \qquad (4)$$

Martens & Harriss (1970) and Seto & Duce (1972) found similar results using $^{131}I^-$ tracer in the laboratory.

In their model ocean-atmosphere studies, Seto & Duce (1972) also cultured the diatom species *Phaeodactylum tricornutum* in the presence of $^{131}I^-$. Organic material incorporating the $^{131}I^-$ was extracted from the diatom culture and added to the model ocean system: the seawater was bubbled and the particles produced were collected using a cascade impactor. $F_{Cl}(I)$ values for these size-separated laboratory aerosol samples are presented in Figure 7. Additional model studies were performed on fresh seawater with no radioactive iodine added, with the natural iodine present analyzed directly in the particles produced. These results are also presented in Figure 7. It is seen that the pattern of iodine enrichment on the particles from both model studies is very similar to that in the marine environment, that is, general increase in iodine enrichment, or fractionation, with decreasing particle size, except for the very largest particles. However, the magnitude of the enrichment is about 20 times greater in the natural environment. These results suggest strongly that at least part of the iodine enrichment in atmospheric sea salt particles results directly from chemical fractionation at the air–sea interface during particle production, probably caused by association of some of the iodine with surface-active organic material. These conclusions agree with those of Dean (1963), who found considerable organic material (primarily algae and plankton debris) in sea spray in New Zealand and believed the high iodine enrichment he measured was due to iodine associated with the organic material.

In their model studies using natural seawater with no added radioactive iodine, Seto & Duce (1972) found that, during bubbling, gaseous iodine comprised 90% of the total iodine released (the rest was particulate) when the surface of the model ocean was irradiated with ultraviolet light and decreased to 75% when the ultraviolet light was absent. When the same experiments were run without bubbling, the absolute concentration of gaseous iodine released decreased significantly, but was not zero and was approximately the same with and without ultraviolet light. Thus a gaseous form of iodine was released from the model ocean surface, but its release was apparently not entirely dependent upon photochemical reactions and was enhanced by bubbling. Further laboratory studies in which the form of this gaseous iodine is determined would be most valuable.

Moyers & Duce (1972b) assumed the gaseous species was I_2 for their thermodynamic equilibria calculations, but Zafiriou (1974) has pointed out that the mean atmospheric lifetime of I_2 would be only a few seconds because of photodissociation during daylight hours. He felt that molecule-aerosol reactions might be important at night but that photodissociation followed by atom reactions (e.g. $X + O_3 \rightarrow XO \times O_2$) would be prevalent during daylight. Lovelock et al (1973) found methyl iodide over the North Atlantic at concentrations of ~7 ng I/m^3. They suggested that CH_3I produced biologically in the sea escapes into the atmosphere and is destroyed photolytically after a residence time of a few days. Zafiriou (1975) has shown by reaction kinetic calculations and laboratory studies that CH_3I in seawater reacts with Cl^- to produce CH_3Cl at about the same rate that CH_3I escapes into the atmosphere. He also showed that reaction of CH_3I with Cl^- in the salt particles after they reach the atmosphere could not account for the high I enrichments observed in the marine aerosol. If CH_3I is photolytically destroyed in the atmosphere, however, as suggested by Lovelock et al (1973) and Zafiriou (1975), the products of this photolysis are probably scavenged rapidly by the marine aerosol and may be the cause of the high iodine enrichments observed. Clearly, the chemical species of gaseous iodine present in the marine atmosphere need to be determined and gas/particle iodine exchange must be studied to fully elucidate the marine atmospheric chemistry of this element.

