Trace constituents in oceanic cloud water and their origin

By A. L. LAZRUS, H. W. BAYNTON, and J. P. LODGE, JR., *National Center for Atmospheric Research, Boulder, Colo.*[1]

ABSTRACT

Samples of oceanic cloud water collected during periods of varying rates of sea salt aerosol production have been analyzed for chloride, sodium, magnesium, calcium, and sulfate ions. For each of the ions, the portions originating from sea salt, chemical fractionation, and advected materials were calculated. Enrichment by chemical fractionation of sea salt was detected only in the case of magnesium. Considerable contributions of calcium and sulfate from origins other than sea salt were observed. Evidence indicates that excess chloride occurs erratically, and originates from volcanic activity.

1. Introduction

The ratios of chemical constituents in aerosols and rainwater over the ocean differ significantly from the analogous ratios in sea water, in spite of the belief that sea salt borne aloft is the principal source of these trace components (Komabayasi, 1962; Sugawara *et al.*, 1949; Koyama & Sugawara, 1953). Numerous theories have been proposed to account for this discrepancy in terms of chemical fractionation of sea salt, either as it leaves the sea surface or while it is borne aloft. These theories at present are largely unsatisfactory and no mechanism adequately explaining the chemical fractionation of sea salt has been proposed. Laboratory experiments have suggested an enrichment of magnesium (Köhler & Båth, 1952) and of calcium (Sugiura, 1965) by chemical fractionation during sea salt aerosol formation. Experiments simulating aerosol formation by the bubble-bursting process at the sea surface indicate a considerable chemical fractionation of phosphate ion depending upon the presence of surface active materials (Baylor *et al.*, 1962). One of the problems in clarifying the mechanism of sea salt fractionation involves inadequate information on the origin of the excess of constituents found over the ocean. Though the number of samples analyzed is comparatively small, they were collected under unique circumstances which permit some conclusions regarding the origins. In the period from September to February, deep, mid-latitude cyclones occasionally cause rough seas around the Antilles. However, the long trajectories of air over the subtropical oceans cause the climatic elements to remain relatively constant. During such episodes, the rate of sea salt aerosol production at the sea surface markedly increases, and the amount of sea salt found in the cloud water increases accordingly. At the same time, the portions of cloud water constituents which are not derived from sea salt do not undergo a similar increase. It is therefore possible to determine what amount of a constituent originated from sea salt aerosol, from chemical fractionation of sea salt, and from non-maritime sources.

The excess represents the increment of a chemical above the concentration expected from the amount of sea salt in a sample:

$$(M)_{xs} = (M)_{obs} - (M/Cl)_{sw}(Cl^-)_{obs} \qquad (1)$$

where $(M)_{xs}$ is the excess concentration; $(M)_{obs}$ is the measured concentration; $(M/Cl^-)_{sw}$ is the ratio of the constituent to chloride ion in sea water; and $(Cl^-)_{obs}$ is the measured concentration of chloride ion in the cloud water. Use of this equation is justifiable if the observed chloride is derived only from sea salt aerosol and has not been selectively depleted by subsequent processes. The relationship between chloride and sodium in the cloud water, discussed in a later section, indicates fulfillment of this requirement.

2. Experimental procedure

The cloud water samples were collected during November and December 1967, at the top of Pico del Oeste, in the Luquillo Mountains of eastern Puerto Rico. This peak is 1020 m above

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sea level and penetrates the base of trade winds cumulus. The recording wind vane indicated northeasterly winds (except for a short period during the collection of Sample 5, when they were northeast to north); and the anemometer registered speeds which deviated very little from 5.4 mps.

Though the wind was relatively constant, rough sea swells occurred, beginning on December 2, increasing during December 3, and reaching maximum intensity from about 0300 h to 1200 h on December 4. The high seas were apparently caused by a very intense North Atlantic cyclone, the center of which travelled some 1200 to 1700 mi north of Puerto Rico December 1 and 2, generating high winds as far south as Bermuda. Sea swells in excess of 20 ft were observed in Bermuda on December 2, and rough seas spread southward to the region of the Antilles in the next 24 h (Colon, 1967).

