Geochemical fractionation during mass transfer from sea to air by breaking bubbles

By FERREN MACINTYRE,[1] *Departments of Chemistry and of Geology and Geophysics, Massachusetts Institute of Technology, Cambridge, Mass. 02139*

(Manuscript received April 23, 1969; revised version April 7, 1970)

ABSTRACT

Physico-chemical hydrodynamics of bubble-breaking and surface chemistry together will explain many of the anomalous ion-ratios reported for the marine component of atmospheric aerosols and precipitation.

The "enrichment" of phosphate in bubble-produced aerosol from a solution containing radioactive P-32 and Na-22 is defined as

$$E = \frac{\text{(P-32/Na-22) aerosol}}{\text{(P-32/Na-22) solution}} - 1$$

and is positive for all solutions studied. Phosphate is always present in excess in drops from breaking bubbles. For jet drops, E lies between 0.01 and 10; for drops from film caps which have drained and lost nearly all of their bulk solution, E may rise as high as 1 000. Phosphate is preferred to chloride as a counter-ion below positively-charged surfactants, and also seems to be bound to peptide-like uncharged materials.

The mechanism is not specific for phosphate, but can be invoked to explain the enrichment of any constituent of marine aerosol whose absolute ionic potential is greater than Na^+ or Cl^-.

Introduction

The ocean yearly puts into the atmosphere something between 2 and 10 billion tons of sea salt (Eriksson, 1959; Blanchard, 1963). This is something more than 3×10^{-11} gm/cm²-sec. These sea-salt particles serve as efficient raindrop nucleators and are returned to earth chiefly in precipitation. Analysis of rainwater for sea-salt components gradually showed that the chemical ratios of seawater are not preserved during this cycle, leading to Carl-Gustav Rosby's observation that "the transport of salts from sea to air is by no means a simple mechanical process", since the components "leave the sea surface in different proportions than those characteristic of seawater" (1959). Eriksson suggested that "some fractionation process seems to take place at the sea-surface, possibly involving organic matter derived from surface films" (1959). Sugawara used the phrase "syn-bubble-bursting fractionation" in an oral presentation (1959), distinguishing this sharply from later events which cause chemical separation during the atmospheric sojourn of a sea-salt particle.

There is, of course, no single process responsible for all chemical differences between oceanic and atmospheric sea salt. Special processes are known for certain elements: Gast & Thompson (1959) showed that boric acid could evaporate directly from the sea surface, and Miyake & Tsunogai (1963) showed that iodide could be photochemically oxidized by ultraviolet to volatile iodine, and so excape from the sea surface. In spite of these special cases—of which many (e.g. fluoride) remain to be elucidated—there is a fundamental process to be sought in the mechanism of the principal transfer agent, which is drop formation by breaking bubbles.

To eject the mass of salt mentioned above requires 10^{-1} jet drop per cm² per second over the world ocean. Using Blanchard's (1963) world-

[1] Present address: Marine Science Institute, University of California, Santa Barbara, Calif. 93106

annual-average whitecap coverage of 10^{17} cm^2, one finds about 3 bubbles breaking per cm^2-sec in whitecaps—which is about what one sees in surf zones.

Blanchard noted that bubble bursting was accompanied by electrical charge separation (1963)—although quantitatively the charge difference is far too small to be detectable chemically as ion-fractionation. Later he observed that droplets downwind from breaking surf carried more than monolayer coverage of surface-active material (1964). Both of these phenomena arise from the hydrodynamics of breaking bubbles.

One of the difficulties with Eriksson's surface-film conjecture is to imagine how a physico-chemical surface phenomenon, acting only over molecular distances, can affect the large-scale transfer of matter from sea to air. A second difficulty lies in visualizing the "surface" of the ocean as a region of different composition from bulk seawater. This is particularly difficult for classical oceanographers, to whom "surface" has traditionally meant any sample collected in an open bucket instead of a Nansen bottle.

Nevertheless, microscopic processes completely dominate the transfer of matter from sea to air. This fact was intuitively understood by the workers who sought chemical fractionation in the bubble-breaking process (Köhler & Båth, 1952; Komabayasi, 1962; Bloch et al., 1966), even though the mechanism remained mysterious. Perhaps some of the bizarre mechanisms proposed caused undue skepticism of otherwise valid experimental results.

The mechanism is simply the "surface mic-

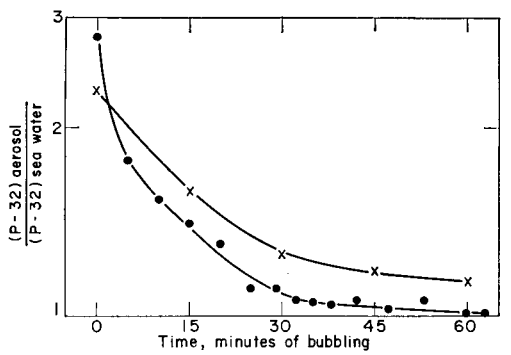

Fig. 1. Enrichment ratio of radioactive phosphorus-32 in spray from breaking bubbles in seawater. The decline in enrichment ratio with time represents loss of a phosphorus carrier from the seawater, not loss of P-32 itself.