FLUORINE There have been very few studies of fluorine in the uncontaminated marine atmosphere. Carpenter (1969) summarized the results of rain analyses for F and pointed out that $E_{Cl}(F)$ in these rain samples, virtually all of which were collected in continental areas, ranged from 10 to 1000. Carpenter (1969) and Sugawara (1965) concluded that F is preferentially injected into the atmosphere from the ocean surface. Wilkniss & Bressan (1971, 1972) have investigated the chemistry of F and Cl in rain as well as atmospheric particles in the field and in the laboratory. At mid-ocean sites, far from the influence of land, they found a mean value for $E_{Na}(F)$ of -0.62 ± 0.07, indicating no positive chemical fractionation of fluorine during sea salt particle production. This was supported by model studies in the laboratory. $E_{Na}(F)$ values in atmospheric particulate samples collected over the ocean but near the east coast of the United States by these authors ranged from 2 to 25. Wilkniss & Bressan note that these apparent high enrichments are probably caused by incorporation of continental material into the marine aerosol they were sampling. Wada & Kokubu (1973) reached a similar conclusion to explain their mean $E_{Na}(F)$ value of 12 ± 9 in the western Pacific. Analyses of aerosol samples collected at various altitudes above sea level in Hawaii support this conclusion (Wilkniss & Bressan 1972). $E_{Na}(F)$ in these samples was near zero up to about 500 m, but increased considerably at 3000 m. The increase is probably related to a relatively greater mass of continental or background aerosol at the higher level. $E_{Na}(F)$ values in rain in Hawaii were often as high as ten and were inversely proportional to the Na concentration in the rain. Wilkniss & Bressan suggest that the high fluorine enrichment

values in rain result from the incorporation of significant quantities of the background aerosol in the precipitation. However, Bewers & Haysom (1974) present mass budget calculations suggesting that terrigenous dust can account for only a few percent of the fluorine in the atmosphere. They postulate that the excess F in the rain may be entering the atmosphere from the ocean as a gas, possibly HF, or on particles with radii less than 0.1 μm. Wilkniss & Bressan (1972) presented laboratory evidence suggesting that gaseous F is released from the atmospheric sea salt particles. The relation, if any, between gaseous F and the high $E_{x_a}(F)$ values in rain is not known. Apparently no attempt has been made to measure gaseous F, except for the freons, in the marine atmosphere, and the geochemical importance of the sea or of sea salt particles as a source for gaseous F has not been investigated. There is no strong evidence for positive enrichment of fluorine during atmospheric sea salt particle production, but additional work on the atmospheric fluorine cycle is clearly needed.

Sulfate

Although several workers have reported occasional samples where the $SO_4^=$/Na ratio in marine aerosols and rain is similar to seawater (e.g. Koyama & Sugawara 1953, Buat-Menard et al 1974), most studies have reported $E_{x_a}(SO_4)$ values greater than zero for marine aerosols (Sugawara et al 1949, Koyama & Sugawara 1953, Junge & Werby 1958, Junge 1963, Tsunogai et al 1972, Buat-Menard et al 1974, Cuong et al 1974). However, in most cases the apparent enrichment has been attributed to $SO_4^=$ sources other than sea salt. As with some other substances, the question of possible $SO_4^=$ enrichment on atmospheric sea salt particles is complicated by the conversion of sulfur gases of both marine and nonmarine origin, e.g. SO_2, H_2S, and perhaps organic sulfides, to particulate $SO_4^=$.

A variety of sulfate-containing particles not originating from the ocean have been detected in the marine atmosphere. For example, the major mass of the background aerosol is probably sulfate, presumably in the form of $(NH_4)_2SO_4$ or H_2SO_4 (Dinger et al 1970). The source of the sulfate in the background aerosol is believed to be the oxidation of SO_2. Anthropogenic $SO_4^=$ (also resulting from the oxidation of SO_2) released by burning of fossil fuels has also been shown to be transported some distance over the ocean. Koide & Goldberg (1971) and Weiss et al (1975) found that non-sea salt $SO_4^=$ in a Greenland glacier began to increase in the mid-twentieth century. The $SO_4^=$ in the snows of 1964–1965 also correlated with the Pb in these samples, which suggests a pollution source for a portion of the excess sulfate (Murozumi et al 1969, Koide & Goldberg 1971). The magnitude of this anthropogenic effect in glacier ice is disputed, however. Some workers (Hamilton & Langway 1967, Junge 1960) found no increase with age in the $SO_4^=$/Na ratios of their ice samples from Greenland. However, marine samples taken downwind of large industrial and urban sites will undoubtedly contain significant quantities of excess anthropogenic $SO_4^=$ (Brosset & Akerström 1972).