The cloud water was collected by impingement on an aluminum screen, approximately 1 m^2, placed in an enclosure to exclude rainwater from the samples. This screen was originally intended only for monitoring the quantity of cloud water (the estimated annual cloud water collection is 325 liters per m^2 per yr); but the device ultimately provided samples for this study as well. Since the screen had been exposed to the clouds approximately one year before our samples were taken, it is probable that the screen surface had reached a steady state condition with respect to cloud water constituents.

The concentration of chloride ion was determined colorimetrically, using mercuric thiocyanate and ferric alum (Iwasaki *et al.*, 1956). The reported results are mean values of three determinations. Coefficient of variation is 0.015.

Sodium ion results are the mean values of four determinations by flame emission photometry. The coefficient of variation is 0.051.

Calcium and magnesium ions were measured by atomic absorption photometry, using lanthanum chloride to suppress interferences. Four determinations per sample were made. The coefficients of variation are 0.028 and 0.020 respectively.

The concentration of sulfate ion was determined colorimetrically, using methyl thymol blue (Lazrus *et al.*, 1968), with three analyses per sample. The coefficient of variation is 0.050.

All samples were refrigerated between collection time and analysis.

Table 1. *Sampling periods and chloride ion concentrations*

No. of sample	Sampling period	Chloride ion (ppm)
1	Nov. 9, 1600 h–Nov. 10, 0800 h	5.4
2	Nov. 10, 1700 h–Nov. 11, 0700 h	7.7
3	Nov. 29, 1500 h–Nov. 30, 1225 h	8.2
4	Nov. 30, 1330 h–Dec. 1, 0800 h	6.9
5	Dec. 2, 1630 h–Dec. 3, 1120 h	15.0
6	Dec. 3, 1130 h–Dec. 4, 1540 h	70.0
7	Dec. 4, 1545 h–Dec. 6, 0830 h	42.7
8	Dec. 9, 0955 h–Dec. 9, 1600 h	30.0

3. Results and discussion

The effect of rough seas on the quantity of sea salt dissolved in cloud water is strikingly illustrated by Table 1.

The increase of sea surface activity on December 2 coincides with increased chloride concentration in the cloud (Sample 5).

Magnesium ion

One expects the magnesium ion concentration in oceanic cloud water to be linearly related to chloride ion concentration if the following assumptions are made. First, the portion of cloud water magnesium inherently associated with sea water aerosol is linearly related to chloride. Second, the increment of magnesium resulting from chemical fractionation which occurs during aerosol production from the sea surface is linearly dependent on chloride, i.e., on the amount of aerosol being produced. Third, if chemical fractionation occurs at a later stage, the increment of enriched magnesium is still linearly dependent on chloride ion, i.e., on the amount of airborne aerosol undergoing the chemical fractionation. Finally, the graph of a linear relationship of magnesium vs. chloride should have an intercept representing the amount of magnesium not originating from sea salt aerosol.

The plot of concentration of magnesium vs. chloride ions is shown in Fig. 1. The regression equation for this line is:

$$(Mg^{++})_{obs} = 0.070\ (Cl^{-})_{obs} + 0.080 \qquad (2)$$

The regression equations are computed assuming random error in both variables (Wald, 1940). If the amount of excess magnesium, as calculated from Eq. (1), is likewise dependent on chloride

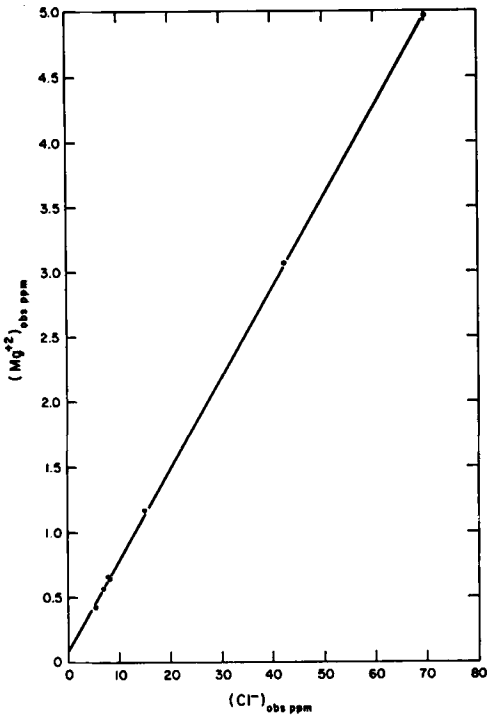

Fig. 1. Observed magnesium ion vs. chloride ion concentrations.