Table 1. *Distribution of phosphate after bubbling*

	Sutcliffe et al. (1963) (conc) sample / (conc) original	This work (counts/ml) sample / (counts/ml) orig.
Original sea water	1.00	1.00
Residual sea water after bubbling	0.87	0.87
Spray	1.41	1.54
"Particulate" (0.45 μm filter)	1.08	0.88
"Soluble"	0.33	0.66

rotome" effect produced by the hydrodynamics of bubble rupture. MacIntyre has discussed the energetics of this process (1968), showing that there is sufficient surface-free energy present to eject the jet drops after dissipating nearly half the available energy by viscosity. The ascending jet that ejects droplets into the atmosphere is composed entirely of material from the upper few microns of the ocean, driven inward not by surface tension gradients (which are both to small and too slow-acting) but by the sharp pressure gradients caused by the changing curvature of the bubble (MacIntyre, unpublished data). High-speed photographs show that the interior surface of the bubble is subjected to an almost scraper-like action by the inward-moving edge of the collapsing cavity, which can crowd surface molecules together with sufficient momentum that multilayer coverage of the resulting jet drops is possible.

Experimental apparatus and results

The first experiments simply verified the reports of Sutcliffe et al. (1963) that fractionation occurred during transfer of phosphate from sea to aerosol. In these experiments, 250 ml of seawater containing 10 μCi of P-32 as H_3PO_4 were vigorously bubbled, and all of the spray collected. The resulting distribution of P-32 after bubbling is compared with the earlier results in Table 1. The time dependence of two such runs is shown in Fig. 1, which plots the radioactivity ratio of the aerosol against time, or, since the rate of bubble production from the glass frit ori-

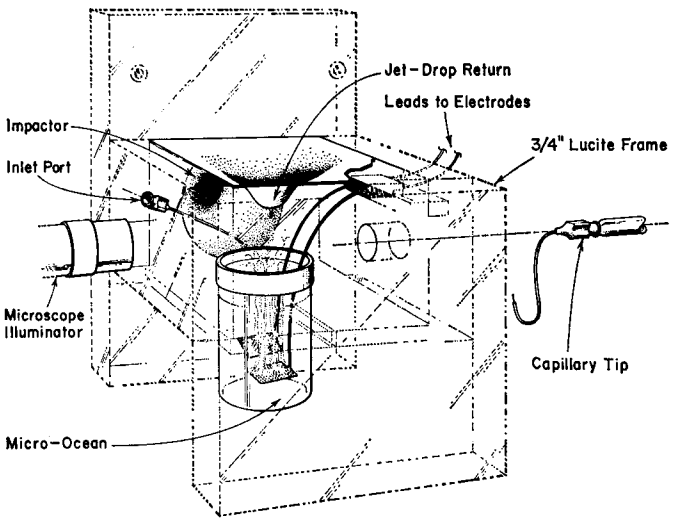

Fig. 2. Experimental "micro-ocean" for collecting bubble-produced spray with minimum contamination. The aerosol impactor behind the micro-ocean has an entrance configuration isokinetic for still air, and collected 1 liter/min of air and nearly all of the droplets produced. The apparatus was operated inside a clean bench, so that air entering the inlet port and other unsealed orifices was nearly free of particles.

fice was constant, against the volume of spray removed. The surface of the seawater was covered with a variety of bubble sizes, some stable, some breaking quickly, much as is observed in the decay of oceanic bubble patches.

Later experiments made use of the "micro-ocean" of Fig. 2. 100 ml of solution containing 10 μCi each of gamma-emitting Na-22 as NaCl and beta-emitting P-32 as Na_3PO_4 were contained in a glass weighing bottle. Two alternate bubble sources were used: an oscillating capillary tip (MacIntyre, 1967) would make monodisperse bubbles, or platinum electrodes would decompose water to make large numbers of extremely fine bubbles of hydrogen and oxygen (with some chlorine). No effects attributable to differences in methods of generating bubbles were detected. More surprising, the size distribution of drops did not seem to reflect either the mode of generating bubbles nor their size at generation. This may be because small bubbles tend to coalesce into larger bubbles before final rupture, so that the size distribution at rupture is relatively independent of size at generation.

The largest jet drops are too heavy to remain airborne. These were collected by a contoured cover of acid-washed "Parafilm" and thence dripped back into the bulk solution.

To prevent adventious contamination from reaching the water surface, the micro-ocean was enclosd in a plastic box, and the box inside a clean bench which filtered the air through activated charcoal and a Cambridge "Absolute" filter. Teflon tubing inserted through the inlet port (a large gauge hypodermic needle) served to replenish the solution or add tracers to it.

The smaller drops are invisible by normal illumination, but scatter light strongly in the forward direction and so can be seen by looking along a beam of collimated light from the microscope illuminator.

Fig. 3 shows the size distribution of droplets as classified by the 7-stage aerosol impactor whose horizontal inlet is visible behind the micro-ocean in Fig. 2. The ordinate scale represents the actual number of drops captured in a given run, as measured by the amount of Na-22 present, referred to the volume of a drop of diameter D. The two bracketing light lines labelled "Beaufort n" are taken from Eriksson (1959) and Woodcock (1953), and represent the relative particle spectra for naturally occurring marine aerosols at different wind forces. Most runs were made with artificial seawater in the vain hope that the trace organic content could thereby be better controlled: these runs are shown by the sets of horizontal lines. A heavy dashed line runs through the mean trend of these results,

with a sharp change of direction at 6 microns. A similar trend line for seawater shows this corner characteristically displaced toward smaller particles, although the slopes of the linear portions are comparable to the artificial solutions. The flatter slopes of the experimental samples compared to the natural distribution represents an excess of large drops and is an artifact of the horizontal location of the impactor entrance. Such large drops are frequently not jet drops, but film drops which are ejected nearly horizontally by the rupturing of the thin film caps. They are too heavy to remain airborne in still air, and although many strike the water surface at high velocity within a cm of the bubble, some will be ejected in the direction of the impactor and be collected.