Another source of $SO_4^=$ in particles over the ocean is continental weathering material or mineral dust. Koyama & Sugawara (1953) found that $E_{c_l}(SO_4)$ in aerosols increased as samples were collected further inland. In addition, Buat-Menard et al (1974) found that $SO_4^=$/Na ratios in most of their samples from off the coast of northwest Africa correlated with Ca/Na ratios. They attribute enrichment of both substances in their samples to gypsum ($CaSO_4 \cdot 2H_2O$) from the desert areas of Africa. Particles resulting from volcanic activity may also contribute significant amounts of $SO_4^=$ to the atmosphere, particularly in marine areas near volcanoes (Pueschel et al 1973) and in the stratosphere up to several years after major eruptions (Cadle et al 1971).

In addition to these nonmarine sources, the sea may release gaseous sulfur compounds into the atmosphere. Release of hydrogen sulfide from the ocean appeared necessary to balance calculated atmospheric sulfur budgets (e.g. Eriksson 1963, Robinson & Robbins 1968). Kellogg et al (1972), however, pointed out that the rapid oxidation of H_2S in surface seawater meant that release of H_2S from the sea would only be significant from biological processes in coastal areas, particularly tidal flats. Hitchcock & Wechsler (1972) showed that H_2S can be liberated from water through the reduction of $SO_4^=$ by anaerobic bacteria from muddy lake bottoms, wet soils and swamps, coastal wet lands and estuaries, and some anoxic fiords.

Because of the anaerobic conditions necessary for H_2S evolution, Lovelock et al (1972) recently suggested that organic sulfides, which can be produced by bacteria under normal aerobic conditions, may be a more significant oceanic source of sulfur to the atmosphere. They reported the presence of dimethylsulfide in seawater and in varieties of the marine alga *Laminaria*. Rasmussen (1974) found that dimethyldisulfide and methyl mercaptan, as well as dimethylsulfide, are produced by aquatic bacteria and Pacific tidal zone seaweeds. Even under anaerobic conditions, when H_2S was released, the organic sulfides were produced in concentrations 100 times greater than H_2S. Rasmussen (1974) concludes that, since organic sulfides are produced during both aerobic and anaerobic conditions, the organic sulfide production by the oceans may be a major source of sulfur in the atmosphere. Dimethylsulfide has yet to be detected in the marine atmosphere, however.

The possibility of a biogenic source for the excess $SO_4^=$ may be indirectly confirmed by the data of Buat-Menard et al (1974), who found significant $SO_4^=$ enrichment over the biologically productive upwelling waters off the Gulf of Guinea. Because this area is south of the intertropical convergence zone and thus not dominated by Sahara dust, they attribute these enrichments to either of two possible mechanisms: (*a*) biological production of sulfur gases which are subsequently converted to SO_3 and H_2SO_4, or (*b*) sea surface enrichment of sulfate due to the association of sulfur containing compounds with surface active organic material.

Although the SO_2/$SO_4^=$ ratio over "unpolluted" land areas varies from 1.3 to 10 (Georgii 1970, Rodhe 1972), recent work by Cuong et al (1974) shows that the SO_2/$SO_4^=$ ratio over oceanic areas is approximately 0.1, suggesting a rapid conversion of SO_2 to $SO_4^=$ or rapid removal of SO_2 from the atmosphere. They state that in some areas, such as the Mediterranean Sea, the ocean is a sink for SO_2. Laboratory studies by Spedding (1972) and Beilke & Lamb (1974) also suggest the ocean is a major sink for SO_2.