ion then it must originate by a chemical fractionation of sea salt rather than by advection from a non-maritime source. Such a relationship does exist as shown in the plot of excess magnesium vs. chloride ion (Fig. 2). The excess magnesium is calculated using Eq. (1) and

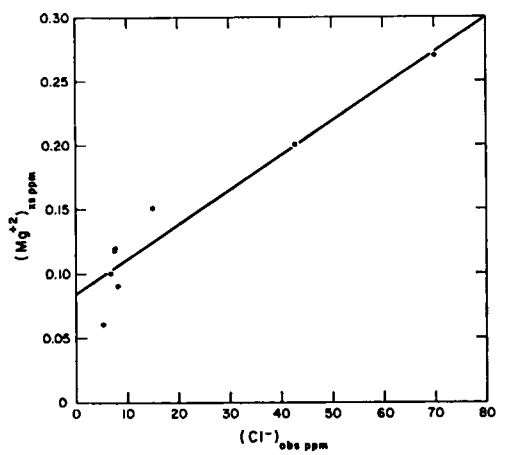

Fig. 2. Excess magnesium ion vs. chloride ion concentrations.

$(Mg^{++}/Cl^-)_{sw} = 0.067$ (Culkin & Cox, 1966). The regression equation for the latter is given by:

$$(Mg^{++})_{xs} = 0.0028\ (Cl^-)_{obs} + 0.079 \qquad (3)$$

The increment due to chemical enrichment of magnesium is thus $0.0028\ (Cl^-)_{obs}$, and these values from the samples are shown in Column 5, Table 2. From Column 6, it appears that the percentage of excess magnesium attributable to chemical fractionation is considerable during periods of high sea salt aerosol production (Samples 6 and 7).

The constants of Eqs. (2) and (3) representing the Y-intercept values indicate that about 0.08 ppm of magnesium in the cloud water is independent of chloride, and probably has an origin other than sea salt. This concentration of magnesium has been calculated for each sample $[(Mg^{++})_{xs} - (Mg^{++})_{En}]$, and the results are shown in Column 7, Table 2. The fairly constant values probably represent magnesium from advected continental aerosol.

Calcium

The concentration of calcium ion found in the cloud water samples are given in Table 3. The excess calcium was calculated from Eq. (1), using $(Ca^{++}/Cl^-)_{sw} = 0.21$ (Culkin & Cox, 1966). A plot of observed calcium vs. chloride ions is

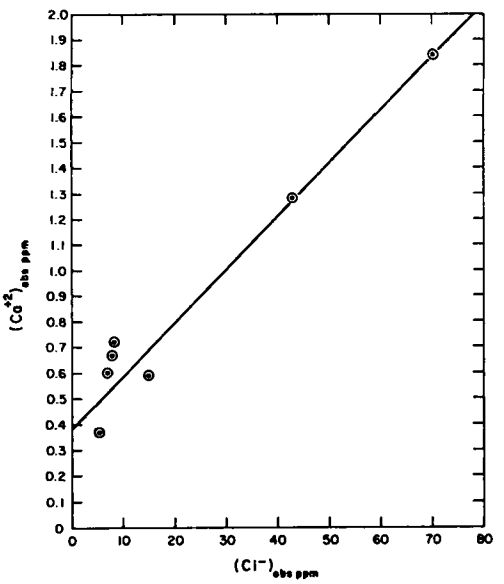

Fig. 3. Observed calcium ion vs. chloride ion concentrations.

Table 2. *Magnesium ion concentrations in oceanic cloud water*

(1) No. of sample	(2) $(Mg^{++})_{obs}$ (ppm)	(3) $(Mg^{++})_{ss}$ [a] (ppm)	(4) $(Mg^{++})_{xs}$ (ppm)	(5) $(Mg^{++})_{En}$ [b] (ppm)	(6) $(Mg^{++})_{En}/(Mg^{++})_{xs}$ (%) × 100	(7) $(Mg^{++})_{ns}$ [c] (ppm)
1	0.42	0.36	0.06	0.015	25	0.04
2	0.63	0.52	0.12	0.021	18	0.10
3	0.64	0.55	0.09	0.023	25	0.07
4	0.56	0.46	0.10	0.019	19	0.08
5	1.16	1.01	0.15	0.042	28	0.11
6	4.96	4.69	0.27	0.196	73	0.07
7	3.06	2.86	0.20	0.120	60	0.08
8[d]						