In order to examine chemical fractionation directly, without introducing handling steps which might themselves lead to fractionation, the following procedure was used. The aerosol drops impacted on the various stages and evaporated, leaving behind a sometimes invisible salt deposit at the center of a 2.5 cm glass plate. Immediately after a run, the plate was sprayed with 0.2 mg/cm² of Krylon lacquer to bind the salt permanently onto the glass, and the slides were counted with the sample chemically unaltered from its condition at capture.

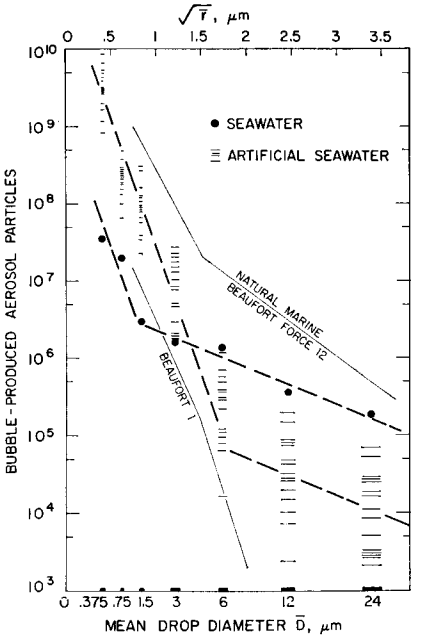

Fig. 3. Drop size distribution for bubble-produced aerosols. The solid lines labled "Marine: Beaufort *n*" are taken from the data of Eriksson (1959) and Woodcock (1953). The horizontal bars represent a number of runs from NaCl solutions. The bar length is the uncertainty in the mean drop diameter collected by a given stage of the impactor. ●, typical run from natural seawater. The plot is linear in $\sqrt{F}$, as shown by the scale at the top.

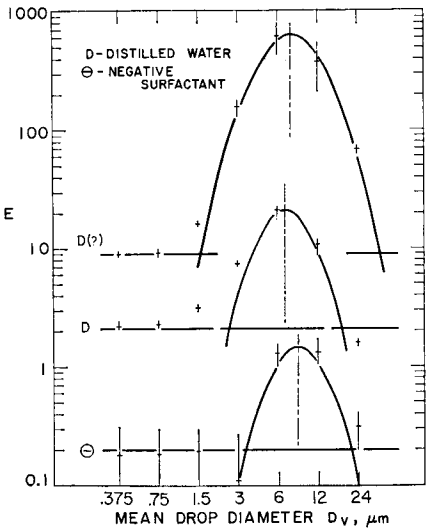

Fig. 4. Enrichment of phosphate *vs.* drop diameter for "distilled water", showing the decrease in enrichment that occurs when a negatively charged surfactant is added. The error bars on the points represent one standard deviation, based on the aggregate errors in counting statistics. The parabolic peak at 8 μm apparently represents a contribution from the well-drained film caps which are nearly free of both water and sodium. (After MacIntyre & Winchester, 1969).

Analysis was by simultaneous beta- and gamma-counting. The data were reduced by a computer program which also provided standard deviation estimates which are shown in Fig. 4 through 6 by the vertical extent of the data points. (The similar uncertainty in the volume-average diameter D of the drops is indicated by the width of the data bars in Fig. 3.) The method of data analysis has been described elsewhere (MacIntyre & Winchester, 1969).

The data are reported as "enrichment" defined as

$$E = \frac{(PO_4^{3-}/Na^+)\ \text{aerosol}}{(PO_4^{3-}/Na^+)\ \text{solution}} - 1$$

An enrichment of 3 means that for every phos-

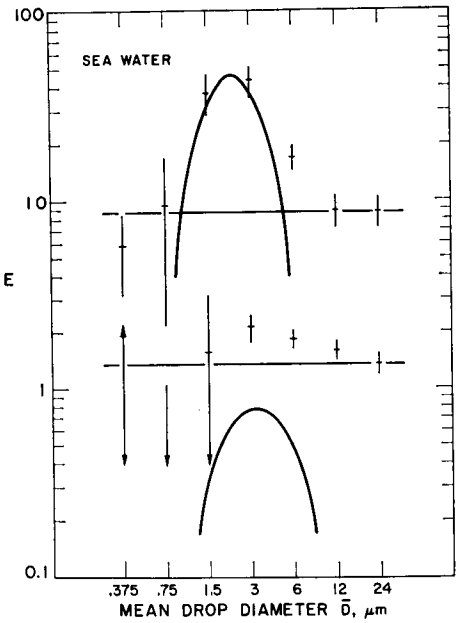

Fig. 5. Enrichment of phosphate *vs.* drop diameter for seawater: The enrichment peak occurs at a smaller drop size for seawater than for any of the artificial solutions used. Bubbles for the lower run were monodisperse in size, and very few small jet drops were formed: hence the large error bars on the three small-diameter points.

phate ion expected in a given volume, there were 3 extra, for a total of four.

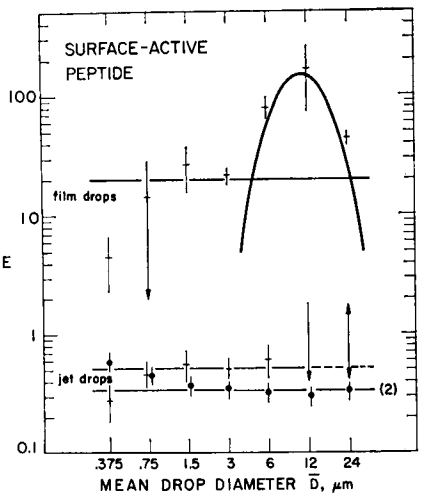

Fig. 6. Enrichment of phosphate *vs.* drop diameter for non-ionic surfactant Maypon 4C in NaCl solution. The lowest run, identified with (2)' represents two nearly identical runs. The upper run resulted from large bubbles with much film-cap area; the lower runs were from small bubbles, which make only jet drops.

