

The origin of the gaseous form of natural atmospheric chlorine

By ROMAN VALACH, *Geological Institute of the Czechoslovak Academy of Sciences, Praha*

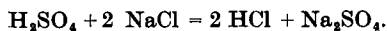
(Manuscript received May 16, 1966)

ABSTRACT

From the evaluation of Junge's experimental data from Florida the conclusion has been drawn that the gaseous form of the natural atmospheric chlorine cannot originate from the particles of sea salt. According to the data by Podzimek and colleagues from the Hradec Králové area (Czechoslovakia) it seems especially improbable that hydrogen chloride would be released from sea salt by action of sulphuric acid; a more accurate re-computation of the original calculation on which the above-mentioned hypothesis was based leads to the same conclusion. Basic reasons supporting the idea that the gaseous form of the atmospheric chlorine results from volcanic action are given. If this new hypothesis is confirmed, the study of processes affecting deep-seated volcanic exhalations will also become significant from the points of view of meteorology, agriculture, transportation, etc.

In studying the contents of some components in the atmosphere of Florida Junge (1956) established that chlorine is present in the atmosphere mostly in the form of giant particles or in the form of gas (Table 1). The proportion of chlorides in large particles is by an order of magnitude smaller than that in the giant ones. In the total sum of chlorides the gaseous ones make up about 50 % (Table 2).

Eriksson (1959 and 1960) in his comprehensive study argues against the earlier opinions that the gaseous form of chlorine in the atmosphere is represented by the elementary chlorine resulting from the action of ozone upon chlorides (probably of marine origin), or the nitrosyl-chloride (NOCl) produced by the reaction $\text{Cl}_2 + \text{NO}$. In his opinion, in the atmosphere the gaseous chlorine exists in the form of hydrogen chloride which was released from sea salt dispersed in the atmosphere according to the reaction



If the gaseous form of the atmospheric chlorine is produced by its release from drops of solutions or solid particles of sea salt dispersed in the atmosphere (be it by action of sulphuric acid or ozone, or by other agents affecting the sea salt), these particles must become impoverished in chlorine. In these particles the ratio

Cl/Na must, therefore, fall below the value of this ratio in the sea (1.80). From the data given in Table 3 (in which Junge's experimental data have been elaborated) a final conclusion may be drawn that the gaseous form of atmospheric chlorine does not get free from sea salt particles.

Analysis of the experimental data

In the giant particles transported by the flow from the sea the relatively greatest amounts of chlorine and sodium were found and the relative analytical error of the individual determinations was minimum. The established value of the Cl/Na ratio (1.86, or 1.78 up to 1.96) can in this case be regarded as the most reliably determined value of this ratio on the basis of Junge's data (Table 3). It is evident that the value 1.86 agrees very well, i.e. within the relative 3 % analytical error, with that of the Cl/Na ratio in the sea.

In the giant particles in the air blown by the wind from the coast a lesser amount of chlorine and sodium has been found (and a relative error in the respective determinations was greater than that in the case of the breeze from the sea). While on the basis of the average value of the Cl/Na ratio it seems that the giant particles blown by the wind from the sea take up an increased amount of gaseous chlorine, in

Table 1. *Mean Cl and Na concentrations in the atmosphere of Florida according to Junge (1956)*

Kind and number of measurements	Mean determination limits in brackets ^a					
	Cl $\mu\text{g}/\text{m}^3$				Na $\mu\text{g}/\text{m}^3$	
	Total	Giant A	Large B	Gas C	Giant	Large
Air blown from the sea (7)	4.62	2.35 (0.038)	0.041 (0.038)	2.23 (0.025)	1.26 (0.044)	0.074 (0.044)
Air blown from coast (6)	1.36	0.500 (0.059)	0.059 (0.058)	0.80 (0.35)	0.34 (0.048)	0.048 (0.048)

^a In the individual determinations certain limits of detection (for instance, $0.5 \mu\text{g}$ X in 25 ml of the analyzed solution) were considered. The amounts of air taken into a certain solution volume differed in the individual determinations and, therefore, the limits of detection of the single determinations of the same component also varied. The estimate of the standard deviation of the individual, as well as average analytical determinations from the correct value has not been given. In some cases, however, the results of the average analytical determinations approach the value of the respective limit of detection. The average limits of detection were, therefore, considered as $\pm$ data approximately determining the range of the possible analytical error.

the same particles from the coast the chlorine content seems to be somewhat less due to a loss of gaseous chlorine. But, if the rather ample range of the Na/Cl ratio values in the giant particles blown from the coast is considered (1.14–1.92), it can be observed that the Na/Cl ratio value in sea water (1.80) lies within the above range of this ratio.

In the large particles (blown from the coast, as well as from the sea) containing amounts of chlorine and sodium by an order of magnitude lesser than those in the giant particles, the range of the Cl/Na ratio values is considerable; it is due to the error of analytical determinations. The value of the Cl/Na ratio in the sea (1.80), also lies within the range of Cl/Na values established in large particles.