A few laboratory studies have investigated $SO_4^=$ fractionation at the air-sea interface. With this problem in mind, Russian investigators have undertaken several

studies that found positive enrichments for sulfate (Bruyevich & Kulik 1967b, Bruyevich & Korzh 1970). These authors believe that the sulfate enrichment observed in the marine aerosol and rain result from fractionation processes occurring at the air/sea interface. Their experimental design did not approximate environmental conditions, however, and evaluation of the results relative to processes occurring at the natural air/sea interface, is rather difficult. Further laboratory studies of $SO_4^=$ fractionation are needed.

In conclusion, although most workers concede that there is a sulfate excess in particles collected over the oceans, the excess has generally been attributed to $SO_4^=$ input from the background aerosol, anthropogenic sources, continental dust, volcanic emissions, and particles derived from oxidation of sulfur gases released by the ocean. The significance of sulfate fractionation at the air/sea interface has not yet been adequately evaluated because of the complicated atmospheric sulfur cycle, which hampers simple environmental studies, and because the laboratory data is meager. Isotopic studies of sulfur in atmospheric sulfate particles can distinguish sources in urban areas (Nielsen 1974). Perhaps, with further work on isotopic ratios, the significance of these various sources to the total composition of sulfur in the marine aerosol will be evaluated.

Heavy Metals

In the past few years interest in the heavy metal content of marine aerosols has increased, largely through concern that man may be affecting the heavy metal composition of atmospheric aerosols on a global basis, as well as through a general interest in the possible importance of eolian transport of trace metals to marine sedimentation. A complete discussion of heavy metals in the marine atmosphere is beyond the scope of this review, but a brief overview, considering the possible importance of the ocean relative to atmospheric trace metals, is worthwhile.

In contrast to studies of alkali and alkaline earth metals, virtually all studies of heavy metals in marine air have assumed that the metals have a continental source. Thus enrichment values such as those calculated for other chemical substances (e.g. $E_{Na}(X)$, where X = heavy metal) have not generally been determined. Comparison of the atmospheric concentration of the heavy metals with that expected on the basis of metal/Na ratios in bulk seawater results in very large enrichments (10^2 to 10^4). With crustal weathering as the main expected source for these elements, enrichments relative to average crustal material have usually been calculated, where enrichment of any element X, $E_{crust}(X)$, is defined as follows

$$E_{crust}(X) = \frac{(X/Al)_{atm}}{(X/Al)_{crust}} - 1, \qquad (5)$$

where X/Al is the mass ratio of X to aluminum in the atmosphere or the Earth's crust. A representative sampling of the crustal enrichment factors, as defined in Equation 5, observed for some selected trace metals in marine aerosols collected on filters is presented in Table 3. To facilitate comparisons, all the reported enrichments in the studies listed in Table 3 have been recalculated using Al as the reference element and utilizing the average crustal abundances of Taylor (1964). Since Al was not determined in the Gulf of Guinea study (Crozat et al 1973), Sc was used as a reference element and enrichments were calculated on the basis of Al, assuming a value of $E_{crust}(Sc)$ of -0.2. (Additional valuable information on the distribution of trace metals in soil-sized particles (radius greater than ~ 4 μm) over the world ocean is given by Chester & Stoner (1974) and Chester et al (1974) but is not included in Table 3.)