Fig. 4 (taken from MacIntyre & Winchester (1969)) is representative of the best data obtained from fractionation experiments in distilled water. Fig. 5 is characteristic of seawater runs, and shows the same qualitative features as Fig. 4 although in less orderly fashion.

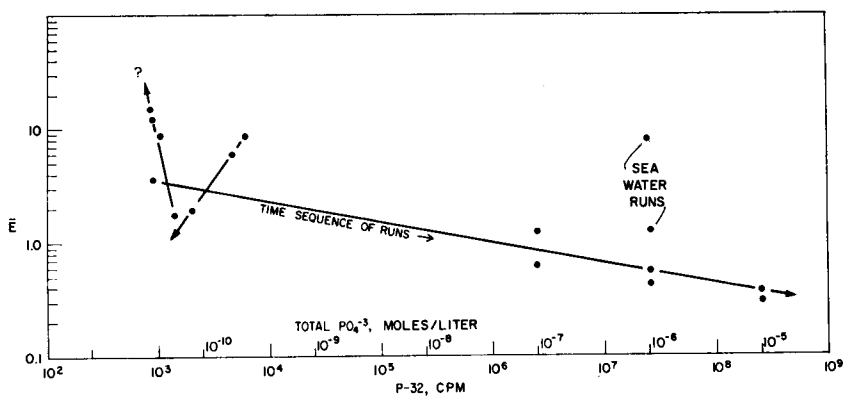

Fig. 7. Phosphate enrichment *vs.* concentration (and time). The arrows connect suites of runs taken from the same solution. Time increases in the direction of the arrows, and it is to be expected that the enrichment will decrease with time, as surfactant is removed. (The one upward-pointing arrow is anomalous.) Macroscopic increments of non-radioactive phosphate were added serially to one suite to bring the total phosphate concentration into the region of seawater to demonstrate that enrichment is not dependent upon having only trace amounts of phosphate present. The enrichment found for natural seawater, although higher than the runs at comparable concentration in artificial solution, is comparable to the enrichment found for the initial runs of all suites.

Fig. 6 shows the results of runs using a non-ionic surfactant similar in some respects to material from the sea surface. It is "Maypon 4C" (Stepan Chemical Co.) and is an ill-characterized material made by reacting coco-acid chloride with hydrolyzed collagen. The resulting material has a 12-carbon hydrophobic chain attached by a peptide bond to 2 to 5 amino acid residues. This structure allows binding of phosphate to an $-NH_4^+$ group on hydroxylysine and to $-OH$ groups on both hydroxylysine and hydroxyproline. (Phosphate is known to form bonds with both of these groups. (Briggs, 1940; Drabikowski, 1963; Katchmann & VanWazer, 1954; Glimcher & Crane, 1964; Perlmann, 1955).

Fig. 7 shows the average enrichment for all size-classes of a run for 16 runs, organized into three suites or sample sets collected sequentially from the same bulk solution. The arrows indicate the time sequence of collection. The abscissa is total phosphate concentration on the assumption that the "carrier-free" P-32 (made from S-32 by an n, p reaction) was indeed free of non-radioactive phosphate. The high concentrations represent additions of non-radioactive Na_3PO_4.

Discussion

Micelles are common structures in colloid chemistry: 50 to 100 hydrophobic molecules with hydrophilic groups on one end cooperate to form a spherical particle with all the hydrophobic portions inside and the hydrophilic group in contact with the water. If these hydrophilic groups are charged, as is frequently the case, the colloidal particle collects around itself a layer of counter-ions of opposite sign to balance the high charge, creating an electrical double layer. Ions of high ionic potential (large charge, small radius) are electrostatically favored as counter-ions.

The same behavior occurs at air–water interfaces. The total energy of the system is lowered by 750 cal/mole of $-CH_2-$ groups which are removed from contact with water, so that in the low energy state the hydrophobic portions will be squeezed into the air phase by the internal pressure of hydrogen-bonding between water molecules. Again, a layer of counter-ions just beneath the surface is required for local charge balance, and small, multiply charged ions are preferentially selected. Calcium and magnesium, for instance, are absorbed with 50- to 200-fold preference to sodium as counter ions beneath negatively charged surfactants (Judson et al., 1953; Walling et al., 1957; Shinoda & Ito, 1961)—but this fact is familiar to anyone who has bathed in hard water and watched sodium stearate turn to a surface scum of calcium stearate. The same behavior of course occurs for negatively charged surfactants, and it is also observable that ions of the same charge are rejected by the surfactant. (Notice in Fig. 4 that the lowest phosphate enrichment is found in the presence of a negatively-charged surfactant.)

In a system containing a single charged surfactant, only oppositely-charged counter-ions will be accepted. But in a mixed system (such as the ocean) with surfactants of both signs, both anions and cations are accepted as counter ions, because they can lower the total energy by fitting between the large surfactant molecules.

In many respects a bubble may be regarded as a peculiar sort of micelle, complete with ordered surfactant, counter-ions, and spherically symmetrical electrical double layer. All three of these components interact with the hydrodynamics of bubble rupture to produce unexpected effects: particle formation (Sutcliffe et al., 1963; MacIntyre, 1965), charge separation (Blanchard, 1963), and chemical fractionation.

