Coherence of iodine and bromine in the atmosphere of Hawaii, northern Alaska, and Massachusetts

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ABSTRACT

Previously reported analyses of rain, snow, aerosols, and gas from Hawaii, Alaska, and Massachusetts, and new analyses of Antarctic and Alaska snow and ice, are compared. Both I and Br appear to be associated with aerosols of smaller particle sizes and longer residence times than Cl-rich aerosols. In most suites of samples there is a clustering at I/Br $\sim$ 0.1–0.2, and Br/Cl exceeds the sea water ratio (3.4×10^{-3}) several-fold. Aerosols collected over open sea water in Hawaii, however, show Br/Cl several-fold *lower* than in sea water. The latter particles are identified as "sea salt" aerosols whereas the Br-rich aerosols are smaller in size and may be basically different in composition, e.g. ammonium sulfate as discussed by JUNGE (1963). It is suggested that Br is "distilled" from the sea spray droplets, possibly by photochemical oxidation to Br_2, and then "condensed" onto the smaller particles, possibly by participating in the oxidation of SO_2 to sulfate. Iodine may engage in similar reactions, and the resulting I and Br-rich particles exhibit a world-wide constancy in I/Br. Precipitation analyses show a similar constancy in I/Br.

The problem

Atmospheric halogens are derived from the sea, but their relative proportions are different from sea water in several important respects. In a series of papers (I, DUCE *et al.*, 1963; II, DUCE *et al.*, 1965; III, LININGER *et al.*, 1966; IV, DUCE *et al.*, 1966) neutron activation analyses of atmospheric samples for iodine, bromine, and chlorine have been reported, and WINCHESTER & DUCE (1965*a* and *b*) have reviewed some of it. Iodine is enriched over chlorine in most atmospheric samples hundreds to thousands of times, and the bromine-to-chlorine ratio is usually, although not always, somewhat greater than the sea water ratio. In suites of samples of aerosol particles, chlorine exhibits a greater degree of variability than either bromine or iodine. Analytical data taken from the widely separated localities of the island of Hawaii, Point Barrow in Alaska, and the city of Cambridge in Massachusetts are strikingly similar in halogen transfer processes in the atmosphere.

New halogen analyses

The method of halogen analysis for data newly cited in this paper is that employed previously (papers I, II, III, and IV), neutron activation analysis (DUCE & WINCHESTER, 1965). Aqueous samples of 5 ml of rain water or equivalent are irradiated in the M.I.T. Reactor, processed radiochemically by solvent extraction, and beta counted, and the analysis of each sample requires one hour giving an accuracy of about ±5 %.

ANTARCTIC SAMPLES

Table 1 presents the halogen composition of six samples collected by Dr. Gunter Faure, Ohio State University, during the antarctic summer 1964–65. In our experience, generalizations based on only a few halogen analyses

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TABLE 1. *Antarctic samples.*

Sample[a]	Cl μg/ml	Br ng/ml	I ng/ml	I/Cl $\times 10^3$	Br/Cl $\times 10^3$	I/Br
Horlick snow	1.26	8.0	0.90	0.70	6.3	0.11
Horlick firn	1.42	3.0	0.65	0.46	2.1	0.22
Horlick ice	0.89	3.3	0.78	0.88	3.7	0.24
Byrd snow	1.20	80.	2.7	2.2	67.	0.033
Scott snow	9.0	16.5	0.67	0.074	1.8	0.040

[a] *Horlick snow:* Freshly fallen snow, Reedy Glacier, Horlick Mts., 127°00′W, 86°05′S. *Horlick firn:* Granular firn snow 40 cm below surface, same locality. *Horlick ice:* Blue glacier ice exposed at the surface, same locality. *Byrd snow:* Granular snow from wall in tunnel 16 m below surface, Byrd Station, 119°31′W, 80°1′S. *Scott snow:* Snow from Scott Base on Ross Island near shore. *Standard deviations:* Concentrations ±5 %, ratios ±7 %.

should be made only with great caution. However, the three inland Horlick samples form a reasonably consistent set. We may expect the coastal Scott snow to have some admixture of sea spray, and the higher Cl concentration may be a reflection of this. The Byrd snow from a tunnel has a very high Br concentration, but (paper III) we cannot say whether it had suffered exposure to leaded motor fuel exhaust.