Judging from the data in Table 3, a number of the heavy metals have weathered crustal material as their source (e.g. Sc, Al, Fe, Th, Mn, Ce, Co, and perhaps Cr). Of course, mean crustal ratios can only be used to crudely approximate the relative composition of crustal material aerosols, owing to different types of crustal material and soils in various source areas and uncertainties concerning chemical fractionation processes during rock weathering. Thus variations of $E_{crust}(X)$ up to an order of magnitude may still indicate a crustal source for these elements. These and other problems in ascertaining the source of trace metals in aerosols utilizing crustal ratios have been discussed in some detail by Rahn (1975) and Duce et al (1975). However, a number of elements are highly enriched relative to both the crust and seawater: Zn, Cu, Cd, Hg, Sb, As, Pb, and Se, among others. Zoller et al (1974) pointed out that these highly enriched elements were rather volatile and suggested that high temperature processes, either natural or anthropogenic, might be responsible for the high concentrations of the elements observed. Indeed, Bertine & Goldberg (1971) and Natusch et al (1974) noted many volatile metals, including As, Sb, Cd, Pb, and Se, that are probably volatilized during coal burning, subsequently adsorbing or condensing primarily on the smallest particles. Duce et al (1975), however, suggested that the similar enrichment factors found for samples collected using identical techniques over the North Atlantic and at the South Pole, coupled with the short residence times of atmospheric particles (on the order of one week or so), long tropospheric mixing time between northern and southern hemisphere (6–12 months), and predominant source of anthropogenic particles in the northern hemisphere ($\sim 90\%$), indicates that the source of the high enrichments for these elements may be natural. Possibilities include volcanism and biological mobilization. Some of these elements may be biologically methylated in either the terrestrial or marine biosphere. Wood (1974) notes that methylated forms of As, Hg, S, and Se have been found in the marine environment. He predicted methylated forms of Hg and As in the atmosphere, and these have been detected by Johnson & Braman (1974; also unpublished data). Clearly, the importance of the biosphere, and in particular the marine biosphere, as a source for these elements in the atmosphere must be investigated in more detail.

Of particular interest to this review is the possibility that some of these elements may actually undergo chemical fractionation during atmospheric sea salt particle production at the sea surface. We have already seen that many heavy metals are concentrated in the surface microlayer, and Piotrowicz et al (1972) suggested that this should result in enrichment of these trace metals on the sea salt particles produced by bursting bubbles. These authors also point out, however, that the effects of any fractionation of trace metals during the bubble-bursting process may be overwhelmed by the presence of these metals in atmospheric particles having a nonmarine source. Relatively little information on the nature of the chemical associations of these

Table 3 Atmospheric heavy metal enrichments [$E_{crust}(X)$] in marine areas

Element	Location						
	South Pole	Atlantic N of 30° N	Lerwick, Shetland Is. (1972)	North coast of Norway	Gulf of Guinea	Oahu, Hawaii
Sc	−0.2	−0.2	−0.1	−0.4	−0.2	—
Al	0.0	0.0	0.0	0.0	0.0	0.0
Fe	1.1	0.4	0.7	0.9	0.7	1.6
Th	−0.1	—	2.8	1.8	—	—
Mn	0.4	1.6	3.6	4.0	—	1.6
Ce	3.4	—	0.7	1.3	1.6	—
Co	3.7	1.4	2.8	5.3	3.0	—
V	0.4	16	23	23	—	14
Cr	5.9	10	14	11	5.8	—
Zn	68	110	790	240	—	—
Cu	92	120	< 77	78	—	450
Cd	—	730	—	1200	—	—
Hg	—	—	< 700	—	1800	—
Sb	1300	2300	3600	3600	2400	—
As	—	—	1500	1900	—	—
Pb	2500	2200	3500	800	—	2900
Se	18,000	10,000	12,000	10,000	—	—
Reference	Zoller et al (1974)	Duce et al (1975)	Peirson et al (1974)	Rahn (1975)	Crozat et al (1973)	G. Hoffman et al (1972)

heavy metals in the sea surface microlayer is available. The possibilities are numerous, ranging from physical adsorption or chemisorption of trace metals on biological and inorganic particulate matter to dissolved metallo-organic coordination complexes with such atoms as N, O, etc. There have been numerous papers published on trace metals in seawater, but, except for some recent results on particulate trace metals, much of the data are rather unreliable; it is difficult to collect uncontaminated samples and to prevent subsequent contamination during storage and analysis. Since most literature on dissolved trace metals is somewhat questionable, data on the speciation of these elements in seawater, particularly with regard to organic complexes, is even less reliable. One possible exception is several papers indicating that a significant fraction of the copper in nearshore, coastal waters may be associated with organic material (Slowey et al 1967, Alexander & Corcoran 1967, Williams 1969, Foster & Morris 1971). Suffice it to say that this will be an interesting and important, as well as difficult, area for future research, both relative to chemical fraction considerations and marine chemistry in general.