The first experiments reported here verified the "Baylor effect", showing again that inorganic phosphate in seawater is adsorbed onto bubbles, partially converted to particulate form (presumably by attachment to surfactant which is then hydrodynamically compressed by the surface flow of bubble rupture into a stable insoluble particle) and ejected into the atmosphere with considerable enrichment compared with the major ions of seawater. The time-decay of this transfer observed upon continued bubbling of small volumes of seawater suggests that the enrichment of the aerosol depends upon some constituent of seawater which is present in lower concentration than the phosphate and which is depleted as it is transferred to the droplets. The variability of the results suggests that this constituent is itself a variable in natural seawater.

If the rate of removal had been directly proportional to the amount of some single constituent remaining in the seawater, Fig. 1 would have been linear (semi-log plot). Instead, the rate of phosphate removal decreases with time, as the nature of the natural surfactant changes with removal of the most active material.

Fig. 3 shows that the drop-size spectrum of the micro-ocean is similar to naturally occurring marine aerosol particles. The observations made in these highly artificial experiments can probably be extrapolated to the real ocean with some confidence, but one characteristic difference should be mentioned. This is the location of the break in the trend curve (----), which is at 6 μm for artificial solutions, but shifts to 1 μm for seawater. A similar downward shift in the peak of the film-drop enrichment parabola is evident upon comparing Fig. 4 (artificial solutions; 9 μm maximum) with Fig. 5 (seawater, 2 μm maximum). This shift is unexplained, but may be related to parameters such as surface-tension/surface-viscosity or surface-viscosity/bulk-viscosity which were not monitored in these experiments.

Fig. 4 (distilled water) is shown because these runs gave the least statistical error (vertical bars at data points are ± 1 standard deviation) and so permitted the parabolas to be fitted most accurately. The "parabolas" are only apparent: on a linear plot they would be seen to be typical Gaussian distributions. The larger error bars at the peaks result from the smaller samples colleted on these impactor stages: the conclusion is that these peaks represent small numbers of relatively large drops from well-drained film caps which have lost most of their bulk water (and sodium). There seems to be no other explanation for the 600-fold enrichment. Some discussion of a mechanism for making such large drops from thin films appears in MacIntyre (1965).

The location of the peaks does not change appreciably upon going from distilled water to various salt solutions, nor are the peaks present in samples which do not form stable large bubbles. These observations are supported by a wider range of runs that are shown here (MacIntyre, 1965), but both can bee seen in Fig. 6.

The decrease in enrichment with time shown in Fig. 1 reappears in Fig. 7 for two of the three suites shown. The remaining suite, which shows a marked increase in enrichment as successive runs were made, is anomalous. The only explanation that comes to mind is that the sources of airborne surfactant aerosol near the laboratory were particularly active that day. (Depending upon wind direction, the MIT laboratory was redolent of burning tires, household detergent, or chocolate candy. A few sub-micron particles of any of these that escaped capture by the air filter would have contained enough surfactant to obscure the removal by bubbling.)

The important conclusions to be drawn from Fig. 7 are three. (1) The enrichment pattern within a suite is orderly; between suites, random, reflecting the variable nature of surfactant contamination. (2) The original enrichment for all runs lies somewhere near 3, which is also the approximate mean value for the seawater runs. (3) Enrichment occurs over a range of phosphate concentrations extending from 3.10^{-11} to 10^{-5} M.

In fact, it is nearly impossible to avoid phosphate enrichment. Attempts were made to produce clean-surfaced water by double distillation (first from alkaline permanganate, then from 50% phosphoric acid), with no exposure of liquid surfaces to the atmosphere. All such attempts failed. However, surfactants can be absorbed on the extensive surface of flocculent precipitates. An effective floc occurred—to be brutally honest—when a stainless steel hypodermic needle in use as a bubble orifice slowly reacted with a 10^{-4} M solution of H_2NaPO_4, added to one of the high-phosphate runs. No enrichment was observed in the presence of such a floc, indicating that the contaminants normally present at the surface were instead held by the active surface of the precipitate, and that in the absence of such organic molecules at the surface, no enrichment of jet drops occurs.

Dean (1963) has given an interesting and relevant recipe for making New Zealand rain: 1 liter of distilled water, 0.5 ml of seawater, and 4 mg of dried plankton and algae. This mix approximates the major ions in rainfall and also accounts for the biologically important nitrogen, phosphate, and iodine. (So much nitrogen falls on coastal New Zealand that artificial fertilizers are not needed for some miles inland (Wilson, 1959.) But 8 mg of organic material per ml is 2 000 times the normal organic concentration of seawater. Either an organic monolayer is compressed onto jet drops (which make admirable raindrop nuclei when dried), or jet drops transfer surface particulate material into the atmosphere. The monolayer hypothesis requires that the ejected surface layer be no more than 0.1 μm thick; on the other hand, Kohn (1969) has shown that jet drops do remove graphite particles from a water surface rather efficiently.

For some purposes it is more convenient to use the fractionation *ratio* $F = E + 1$ but mechanistic studies E is the natural measure. Consider

calcium enrichment from seawater; the sodium concentration [Na] remains unchanged from bulk seawater to jet drop but the calcium concentration [Ca] is increased by the addition of a purely surface component. If we examine a volume of jet drops which have come from, say, 1 cm² of bubble interior surface, we can associate a thickness t (cm) with this sample. Then the total calcium is the sum of the bulk concentration $[Ca^\circ]\cdot t$ (ions/cm³·cm) plus the surface contribution [Ca*] (ions/cm²), and

$$E=\frac{[Ca^*]+[Ca^\circ]\cdot t}{[Ca^\circ]\cdot t}-1=\frac{[Ca^*]}{[Ca^\circ]\cdot t}$$

where $[Ca^\circ]=M\cdot 6.10^{20}$ ions/cm³ if M is the molarity, $t=\delta\cdot 10^{-4}$ cm if δ is in μm, and $[Ca^*]=n.\ 10^{14}$ ions/cm² if n is in units of ions/100 A², which is typical of surfactants ionic areas at low surface pressures.