ALASKAN AND MASSACHUSETTS SNOWS

Table 2 shows a freshly fallen snow from Concord, Massachusetts 30 km from the sea with halogen content not atypical of other near-coastal data. The Fairbanks, Alaska average snow profiles are our only analyses to date of inland and unpolluted precipitation. In contrast to more maritime samples, these are relatively Cl-poor and exhibit high Br/Cl ratios. Like most maritime samples, however, I/Br is of the order of 10^{-1}. The single freshly falling snow from Fairbanks in January is anomalous compared to the averages for the preceding autumn when most snow fell. Its fall came at a time of air movement from the Gulf of Alaska lying to the south, although normally air moves from Canada lying to the east during fall and winter. Without knowing in detail the meteorology during each snow fall of the season, however, no more should be said.

TABLE 2. *Alaskan and Massachusetts snows.*

Sample[a]	Cl μg/ml	Br ng/ml	I ng/ml	I/Cl $\times 10^3$	Br/Cl $\times 10^3$	I/Br
Concord, Mass.	0.71	5.2	0.62	0.87	7.2	0.12
Fairbanks, Alaska						
No. 2[b]	5.1	11.2	2.6	0.52	2.2	0.23
No. 5	0.090	3.9	0.51	5.7	43.	0.13
No. 6	0.116	3.0	0.60	5.2	26.	0.20
No. 7	0.16	4.1	0.54	3.4	26.	0.13

[a] Concord, Mass.: freshly fallen snow at 2 River Street, 2 January 1965.

Fairbanks, Alaska: No. 2, falling snow on roof of Institute of Marine Sciences, College, 15 January 1965, 10:25–10:40 A.M. No. 5, ground snow 60 m from Farmer's Loop Road, average of 39 cm depth. No. 6, ground snow at Goldstream Creek north of College, average of 44 cm depth. No. 7, ground snow at Tanana River near Chena Ridge west of Fairbanks, average depth profile. All samples collected on 15 January 1965 at sites remote from local pollution.

[b] We have now analyzed several freshly falling snows from Fairbanks, Alaska, and the Cl concentration of sample #2 given in Table 2 is anomalously several-fold higher than the other samples collected at about the same time and place. We therefore regard the sample #2 Cl value to be in error.

Data comparison

PRECIPITATION

In Hawaiian rains (papers I and II) the concentration of Cl is of the order of 1 μg Cl/ml (II, Fig. 4), and the trend of data is a decrease from 5 μg Cl/ml at 1000 feet to 0.5 μg Cl/ml at 6000 feet altitude of collection within the orographic rain cloud. Br and I likewise decrease with increasing altitude (II, Figs. 5 and 6), the ranges of the trends between 6000 feet and 1000 feet being 5–20 ng Br/ml and 2–8 ng I/ml. The average weight ratio I/Br ~ 0.4 independent of altitude but I/Cl and Br/Cl both increase with increasing altitude 2.5-fold over this range. The ratio Br/Cl extrapolates well to the sea water value (3.4×10^{-3}) at zero altitude, but I/Cl extrapolates to about 1.5×10^{-3} at zero altitude, exceeding the sea water value (4×10^{-6}) by 400 times. The snow from Concord, Mass. (Table 2) is not unlike the Hawaiian rains.

The freshly falling snow in Fairbanks, Alaska, is similar to Hawaiian rains, and the three average ground snow samples for the winter show Hawaii-like Br, I, and I/Br. However, Cl is much lower in the ground snows, and the ratios Br/Cl and I/Cl exceed the falling snow values by an order of magnitude. Ground-lying Barrow snows (IV, Figs. 6 and 7) are mixed with sea salt, especially nearest the coast, but I is still very high and Br somewhat high compared to sea water. The data imply a mixture of the sea salt component and a component with I/Br $\sim 10^{-1}$. The concentrations of this component are accordingly I ~ 1 ng/ml and Br ~ 10 ng/ml, not unlike the Hawaii, Massachusetts, and Fairbanks results.

AEROSOLS

Aerosols collected by cascade impactor in Hawaii on land-based stations well removed from the sea and up to 5000 feet (II, Table 4) contain 1–4 μg Cl/m³ STP, 12–24 ng Br/m³ STP, and 0.4–2 ng I/m³ STP. Concentrations by a similar impactor in Cambridge, Massachusetts (III, Table III and IV) are 1–6 μg Cl/m³ STP and 2–10 ng I/m³ STP, but local pollution from automobile exhaust gives rise to the high values 20–800 ng Br/m³ STP, and the high Br is correlated with Pb and the haziness of the air (III, Fig. 10). In Barrow, Alaska during January when the sea surface was frozen, concentrations measured (IV, Table 5) using a Millipore filter were < 0.02–4 μg Cl/m³ STP, 1–30 ng Br/m³ STP and 0.3–10 ng I/m³ STP. The concentrations in all three localities are strikingly similar, except for Barrow Cl which is sometimes very low. In the Hawaii and in the Barrow aerosol samples cited the data cluster in the vicinity of I/Br ~ 0.1–0.2. Generally the ratio Br/Cl is greater than in sea water, and sometimes very much greater.