On the basis of four values of the “mean” Cl/Na ratios it can be assumed that in three cases investigated release of gaseous chlorine and in one case enrichment of particles in chlorine could have taken place. This is why the ratio of the gaseous chlorine which theoretically could be set free from giant and large particles to the amount of the gaseous chlorine found has been computed (Table 3). In the air transported by the flow from the sea the amount of chlorine evidently only apparently consumed by the giant particles and the chlorine amount (apparently) released by the large particles perfectly compensate each other. In the air blown from the coast which contained approximately four times less chlorine than that from the sea (and the analyses of which were affected by a

Table 2. *Relative representation of the individual forms of chlorine in the atmosphere of Florida (on the basis of Table 1)*

Air blown from	A/B	A/C	$\frac{100 \cdot C}{A + B + C}$	$\frac{A \text{ from sea}}{A \text{ from coast}}$	$\frac{C \text{ from sea}}{C \text{ from coast}}$
Sea	57 (51–65)	1.19 (0.93–1.21)	48.5		
				4.7	2.8
Coast	8.5 (3.7–560)	0.62 (0.53–0.73)	59	(4.1–5.4)	(1.7–5.5)

Symbols A, B and C have the same meaning as those in Table 1.

Table 3. *Tabular evaluation of the amount of the gaseous form of chlorine possibly released from sea salt according to the Cl/Na ratio (on the basis of data from Table 1)*

Air blown from	Cl/Na in			Cl $\mu\text{g}/\text{m}^3$ released from particles ^a		100·Cl (released)	100·Cl (total released)
	Particles		Atmosphere (total)			Cl (found in gaseous form)	Cl (total found in gaseous form)
	Giant	Large		Giant	Large		
Sea	1.86 (1.78–1.96)	0.55 (0.02–2.63)	3.47	0.09 (–0.03 to 0.19)	–0.09	0	–4.5
			1.80				
Coast	1.47 (1.14–1.92)	1.23 (0.01– ∞)	3.50	–0.11 (–0.25 to 0.39)	–0.027	–17 (c. –35 to 45)	

^a The calculation has been carried out according to the relation $\text{Cl (released)} = \text{Cl (found in particles)} - 1.8 \cdot \text{Na (found particles)}$; the negative values in columns then express which amount of gaseous chlorine could be released from the salt particles.

greater analytical error than the determination of chlorine in the air from the sea)—(Table 1), approximately 17 % of gaseous chlorine may have originated by release from sea salt. The total amount of gaseous chlorine found in the air from the coast and that from the sea which may have originated from sea salt is then about 5 %.

The maximum amount of gaseous form of chlorine which could be released from sea salt particles in the sense of Eriksson's hypothesis can also be computed from the value of the SO_4/Na ratio in these particles. The greater is the difference between the value of the SO_4/Na ratio in the particles coming from the sea and

the value of this ratio in the sea water (and, of course, the greater is the higher sodium amount in the air volume unit investigated) the greater quantity of hydrochloric acid could be set free by sulphuric acid action.

The analytical error in Junge's determinations of sulphates in particles in the air transported by breeze in Florida is, unfortunately, considerable; the amounts found being 0.27–0.37 $\mu\text{g SO}_4/\text{m}^3$ (Table 4), the determination limits ranged between 0.26–0.37 $\mu\text{g SO}_4/\text{m}^3$. The conclusions drawn on the basis of these results furnish, therefore, less evidence than those based on the determinations of chlorides.

In the gigantic particles in the air blown

Table 4. *Tabular evaluation of the amount of the gaseous form of chlorine possibly released from sea salt according to the SO_4/Na ratio*

Air blown from	SO ₄ μg/m ³ after Junge (1956) in particles		SO ₄ /Na in		SO ₄ μg/m ³ from the sea ^b in particles		Maximum Cl μg/m ³ released by action of H ₂ SO ₄ from particles ^c		100 · Cl _{H₂SO₄} Cl (in gaseous form)	
			Particles							
			The sea ^a							
	Giant	Large	Giant	Large	Giant	Large	Giant	Large		
Sea	0.37 (0.37)	0.32 (0.32)	0.294 (0 to 0.59)	4.3 (0 to 21.3)	0.25	0.316	0.018	0.04	0.224	11.7
Coast	0.27 (0.26)	0.33 (0.26)	0.79 (0 to 1.82)	6.9 (0 to ∞)		0.085	0.012	0.137	0.236	46.6
Total										21.0

^a According to Rankama & Sahama (1952) 1 kg of sea water contains 2.648 g SO_4^{2-} and 10.554 g Na^+ .

^b SO_4 from the sea = 0.25 Na (in particles).