Then

$$E=\frac{n\cdot 10^{14}}{M\cdot 6\cdot 10^{20}\cdot\delta\cdot 10^{-4}}=\frac{n\cdot 10^{-2}}{6M\delta} \qquad [1]$$

and if $M=10^{-2}$ as in seawater, $n=1$ and $E=2$, we obtain

$$\delta\doteq\frac{1}{12}\mu\text{m}$$

This agrees well with the monolayer hypothesis, but seems remarkably thin. Another estimate of the thickness is a simple mass balance between the jet drop and the bubble interior. This estimate is very sensitive to the relation between drop size and bubble size, which is not well known. For bubbles near 1 mm, the drop is roughly one-tenth the bubble diameter. If this drop is assumed to come from a uniform thickness t destributed over some fraction f of the bubble interior, we have for a mass balance

$$f\cdot t\cdot\pi D^2=\frac{\pi}{6}\left(\frac{D}{10}\right)^3$$

$$t=\frac{D}{6f}10^{-3}$$

and if $f=1/6$ and $D=0.1$ cm, we find $t=10^{-4}$ cm $=1$ μm.

On the other hand, an expression which fits the small-diameter end of Blanchard's (1963) drop-size data is

$$d^3=0.1\ D^2$$

where both the drop diameter d and the bubble diameter D are in microns, so that the constant 0.1 carries a hidden dimension of 1 μm. Then

$$f\,t\,\pi D^2=\frac{\pi D^2}{6\,10}$$

and

$$t=\frac{1}{10}\mu\text{m}$$

Iribarne & Mason (1967) have used the relation (also based on a mass balance)

$$t=\frac{D}{600}\text{cm}$$

for a thickness of 1.6 μm if $D=0.1$ cm.

MacIntyre (1969) concluded from an energy analysis that the thickness should lie between 0.5 and 20 μm, but was unable to narrow the range because the true mechanism of rupture is more complicated than these simple models can cope with. For instance, physically the jet-drop material is more likely to come from a cup-shaped region whose thickness varies with distance from the bubble axis. Chemically, there will be a distribution constant $K_d=[Ca^*/Ca^\circ]$ which relates M and n of equation [1] and which differs for each surfactant and each counter ion.

However, it seems safe to conclude that the ejected surface thickness is small compared to the usual oceanographic concepts of "surface water".

Implicit in these considerations of mechanism is a process of surface compression, so that there need not be complete monolayer coverage to produce observable enrichment. This is important to geochemical processes because the ocean is not covered by a monolayer (Adam, 1963) except in unusual situations such as polluted inshore waters and near petroleum-handling installations. Enrichment has been observed at surface concentrations as low as 10^{-4} monolayer (MacIntyre & Winchester, 1969).

There are several myths (or semantic quibbles) which have perhaps made enrichment appear unduly mysterious. First, one sees such sentences

Table 2. *Enrichment of selected seawater ions in aerosol, precipitation or physico-chemical systems*

Cations are referred to Na, anions to Cl, because the marine aerosol Cl/Na ratio is not firmly known. Seto et al. (1969) suggested that the Cl/Na ratio in Hawaiian rain is about 1.66 (seawater = 1.80), which agrees with Junge & Werby's (1958) value for coastal rains.

Sample type (no. of samples)	Enriched ion						Reference	Notes
	Ca	Mg	K	SO_4	Br	PO_4		
Adsorption at interface	72 252	— —	— —	— —	— —	— —	Shinoda & Ito (1961)	Interface taken as 1 μm thick for calculations.
Adsorption at interface	—	—	—	1.2 4.0	—	—	Judson et al. (1953)	
Enrichment in foam	8.8 30.3	28.2 49.0	— —	— —	— —	— —	Walling et al. (1957)	
Aerosol carryover in distillation	1.85 2.04	—	1.62 4.72	— —	1.75 25.1	— —	Bloch et al. (1966)	
Aerosol carryover from boiling seawater (17 liters)	—	—	12.4	1.65	1.41	—	Bruyevich & Kulik (1967)	Distilled in quartz
Annual average, coastal rains (5)	1.55	—	0.47	—	—	—	Junge & Werby (1958)	Selected to minimize continental contribution.
Bubbled seawater (4)	—	—	—	—	—	0.22	Bruyevich & Kulik (1967)	
Mid-Pacific rain (5)	—	—	0.52	4.6	—	—	Bruyevich & Kulik (1967)	Authors do not comment on the difference between Pacific and Indian ocean rains. Samples taken along longitudinal transects.
Mid-Indian Ocean rain (4)	—	—	4.5	1.8	—	—	Bryuevich & Kulik (1967)	
Antarctic snow (7)	3.15	5.5	—	3.8	—	—	Matveyev (1961)	An excess of anions argues against aluminosilicate dust contamination

as "the Na/K ration is greatly reduced, while the SO_4/Cl ratio is increased". The phrasing seems to imply that there are two processes at work, whereas if the minor constituent is referred to the major, the ratios uniformly increase (see Table II) and only a single mechanism seems called for. Second, the terms "distillation" and "mechanical evaporation" are misleading when used to describe the entrainment of jet drops into the gas phase. It should be clear that non-volatile ions are unaffected by evaporative processes. Third, there have been reports that enrichment is mass-dependent, perhaps increasing linearly with the log of ionic weight. This last point is of sufficient interest to warrant more discussion.