Aerosols collected by aircraft over the open ocean near Hawaii (I, Table 5; II, Table 5) contrast with these data by exhibiting Br/Cl *lower* than in sea water, up to 10 times lower. In these samples the total concentrations are roughly in the same range as the aerosols cited above, but Br seems singularly depleted relative to both Cl and I. On the other hand, Barrow aircraft aerosols in winter (IV, Table 6 and Fig. 5) do not show this effect but on the whole agree with the Millipore filter data.

Among miscellaneous samples collected in Hawaii (II, Table 7), two analyses of salt from a cliff, believed to be derived from airborne sea salt crystals, show Br/Cl = 3.6×10^{-5}, a hundred times lower than in sea water. The relations among all the Hawaii samples are shown in Fig. 12 of paper II.

GAS

Only in Hawaii has successful sampling of halogens in the gas phase been carried out. The data (II, Table 6) indicate that about half the Cl and Br and somewhat more than half the I of the land aerosols and gas was in the gas phase, defined as that which passes through 0.1 μ Millipore filters.

Model for halogen fractionation

Iodine and bromine exhibit great uniformity in their concentrations and I/Br ratios in localities widely differing in climate and distance from the sea, but chlorine is much more variable, tending to decrease in concentration with increasing distance from the sea. These relations suggest a simple model where two aerosol components are present in varying mixing ratios: (1) a Cl-rich, or Br-poor, component with short residence time and (2) a Cl-poor, or I and Br-rich, longer residence time component. The sea must be the ultimate source for both components, but the first is more immediately derived from sea spray.

If we compare the properties of the two halogen components in detail with the general properties of aerosols as thoroughly discussed by JUNGE (1963), a strikingly consistent picture emerges. As Junge reviews the evidence, tropospheric aerosols of natural origin may (1) be derived from sea spray and exist in the range of radius $1 < r < 20\ \mu$ ("giant" particles) and (2) be derived from other sources and have equal mass concentrations in the ranges $0.1 < r < 1\ \mu$ and $1 < r < 20\ \mu$ ("large" and "giant" particles). Particles of giant size are more effective as rain drop nuclei than large particles, but both are removed from stable suspension in the atmosphere by precipitation. The residence time of large particles in the atmosphere is 20–40 days whereas giant particles remain aloft at most a few days. Chemical data indicate that Cl^- is the principal anion in the giant sea spray particles, whereas the composition of large particles is well represented by $(NH_4)_2SO_4$.

The halogen evidence indicates that sea spray, which gives rise to giant Cl^--rich particles, loses Br more rapidly than Cl to the gas phase, and the residual particles come to have a Br/Cl ratio lower than in sea water. Iodine is also present in the gas phase either by a similar inorganic distillation from sea spray or from the sea surface or by an organic mechanism.

The Cl-rich residual particles will fall out more or less rapidly depending on particle size and air movement, but the Br* and I* (where * indicates vapor without commitment as to chemical species) will stay aloft and be carried with the air. Now, Br* and I* may be chemically reactive, e.g. Br_2 and I_2 are oxidizing agents for inorganic and organic substances, and a chemical reaction may cause creation of new particles or a recombination of Br and I preexisting with particulate material. If the particle substrate is different from sea salt, it may have a different particle size distribution and a residence time in the atmosphere different from the Cl-rich residual particles.

We suggest that the Br and I distillate particles are smaller in radius than the Cl-rich residual particles, with supporting evidence from Hawaii, Barrow, and the M.I.T. campus (papers II, IV, and III). Aerosols collected over land in Hawaii tend to have greater I/Cl and Br/Cl at greater altitudes, and the greatest values were found at 11,000 feet, above cloud level, and in the smallest particle sizes. Aircraft aerosols from Barrow show roughly half the Br not collected by the L-strip that is collected by the S-strip, indicating substantial Br in particles of radius $\leq 1\ \mu$. Cl is mainly in larger particles, as L-strip and S-strip collectors show the same Cl concentrations. Aerosols at M.I.T., with 1 or 2 exceptions, show greater I/Cl in the smaller particles; Br is not comparable because of motor fuel pollution.