[a] $(Mg^{++})_{ss}$ represents inherent magnesium in sea salt or $(Mg^{++}/Cl^{-})_{sw}\,(Cl^{-})_{obs}$.
[b] $(Mg^{++})_{En}$ represents magnesium enriched by fractionation or $0.0028\,(Cl^{-})_{obs}$.
[c] $(Mg^{++})_{ns}$ represents magnesium not related to sea salt or $(Mg^{++})_{xs} - (Mg^{++})_{En}$.
[d] The volume of sample No. 8 was sufficient only for chloride and sodium analyses.

shown in Fig. 3. The regression equation is represented as:

$$(Ca^{++})_{obs} = 0.021\ (Cl^{-})_{obs} + 0.38 \qquad (4)$$

Excess calcium, however, is not related linearly to chloride ion, as can be seen from Fig. 4. This is confirmed by the low coefficient of correlation, which is 0.19. The value for excess calcium averaged over all samples is 0.40 ppm, while the intercept of Eq. (4) is 0.38 ppm. It is therefore possible to attribute all of the excess calcium to a source unrelated to sea salt.

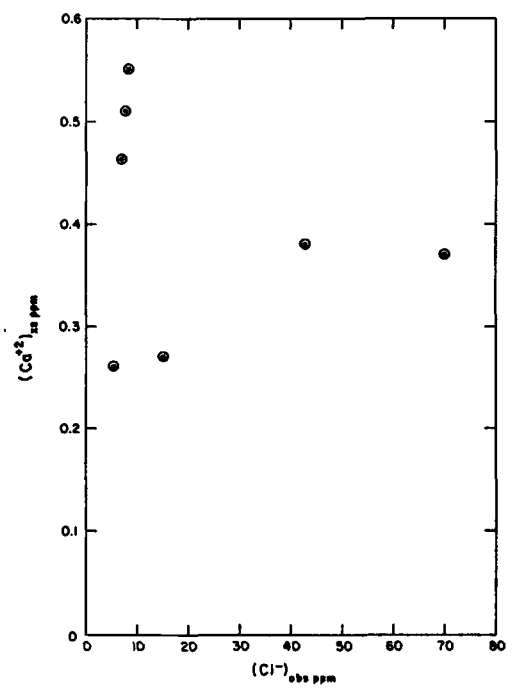

Fig. 4. Excess calcium ion vs. chloride ion concentrations.

There is more magnesium than calcium in sea water, the ratio being 3.16 (Culkin & Cox, 1966). However, there is less magnesium than calcium in the lithosphere, the average ratio being 0.57. The ratio of magnesium unrelated to sea salt to the comparable calcium value is given in Column 6, Table 3. The ratio is about 0.2, further suggesting a continental origin for these portions of magnesium and calcium. There is increasing evidence for the aeolian transport of continental aerosol from arid Africa to the Caribbean area (Junge, 1956; Delany *et al.*, 1967). The values in Column 5, Table 3 indicate the large contribution which continental dust may make to calcium content of oceanic cloud water.

Since calcium and magnesium are such similar alkaline earth elements, it is surprising that only the latter manifests a significant enrichment by chemical fractionation. Conceivably, the enriched increment of magnesium ascribed to chemical fractionation is an artifact. If the $(Mg^{++}/Cl^{-})_{sw}$ ratio used had been higher it would have accounted for all of the sea salt-dependent magnesium. This ratio, however, is remarkably constant throughout the world: it varies from 0.06670 to 0.06703, with most of the values lying between 0.06690 and 0.06669 (Culkin & Cox, 1966). By comparison, the 95% confidence limits of the slope of Eq. (2) are 0.069 to 0.071, making unlikely this explanation for the different behaviors of magnesium and calcium.