The slope of the enrichment-*vs.*-log(mass) curve of one author (Komabayasi, 1962) predicts a two-fold increase of the heavy calcium isotope Ca-48 over the common light isotope Ca-40. Such a purely physical enrichment would eliminate any complicating chemical effects—and, of course, would be of immediate interest to weapon-makers. Careful experiments looking for such an isotopic effect, using techniques developed for examining calcium isotopes in the natural environment (Corless, 1963) were undertaken, and no such mass-dependent enrichment was found (MacIntyre & Corless, unpublished results). The original reports of mass-dependence (whose data looked very convincing) are probably to be attributed to the fact that heavy ions tend to be enriched because they also have a high ionic potential. This tendency, plus the wide and uncontrollable variability of enrichment, seems to have given a coincidental log-linear relationship. The later data do not indicate that enrichment is sufficiently reproducible to make such a correlation meaningful.

The experimental work described here treats

only of the phosphate/sodium ratio. Nevertheless, it is suggested that the mechanism described is a general one which can be used to explain much related data. For convenience, some of the more pertinent and reliable enrichment data from other investigations are summarized in Table 2. Perhaps the only conclusions that can be drawn from such a compilation are the now familiar pair: enrichment is favored by high ionic potential, and the data are typically unreproducible. However, it seems probable that the major ions of seawater are enriched in the marine aerosol with respect to Na^+ and Cl^-.

In particular, both MacIntyre (1966) and Brujevich & Kulik (1967) have suggested before that the normal sea surface must be a source of a considerable portion of the so-called "excess sulfate" in the atmosphere. It appears that the sea-surface contribution might easily be double the expected value. However, it must be emphasized that there still exist no reproducible unexceptionable analyses of precipitation or aerosol far from land which distinguish satisfactorily between terriginous and marine material with sufficient accuracy to allow an unequivocal answer to the origin of the excess sulfate, nor has sulfate enrichment been studied in the laboratory. It may be significant that sulfate is known to bond to the sugar moiety of surfactants such as sucrose monolaurate (Ossipow et al., 1957).

Conclusions

The combination of counter-ion attraction to surfactant films, and the ability of small bubbles to eject a micron-thin slice of the bubble interior surface as jet drops, is sufficient to account for much of the reported chemical fractionation in the transfer of salt from sea to air. This mechanism does not rule out special processes for certain substances (such as boric acid, iodine, and fluorine), but it provides a simple and unifying hypothesis for the anomalies of ion-distributions in the marine atmosphere.

The extreme variability of enrichment in the field is matched by a similar variability in "carefully controlled" experiments in the laboratory. This intractability apparently reflects the difficulty of monitoring the nature and quantity of surface-active contaminants.

The ubiquity of enrichment suggests that the whole concept of ionic "excess" deserves attention. Traditionally, the amount of any ion above that required to make its enrichment relative to chloride equal to zero has been thought of as an excess, and special hypotheses have been postulated to account for it. The rather scanty data reviewed here suggest that excess of 10% to 400% require no such explanations, since such enrichments are observed during the process of forming the primary aerosol. Before a clear picture of atmospheric geochemistry can be drawn, it will be necessary to establish meaningful oceanic time-and-space average enrichment patterns for the major components of seawater.

In closing it is important to note the possibility of removing phosphate from sewage effluent by bubbling after adding an appropriate surfactant "collector". Phosphate in effluent is the nutrient primarily responsible for the increasingly common dystrophication of natural waters in which an uncontrollable growth of slime algae is followed by complete oxygen consumption and sulfide production as organic matter decomposes in the lower levels, leading ultimately to the complete destruction of life, as in Lake Erie. Such a phosphate removal process is under investigation by Winklehaus (1970): it may be possible to prevent sewage dystrophication of natural waters. Lake Tahoe may yet be kept blue.

Acknowledgements

This work owes much to discussions with John Winchester, Edward Baylor, Duncan Blanchard, Gordon Riley, and Peter Wangersky. Various aspects have been supported by the ONR (Project NR 083-157), by the MIT Computation Center, and by the NSF (GA-968).

REFERENCES

Adam, N. K. 1963. The Pollution of the Sea and Shore by Oil: A Report Submitted to the Council of the Royal Society. Roy. Soc. London, 27 pp.

Blanchard, D. C. 1963. The electrification of the atmosphere by particles from bubbles in the sea. In *Progress in Oceanography* (ed. M. Sears) *1*, Chapter 2, 71–202. Pergamon Press, N. Y.

Blanchard, D. C. 1964. Sea-to-air transport of surface-active material. *Science 146*, 396–397.

Bloch, M. R., Kaplan, D., Kertes, V. & Schnerb, J. 1966. Ion separation in bursting bubbles: An explanation for the irregular ion rations in atmospheric precipitations. *Nature 209*, 802–803.

Brujevich, S. V. & Kulik, Ye. Z. 1967. Chemical interaction between the ocean and the atmosphere (salt exchange). *Oceanology 7*, 279–293.

Corless, J. T. 1963. Variations in the ratio Ca-48/(total calcium) in the natural environment. Thesis, MIT. 59 pp.

Dean, G. A. 1962. The iodine content of some New Zealand drinking waters with a note on the contribution from sea spray to the iodine in rain. *New Zealand J. Sci. 6*, 208–214.

Eriksson, E. 1959. The yearly circulation of chloride and sulfur in nature: meteorological, geochemical, and pedological implications. Part. I *Tellus II*, 375–403.

Gast, J. A. & Thompson, T. G. 1959. Evaporation of boric acid from seawater. *Tellus II*, 344–347.

Iribarne, J. V. & Mason, B. J. 1967. Electrification accompanying the bursting of bubbles in water and dilute aqueous solutions. *Trans. Farad. Soc. 63*, 2234–2245.