Finally, we suggest that we have observed the residual Cl-rich particles, from sea spray after Br depletion, only by aircraft sampling over the open sea near Hawaii. The observations were made on two separate occasions (papers I and II) using two different impaction collectors of similar design, and flights were offshore and at 300 to 1500 meters altitude. In these samples most of the mass occurred at the small end of the giant range, at 1 μ or slightly less, and Br/Cl varied from the sea water value to 10-fold less than that. In Barrow we believe these particles were not present owing to the absence of open sea water in winter, and aircraft aerosols consisted of the distillate component, probably more or less mixed with sea salt blown up from ground-lying snow or residue of evaporated sea ice. If the Hawaii cliff salt were derived from air-borne sea salt, its very low Br/Cl ratio suggests it is derived from the Cl-rich residual particles. The tendency for Br loss from aerosols is supported by the Pb and halogen pollution results (paper III).

The average profiles of Fairbanks snow (Table 2) show exceptionally high Br/Cl and a low overall Cl concentration. In our view, the aerosols contained in this snow had lived in the atmosphere for a long time and contained less Cl-rich material than samples from any of the other locations studied.

Chemical considerations

Generation of gaseous iodine from the sea surface has been extensively discussed in the literature, and paper II reviews some of the possibilities that have been proposed. Probably an inorganic form such as I_2 is predominant, but organic species may also contribute. Gaseous bromine in the atmosphere has not been discussed prior to paper II, but there it is suggested that photochemical oxidation of Br^- to Br_2 is a distinct possibility. Paper III dismisses motor fuel exhaust as an important source of particulate bromine seen in the non-urban samples.

I_2, Br_2 and Cl_2 are all oxidizing agents increasing in strength in that order, and in the atmosphere, compounds of sulfur, nitrogen, and carbon are found which are reducing agents capable of reacting with these halogen gases. Important in determining which reactions are likely to be the principal ones are the relative concentrations of oxidizing and reducing agents and the reaction rates, which are subject to catalysis by other substances present.

Ammonium sulfate, the most abundant aerosol material in the troposphere except for sea salt in marine areas, is formed presumably by oxidation of SO_2 gas to SO_3 and then neutralization by NH_3 gas in the presence of H_2O to form $(NH_4)_2SO_4$. I_2, Br_2, and Cl_2 are all thermodynamically able to oxidize SO_2 to SO_3, and the halogen gases tend to react quickly. The abundance of SO_2 in the atmosphere is of the order of 1–10 μg S/m^3 of air considerably in excess of Br or I concentrations. It is reasonable to believe that during such reactions bromide and iodide may remain associated with the sulfate in the newly-formed particles.

In the land aerosols of Hawaii and the Barrow aerosols the data cluster near I/Br $\sim$0.1–0.2. In the Hawaii rains, however, the mean value is nearer I/Br $\sim$0.4. The difference is real and may reflect a more efficient uptake of I^* vapor by the droplets than the aerosols, or it may result from the tendency of raindrops to form from giant aerosols, which are Br-poor but not so I-poor, than from the Br-rich large particles.

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СВЯЗЬ МЕЖДУ ИОДОМ И БРОМОМ В АТМОСФЕРЕ ПОД ГАВАЯМИ, СЕВЕРНОЙ АЛЯСКОЙ И МАССАЧУСЕТСА

Сравниваются предварительно сообщенные анализы дождя, снега, аэрозолей и газа с Гаваев, Аляски и Массачусетса и новые анализы снега и льда из Антарктиды и Аляски. Оба и иод и бром связаны с аэрозолями меньших размеров, но с большим временем нахождения в атмосфере, чем хлор. В наиболее удачных пробах имелся рост группами (clustering) при отношении I/Br ~ 0,1 – 0,2, а отношение Br/Cl превышало значение для морской воды в несколько раз.

Однако аэрозоли, собранные над поверхностью моря в Гаваях дают значение Br/Cl в несколько раз меньшее чем для морской воды. Последние отождествляются с аэрозолями «Морской соли», тогда как богатые бромом аэрозоли меньше по размерам и могут существенно различаться по химическим соединениям, например, содержать сульфат аммония как исследовал Junge (1963 г.). Можно предположить, что бром «испаряется» из морских брызг посредством фотохимического окисления до Br_2, а затем «конденсируется» в меньшие частицы посредством окисления SO_2 в сульфат. Иод возможно захватывается при аналогичных реакциях и поэтому богатые иодом и бромом частицы повсеместно характеризуются одним и тем же отношением I/Br. Анализ осадков дает аналогичное постоянство этого отношения.