Table 3. *Calcium ion in oceanic cloud water*

(1) No. of sample	(2) $(Ca^{++})_{obs}$ (ppm)	(3) $(Ca^{++})_{ss}$ [a] (ppm)	(4) $(Ca^{++})_{xs}$ (ppm)	(5) $100(Ca^{++})_{xs}/(Ca^{++})_{obs}$ (%)	(6) $(Mg^{++})_{ns}$ [b]$/(Ca^{++})_{xs}$
1	0.37	0.11	0.26	70	0.2
2	0.67	0.16	0.51	76	0.2
3	0.72	0.17	0.55	76	0.2
4	0.60	0.14	0.46	77	0.2
5	0.54	0.32	0.27	46	0.1
6	1.84	1.47	0.37	20	0.2
7	1.28	0.90	0.38	30	0.4

[a] $(Ca^{++})_{ss}$ represents inherent calcium in sea salt or $(Ca^{++}/Cl^{-})_{sw}(Cl^{-})_{obs}$.
[b] $(Mg^{++})_{ns}$ represents magnesium not related to sea salt.

A more plausible explanation is the supersaturation of calcium carbonate at the sea surface in low latitudes (Berner, 1965; Broecker & Takahashi, 1966). It is likely that carbonate at the sea surface makes calcium unavailable to the fractionation process. By comparison, the solubility product of magnesium carbonate is five orders of magnitude larger than that of calcite.

The acidity of the samples (pH 4.9–5.4) prevents the removal of calcium ion from the cloud water by insoluble carbonate formation.

Simulated sea salt aerosol production in the laboratory has shown significant increases in the calcium/sodium ratio in aerosol relative to the ratio in sea water (Sugiura, 1965). Unless organic components of seaweed (or a synthetic chelating agent) were present, no chemical fractionation occurred. The possibility that the enriched calcium originated from particulate biological material in the aerosol is unlikely, since fractionation occurred using only organic extracts of seaweed. A continuous stream of nitrogen (10–20 days) was bubbled through the sea water in order to generate the aerosol, and no carbon dioxide was available to react with calcium at the surface. Indeed the purging by nitrogen may have reduced the carbonate alkalinity by removing dissolved carbon dioxide from the equilibrium:

$$H^{+} + HCO_3^{-} = CO_2 + H_2O$$

The experiment nevertheless indicates that calcium can be chemically fractionated at the sea surface, and further suggests that association with carbonate ion may be the cause of our failure to observe this fractionation.

Sulfate

The sulfate ion data are compiled in Table 4. For calculating excess sulfate, the ratio of sulfate to chloride in sea water was taken as 0.14 (Morris & Riley, 1966). The negative value of Sample 7 may be the result of error; it should be noted, however, that sulfate ion deficiencies in precipitation have been systematically observed during stormy seas (Miyake & Sugiura, 1954). Though the range of chloride concentra-

Table 4. *Sulfate ion in oceanic cloud water*

(1) No. of sample	(2) $(SO_4^{=})_{obs}$ (ppm)	(3) $(SO_4^{=})_{ss}$ (ppm)	(4) $(SO_4^{=})_{xs}$ (ppm)	(5) $100(SO_4^{=})_{xs}/(SO_4^{=})_{obs}$ (%)
1	4.3	0.76	3.5	81
2	3.4	1.1	2.3	68
3	4.2	1.1	3.1	74
4	3.5	0.97	2.5	71
5	3.6	2.1	1.5	42
6	9.1	9.8	−0.7	
7	8.2	6.0	2.2	27

Table 5. *Rainout and washout contribution to oceanic rainwater (Miyake and Tsunogai, 1965)*

	Rainout	Washout	Rainout	Washout	Rainout	Washout	Rainout	Washout
(Cl^-)	0.82	9.6	0.19	0.60	0.30	0.26	0.88	0.72
(Na^+)	0.45	5.3	0.04	0.32	0.07	0.15	0.44	0.39
$(Cl^-)/(Na^+)$	2.0	1.8	4.8	1.8	3.9	1.7	2.0	1.8
	0600–1330 h May 5, 1964		1330–1536 h		1536–1850 h		1850–0410 h May 6	

tion in these samples extends over an order of magnitude, the excess sulfate concentration is nearly constant, the average being 2.1 ppm, and therefore appears independent of sea salt. This excess sulfate may comprise a very high percent of the total sulfate ion, Column 5, Table 4.