A few laboratory studies were designed to investigate certain aspects of chemical fractionation of heavy metals. Van Grieken et al (1974) added carrier-free quantities of inorganic ^{65}Zn, ^{75}Se, and ^{22}Na to unfiltered coastal seawater and collected the particles produced by bursting bubbles of air generated below the water surface. Both ^{75}Se and ^{65}Zn showed enrichment in the bulk aerosol relative to the seawater, with ^{65}Zn generally having the greater enrichment. Higher enrichments were often observed when the bubble path length before bursting was increased from 1 cm to 10 cm. ^{65}Zn enrichments were generally less than ten and ^{75}Se less than three.

Wallace & Duce (1975) investigated the transport of particulate organic carbon (POC) and particulate trace metals (PTM) to the sea surface by rising bubbles in samples of surface water from Narragansett Bay using an adsorptive bubble separation technique. Nitrogen bubbles of ~1 mm diameter were allowed to rise through the sample contained in an all-glass column 70 mm in outside diameter and 2.4 m high. The froth or foam that accumulated at the surface was analyzed for particulate materials, as was the original sample and the bubble-stripped residue. Recoveries of POC in the foam ranged from 30% to 59%, whereas those of particulate Al, Mn, Fe, V, Cu, Zn, Ni, Pb, Cr, and Cd were generally greater than 50%. Wallace & Duce (1975) extrapolated their laboratory results to obtain a crude order of magnitude extimate of the bubble transport of POC and PTM to the ocean surface under open ocean conditions and suggested that this may be the primary mechanism by which the sea surface microlayer is enriched in particulate trace metals. Their study and that of Van Grieken et al (1974) illustrate the potential importance of bubble transport of certain forms of some heavy metals to the air sea interface and suggest that further work is necessary before ruling out chemical fractionation at the air sea interface as a cause for the apparently anomalous atmospheric concentrations of a number of these metals.

Boron

There has been relatively little interest in the atmospheric chemistry of boron, although several Japenese workers have reported $F_c(B)$ values in rain that vary from

50 to several hundred in marine areas (Sugawara 1948, Muto 1952, 1953, 1956). Attempting to explain these results, Gast & Thompson (1959) distilled seawater containing boric acid in the laboratory and found considerable boric acid boron but no detectable chloride in their distillate. They proposed that boric acid vaporizes from the sea surface into the atmosphere and is subsequently scavenged by rain. To support this suggestion, they passed air over the surface of dilute solutions of boric acid in distilled water at 25–32°C and collected the condensate from the subsequent evaporation. The condensate contained considerable quantities of boric acid, equivalent to ~60 μg B/liter. Gast & Thompson point out that the evaporation of boric acid from a seawater surface would be a function of both the boric acid concentration in seawater and the water temperature and suggest that this temperature effect might have caused the environmental differences observed by the Japanese investigators. Creac'h & Point (1966) measured boric acid in the gas phase in surface air on the coast of France and found a mean concentration of 56 ± 22 μg B/m^3, which is extremely high. They believed the source of the H_3BO_3 was the ocean.

Nishimura & Tanaka (1972) repeated the evaporation experiments of Gast & Thompson (1959) using seawater containing 20–60 times as much boric acid-boron as normal seawater. Assuming that the vapor pressure of boric acid varied linearly with concentration, they extrapolated their results to seawater containing normal boron concentrations, concluding that at equilibrium the evaporation condensate should contain $\leqq 1.1$ μg B/liter at 25°C, considerably less than that found by Gast & Thompson (1959). The condensate concentration of $\leqq 1.1$ μg B/liter is less than the excess B (i.e. the quantity of boron above what is expected on the basis of the B/Na ratio in seawater) found in precipitation over the ocean, 4.7 ± 1.1 μg B/liter. Nishimura & Tanaka (1972) therefore concluded that the ocean is not a source of boron but a sink.