Judson, C. M., Lerew, A. A., Dixon, J. K. & Salley, D. J. 1953. Radiotracer study of sulfate ion adsorption at the air/solution interface in solutions of surface-active agents. *J. Phys. Chem. 57*, 916–923.

Junge, C. E. & Werby, R. T. 1958. The concentration of chloride, sodium, potassium, calcium, and sulfate in rain over the United States. *J. Meteor. 15*, 417–425.

Köhler, H. & Båth, M. 1952. Quantitative chemical analysis of condensation nuclei from seawater. *Nova Acta Regiae Soc. Sci. Upsaliensis, Ser. IV*, 15, 4–24

Kohn, H. W. 1968. Bubbles, drops, and entrainment in molten salts. ORNL-TM-2373, 19 pp.

Komabayasi, M. 1962. Enrichment of inorganic ions with increasing atomic weight in aerosol, rainwater, and snow in comparison with sea water. *J. Meteor. Soc. Japan 40*, 25–38.

MacIntyre, F. 1965. Ion fractionation in drops from breaking bubbles. Thesis, MIT. 271 pp.

MacIntyre, F. 1966. Fractionation in chemical transport from sea to air: phosphate, organic matter, and bubbles. In *Abstracts of papers, II International Oceanographic Congress, 30 May–9 June 1966*. Nauka, Moscow.

MacIntyre, F. 1967. Vibrating capillary for production of uniform small bubbles. *Rev. Sci. Inst. 38*, 969–970.

MacIntyre, F. 1969. Bubbles: A boundary-layer "microtome" for micron-thick samples of a liquid surface. *J. Phys. Chem. 72*, 589–592.

MacIntyre, F. & Winchester, J. W. 1969. Phosphate ion enrichment in drops from breaking bubbles. *J. Phys. Chem. 72*, 2163–2169.

Matveyev, A. A. 1961. The chemical composition of snow in the Antarctic. *Gidrokhimicheskiye materialy, Novocherkassk, 34*, cited in Bruyevich & Kulik, 1967.

Miyake, Y. & Tsunogai, S. 1964. Evaporation of iodine from the ocean. *J. Geophys. Res. 68*, 3938–3993.

Ossipow, I., Snell, F. D. & Hickson, J. 1957. The surface chemistry of alkyl esters of sucrose. *2nd Internat. Cong. on Surface Activity 1*, 50–55.

Rossby, C.-G. 1959. Current problems in meteorology. In *The Atmosphere and the Sea in Motion* (ed. B. Bolin), p. 44. Rockefeller Inst. Press, N. Y.

Seto, Y., Duce R. A. & Woodcock, A. H. 1969. Sodium-to-chlorine ratio in Hawaiian rain as a function of distance inland and of elevation. *J. Geophys. Res. 74*, 1101–1103.

Shinoda, K. & Ito, K. 1961. Selective adsorption studies by radiotracer technique: The selective adsorption between calcium and sodium ion at the ionized interace. *J. Phys. Chem. 65*, 1499–1502.

Sugawara, K. 1959. Syn-bubble-bursting fractionation of sea salt. *Internat. Oceanographic Congress Preprints*, 875–877.

Sugawara, K. 1961. Chemistry of ice, snow and other water substances in Antarctica. *Antarctic Record (Japan) II*, 116–120.

Sutcliffe, W. H., Jr., Baylor, E. R. & Menzel, D. W. 1963. Sea-surface chemistry and Langmuir circulation. *Deep sea Res. 10*, 232–243.

Walling, C., Ruff, E. E. & Thornton, J. L. Jr. 1957. The adsorption of cations by anionic foams. *J. Phys. Chem. 61*, 486–489.

Wilson, A. T. 1959. Surface of the ocean as a source of air-borne nitrogenous material and other plant nutrients. *Nature 184*, 99–101.

Winklehaus, C. 1970. Phosphate stripping from dilute solutions by surface active materials. Thesis, Department of Civil Engineering, University of Michigan.

Woodcock, A. H. 1953. Salt nuclei in marine air as a function of altitude and wind force. *J. Meteor. 10*, 362–371.

ГЕОХИМИЧЕСКОЕ ФРАКЦИОНИРОВАНИЕ ВО ВРЕМЯ ПЕРЕНОСА МАССЫ ОТ МОРЯ И ВОЗДУХА ПРИ ДРОБЛЕНИИ ПУЗЫРЕЙ

Физико-химическая гидродинамика дробления пузырей вместе с химией поверхностных явлений могут объяснить многие аномальные отношения ионов, наблюдаемые в осадках и в атмосферных аэрозолях над морем. Обогащение фосфатами аэрозоля, получающегося из таких пузырей из растворов, содержащих радиоактивные P-32 и Na-22 определяется как

$$\frac{(\text{P-32/Na-22})\ \text{аэрозоль}}{(\text{P-32/Na-22})\ \text{раствор}} - 1$$

и является положительным для всех изученных растворов. Фосфаты всегда присутствуют в избытке в каплях от дробящихся пузырей. В каплях от струй величина E находится в пределах от 0,1 до 10; для капель из поверхностных пленок, раствор из-под которых был почти весь высушен, значение E может возрасти до такой большой величины как 1 000. Фосфаты всегда предпочтительнее хлоридам под положительно заряженными пленками и проявляют тенденцию связываться с пептидоподобными незаряженными веществами. Этот механизм не является специфичным только для фосфатов, но может быть привлечен для объяснения аэрозоля над морем любым веществом с абсолютным ионным потенциалом, большим, чем у Na^+ в отношении Cl^-.