Excess sulfate has been found in remote areas of the world where minimum industrial and soil contribution would be expected. For example, ice deposited on the Greenland ice cap during the years 1915–1957 was obtained from depths ranging up to 100 ft. The sampling site, 200 mi east of Thule, was 7600 ft high. The average excess sulfate ion content was 2.5 ppm, similar to the average found in the cloud water samples (Diamond, 1958).

Although continental aerosols and advected sulfur dioxide must account at least partially for this excess sulfate, there are other likely sources. Oceanic sulfate is not in equilibrium with sea water with respect to oxygen-18 content. Isotope measurements of sulfate formed by oxidation of hydrogen sulfide in sea water suggest that a continuous chemical cycling of oceanic sulfur may account for the lack of equilibrium (Lloyd, 1967). The cycle involves biological reduction of sulfate ion to hydrogen sulfide and subsequent oxidation, primarily by air, to sulfate. Since hydrogen sulfide may escape from the sea surface unassociated with aerosol, the sulfate resulting from its oxidation would appear as excess. Measuring the oxygen and sulfur isotope ratios in several samples of cloud water sulfate will permit calculation of these ratios in the excess sulfate portion. Hopefully, this will help explain its origin.

Chlorine

Valach (1967*a*) discussed the origin of gaseous chlorine in the atmosphere. By an analysis of earlier data he demonstrated the unlikelihood of theories which attribute gaseous chlorine to generation from sea salt. He points out, for example, that measurements of both particulate and gaseous forms of chlorine in Florida (Junge, 1956) showed a loss of chloride ion from sea salt aerosol sufficient to account for only a small percentage of the gaseous chlorine observed.

There is, however, another set of data which strongly suggests that chlorine gas is present over the open ocean, and therefore that sea salt may be its source. Rainwater was collected on Hachijo-jima Island (33°06′ N, 139°47′ E) simultaneously at 800 m and at 80 m above sea level (Miyake & Tsunogai, 1965). The chemical composition of samples obtained at the higher altitude represented primarily constituents entrained in the cloud droplets (rainout process); the composition of the lower altitude samples resulted from the rainout process plus capture of trace substances by the falling raindrops (washout process). By subtracting the ion concentrations in each sample collected at 800 m from the analogous concentrations in the lower altitude sample, it was possible to report reasonable estimates of the separate contributions of the rainout and washout processes (Table 5).

The $(Cl^-)/(Na^+)$ ratios for washout remain throughout the storm at about the value for sea water, 1.80 (Culkin & Cox, 1966), consistent with the capture of sea salt particles by the falling raindrops. However, the ratios associated with rainout increase to more than twice this value during the storm, suggesting that much of the chloride entrained in the cloud droplets is not derived from sea salt. Moreover, since the total equivalents of cations do not reasonably account for the excess chloride, the latter probably results from dissolution of a chlorine-containing gas in the cloud water.

It was initially because of these observations that cloud water samples were collected at Pico del Oeste for chemical analysis. The sodium ion concentration measured in these samples is plotted against chloride ion concentration in

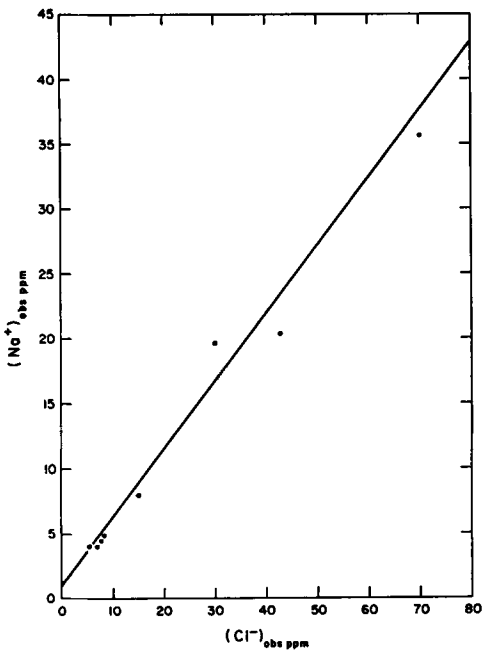

Fig. 5. Observed sodium ion vs. chloride ion concentrations.