Both investigations considered only evaporation of boron to the atmosphere and not chemical fractionation of boron on particles produced during bubble bursting. No studies have evaluated this possible mechanism for boron enrichment. However, Gast & Thompson (1959) note that atmospheric boron has been attributed to sources other than the sea, including dust, volcanic activity, pollution, and evaporation of boron compounds from plants. Our understanding of boron in the marine atmosphere is minimal at best.

CONCLUSIONS

Evaluation of the occurrence and extent of chemical fractionation of various substances during the production of atmospheric sea salt particles by bursting bubbles is difficult indeed. Two factors emerging from our discussion of the available data are perhaps most responsible for this difficulty:

1. Atmospheric particles that are not produced by the ocean but may contribute significantly to the concentration of a number of trace substances in the marine aerosol are present throughout the atmosphere over the world ocean. These particles include the so-called background aerosol and mineral dust, among others. Care in the selection of sampling sites and the collection of samples may greatly minimize the effects of non sea salt aerosols, but these particles are consistently present throughout the marine atmosphere.

2. Gaseous forms of many of the trace substances of interest in the particles coexist in the marine atmosphere, and extensive gas-particle exchange is likely. This may be most important for the halogens, sulfate, nitrogen compounds, boron, and even organic carbon and some trace metals such as Se, Hg, As, etc.

Certainly, the well-documented enrichment in the ocean surface microlayer of many of the substances we have discussed suggests that they should be enriched on the particles produced when bubbles burst through this layer. However, in many cases enrichments are likely to be swamped by the high concentrations of these substances already present in the atmosphere from other sources. Based on the available data, the only substances having positive enrichments of more than a few percent in the atmosphere that can be clearly ascribed to chemical fractionation occurring during sea salt particle production are I, $PO_4^{=}$, probably organic nitrogen and organic carbon, and possibly some heavy metals and K in biologically productive waters. The evidence suggests that the other substances discussed either show no enrichment in the environment, or if an enrichment is observed, it is apparently due to the presence of particles with a nonmarine source or to gas/particle interactions.

Further research in a number of areas should significantly enhance understanding of chemical fractionation processes. For example, we know virtually nothing about the chemical composition of particles less than about 0.5 μm radius over the ocean. Although many of these particles are known to have a nonmarine origin, the size of the smallest particles that can be produced by the ocean remains unknown. Investigation of the chemical composition of these very small particles is also critical in evaluating the importance of gas/particle interactions as a source for the apparent enrichment observed for some substances. Obviously simultaneous measurements of the gas and particulate phase of these substances are required in the field.

Surface-active organic material in the surface layers of the ocean plays a major role in the transport of certain trace substances from the ocean to the atmosphere. However, our knowledge of the chemical form and quantity of this surface-active material in ocean surface water is fragmentary. We know even less about the concentration and composition of organic material in the atmosphere and the chemical and physical nature of its associations with other trace substances. Further work is urgently needed in this area.

Finally, continued laboratory studies of air/sea exchange of matter in both directions are certainly necessary, and chemical fractionation experiments should be continued as well. A word of warning is crucial here, however. MacIntyre (1974b) has recently pointed out the many dangers and pitfalls that can arise in laboratory studies, particularly with regard to contamination of the model water system with surface active organic material – especially organic material with properties unlike those of surfactants actually found in the sea. MacIntyre (1974b) points out that only once in a decade has he been able to produce "a solution surface which was not detectably dirty by bubble-experiment criteria." His description of how this was accomplished only once should impress the problems of laboratory simulation of

air/sea exchange processes indelibly on the minds of all investigators working in this field.

As in all areas of natural science, studies of chemical fractionation at the air/sea interface require carefully planned field and laboratory programs. Many of the problems that result from improper sampling sites, poor collection techniques, inadequate analytical procedures, and contamination in all phases of field and laboratory work are now well documented. New problems will certainly arise, but the marked increase in overall quality of studies in this field over the past five years suggests that the next five to ten years should result in some definitive answers to many of the most important questions concerning chemical fractionation at the air/sea interface.

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