Fig. 5. The regression equation for this plot was calculated assuming random error in both variables:

$$(Na^+)_{obs} = 0.53\ (Cl^-)_{obs} + 0.6 \qquad (6)$$

The 90 % confidence interval of the slope is 0.49 to 0.61, and therefore brackets the sea water ratio $(Na^+/Cl^-)_{sw} = 0.55$. The results therefore fail to confirm a significant excess of chloride ion in the cloud water, and one concludes that gaseous chlorine is not consistently present in the oceanic environment. In view of this, gaseous chlorine probably does not originate from sea salt.

In trying to explain the presence of gaseous chlorine, it was found that several volcanic incidents occurred at about the time of sampling on Hachijo-jima. Osima, approximately 120 miles north of Hachijo-jima, erupted in January, March, May, July through September, and in December 1964 (Suwa, 1965). Though the May eruptions began two days after the sampling period, the frequency of eruptions indicates that fumaroles were probably injecting volcanic gases into the atmosphere before and during the sampling period. On April 14, 1964, a large submarine volcano erupted about 1300 miles south of Hachijo-jima (Suwa, 1965). In addition, hot springs and fumarole activity are reported on Aoga-Shima, about 62 miles south of Hachijo-jima (Kuno, 1962).

Assuming that sodium ion is a reasonably approximate indicator of sea salt undergoing rainout, the excess chlorine entrained by the cloud droplets over Hachijo-jima may be calculated by Eq. (7):

$$(Cl^-)_{xs} = (Cl^-)_{obs} - (Cl^-/Na^+)_{sw}(Na^+)_{obs} \qquad (7)$$

Excess fluorine may be calculated in a similar way from the data of Miyake & Tsunogai. These calculated excesses of both chlorine and fluorine will be slightly low, since non-maritime sources make a small contribution to sodium over the ocean as indicated by the intercept in Fig. 5. The calculated values are given in Table 6.

Though the ratio of chlorine of fluorine in sea water is 10^4, the average ratio of excess chlorine to excess fluorine is five. The ratio of hydrogen chloride to hydrogen fluoride in the gases of several Japanese volcanoes is 7 (Iwasaki *et al.*, 1965). Both this similarity and the observation that excess chlorine is not consistently entrained by rainout over the ocean, support the contention that the gaseous forms of chlorine and fluorine in the atmosphere result largely from volcanic activity (Valach, 1967*b*).

Table 6. *Excess chlorine and fluorine entrained by rainout (calculated from data of Miyake and Tsunogai, 1965)*

	1 Rainout	2 Rainout	3 Rainout	4 Rainout
$(Cl^-)_{xs}$	0.01	0.1	0.17	0.09
$(F^-)_{xs}$	0.017	0.015	0.023	0.021
$Cl^-)_{xs}/(F^-)_{xs}$	0.6	8	8	4

Conclusions

Magnesium in oceanic cloud water in excess of the amount expected from dissolved sea salt is partly of non-maritime origin and partly from a chemical fractionation of sea salt. Calcium excess appears to originate entirely from non-maritime origins.

Sulfate ion is present in excess amounts in accordance with previous observations. However, the cloud water data eliminate chemical fractionation of sea salt as a possible source.

Neither enrichment nor depletion of chlorine ion by chemical fractionation was detected. Since no excess chloride was observed but has been noted in other investigations, its origin must be intermittent and/or localized. Ratios of excess chloride to excess fluoride in one set of observations suggest that geothermal activity is sometimes the origin.

REFERENCES

Baylor, E. R., Sutcliffe, W. H. & Hirschfeld, D. S. 1962. Adsorption of phosphates onto bubbles. *Deep Sea Research 9*, 120–124.

Berner, R. A. 1965. Activity coefficients of bicarbonate, carbonate, and calcium ions in sea water. *Geochim. Cosmochim. Acta 29*, 947–966.

Broecker, W. S. & Takahashi, T. 1966. Calcium carbonate precipitation on the Bahama banks. *J. Geophys. Res. 71*, 1575–1602.

Colon, J. A. 1967. Report on the sea conditions observed along north coastal sections of Puerto Rico on December 3–4, 1967. Official Report, ESSA Weather Bureau Office, San Juan, Puerto Rico, 2 pp.

Culkin, F. & Cox, R. A. 1966. Sodium, potassium, magnesium, calcium and strontium in sea water. *Deep Sea Research 13*, 789–804.

Delany, A. C., Delany, A. C., Parkin, D. W., Griffin, J. J., Goldberg, E. D. & Reimann, B. E. F. 1967. Airborne dust collected at Barbados. *Geochim. Cosmochim. Acta 31*, 885–909.

Diamond, M. 1958. Precipitation trends in Greenland during the past 30 years. *Research Report 22*, Snow, Ice, and Permafrost Research Establishment, Wilmette, Illinois, 1956.

Iwasaki, I., Utsumi, S., Hagino, K. & Ozawa, T. 1956. A new spectrophometric method for the determination of small amounts of chloride using the mercuric thiocyanate method. *Bull. Chem. Soc. Jap. 29*, 860–864.

Iwasaki, I., Ozawa, T., Yoshida, M., Katsura, T. & Kamada, M. 1965. Chemical analysis of volcanic gases. *Bulletin Volcanologique 28*, 5–16.

Junge, C. E. 1956. Recent investigations in air chemistry. *Tellus 8*, 127–139.

Köhler, H. & Båth, M. 1952. Quantitative chemical analysis of condensation nuclei from sea water. *Nova Acta Regiae Soc. Sci. Upsaliensis, Ser. 4, 15*, 2–24.

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

Koyama, T. & Sugawara, K. 1953. Separation of the components of atmospheric salt and their distribution. *Bull. Chem. Soc. Jap. 26*, 123–126.

Kuno, H. 1962. Catalogue of the active volcanoes and sulfatura fields of Japan, Taiwan and Marianas, Part XI of Catalogue of the Active Volcanoes of the World (ed. by International Assoc. Volcanolog). Stabilimento Tipografico Francesco Giannini and Figli, Napoli.

Lazrus, A. L., Lorange E. & Lodge, J. P. Jr., 1968. New automated techniques for sulfate ion and for total inorganic fixed nitrogen in trace inorganic chemicals in water. *Advances in Chemistry Series* (ed. R. F. Gould), American Chemical Society Publications, Washington, D.C.

Lloyd, R. M. 1967. Oxygen-18 composition of oceanic sulfate. *Science 156*, 1228–1231.

Miyake, Y. & Sugiura, Y. 1954. Chemical studies of rain water accompanied by a typhoon. *Geophys. Mag. 26*, 29–34.

Miyake, Y. & Tsunogai, S. 1965. Chemical composition of oceanic rain. *Proc. Int. Conf. Cloud Physics, Tokyo and Sapporo, May 24–June 1, 1965*, 73–78.

Morris, A. W. & Riley, J. P. 1966. Bromide/chlorinity and sulphate chlorinity ratio in sea water. *Deep Sea Research 13*, 699–705.

Sugawara, K., Oana, S. & Koyama, T. 1949. Separation of the components of atmospheric salt and their distribution. *Bull. Chem. Soc. Jap. 22*, 47–52.

Sugiura, Y. 1965. Effect of organic matter on composition of sea salt in sea water bubbles. *Proc. Int. Conf. Cloud Physics, Tokyo and Sapporo, May 24–June 1, 1965*, 47–51.

Suwa, A. 1965. *Bulletin of Volcanic Eruptions, No. 5.* Volcanological Society of Japan, International Assoc. of Volcanology, IUGG.

Valach, R. 1967 *a*. The origin of the gaseous form of natural atmospheric chlorine, *Tellus 19*, 509–516.

Valach, R. 1967 *b*. Fluoride und Chloride in Niederschlagen von Böhmen. *Studia Geoph. et Geod. 11*, 241–251.

Wald, A. 1940. The fitting of straight lines if both variables are subject to error. *Annals of Mathematical Statistics 11*, 284–300.

НЕКОТОРЫЕ ХИМИЧЕСКИЕ ТРАССЕРЫ НАД ОКЕАНОМ И ИХ ПРОИСХОЖДЕНИЕ

Пробы воды из облаков над океаном, взятые в периоды различной скорости генерирования аэрозоля морских солей, были проанализированы на ионы хлоридов, калия, магния, кальция и сульфатов. Для каждого вида ионов были вычислены части, возникающие из морской соли, химического фракционирования и адвекции вещества. Наблюдался значительный вклад кальция и сульфатов происхождения помимо из морской соли. Имеются данные, что избыток хлоридов наблюдается случайным образом и обязан своим происхождением вулканической активности.