^c $\text{ClH}_2\text{SO}_4 = 0.738$ ($\text{SO}_4 \text{ found} - \text{SO}_4 \text{ from sea}$), as $\text{SO}_4^{2-} \sim 2 \text{ Cl}^-$, i.e. 1 mg $\text{SO}_4 \sim 0.738$ mg Cl.

Table 5. Mean NH_4 concentration in the atmosphere of Florida

Air blown from	$\text{NH}_4 \mu\text{g}/\text{m}^3$ after Junge (1956) in particles		NH_4/Na in	
			Particles	The sea ^a
	Giant	Large	Giant	Large
Sea	0.057 (0.034)	0.034 (0.034)	0.045 (0.017 to 0.075)	0.46
Coast	0.12 (0.38)	0.038 (0.038)	0.35	0.79

^a According to Rankama & Sahama (1952) in 1 kg of sea water there is $>0.05\text{--}0.005 \text{ g NH}_4$.

from the sea which contain the greatest amount of chlorine, sodium and sulphates, the value of the "average" SO_4/Na ratio is 0.29, i.e. very approaching that in the sea (0.25). The SO_4/Na value in the sea appears within established intervals of values of this ratio which could be due to an analytical error in three of the four cases (Table 4); only in the giant particles blown from the coast the value 0.25 lies beyond the considerably wide range 0.75– ∞ .

The amount of gaseous chlorine which could be released from the sea salt particles in consequence of the increasing concentration of sulphates corresponds in the case of air from the sea to 12 % of gaseous chlorine really found in this air. In the air transported by the flow from coast which contained less chlorine and sodium than that from the sea, up to 50 % of the gaseous chlorine established may have originated from the sea salt; on the whole, 21 % of gaseous chlorine found may have at the maximum been released by the action of sulphuric acid upon sea salt.

The above values of the possibly released gaseous chlorine are the maximum possible mean values, as in reality part of the acidity of the sulphuric acid contacting in the sea salt solution would be consumed for the neutralization of its weakly alkaline reaction and the overwhelming of buffer effects in this solution. From the data shown in Table 5 it may be gathered that part of the sulphuric acid which would enter into the atmospheric particles of marine origin would be neutralized by NH_4^+ ions which probably also enter there from the atmosphere (since $\text{SO}_4^{2-} \sim 2 \text{ NH}_4^+$, 1 mg $\text{NH}_4 \sim 2.66 \text{ mg SO}_4$).

The amount of gaseous chlorine in the atmosphere of Florida which could be released from sea salt, be it by means of whatever mechanism, is, therefore so small, that the sea salt (the sea) cannot be regarded as a source of the greatest part of the atmospheric gaseous chlorine. The values of gaseous chlorine which according to Junge's basic experimental data could originate from sea salt may be considered to result most probably from analytical errors.

It may therefore be stated that the above analysis of Junge's (1956) results clearly attests the right assertion of this author (1960) in his comments to Eriksson's (1959 and 1960) study that "there is no basis for the assumption that the ionic composition of sea spray particles deviates much from that of sea water".

The correctness of Eriksson's hypothesis on the origin of the gaseous form of the atmospheric chlorine can also be recognized from the values obtained on the basis of a great number of measurements carried out by J. Podzimek, L. Šrámek & E. Volfová (1964). From Table 6 it follows that in the Hradec Králové area in the precipitations during the summer months of 1960 the ratio Cl/Na was somewhat higher than that in Florida (3.7×3.5). The conclusion may, therefore, be drawn that during the summer season mentioned in the atmosphere of the Hradec Králové area about 50 % of chlorine existed in gaseous form. During the winter months of the same year the value of the ratio studied fell as low as to equal its value in the sea; from this it may, therefore, be concluded that in winter season in our area there was practically no gaseous chlorine.

As far as Eriksson's hypothesis that the

Table 6. *Some data on precipitations in the Hradec Králové area (according to Podzimek et al., 1966)*

Season	Average contents (mg/litre) in samples from 11 localities			Cl/Na	Cl/SO ₄	pH
	Cl	Na	SO ₄			
IV-IX	5.98	1.61	12.62	3.71	0.47	4.87
X-III, 1960	1.76	0.97	11.71	1.81	0.15	4.71
Sea (average)				1.80	0.25	8.17

origin of atmospheric gaseous chlorine is conditioned by the action of sulphuric acid upon sea salt would be correct, the rise of the Cl/Na value would be accompanied by a proportional increase of the SO₄/Na value, or the Cl/SO₄ value would be approximately constant in time-spans with fairly great or negligible amount of gaseous chlorine. From Table 6, however, it follows that a marked change in the value of the Cl/Na ratio is in connection with a pronounced variation of the Cl/SO₄ ratio. While in the precipitations in the Hradec Králové area in the summer and the winter of 1960 the chloride contents differed three times, the sulphate concentrations showed very small variations only ($\pm 3.7\%$ of the result).

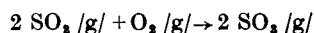
The dependences (following especially from Eriksson's hypothesis) between the content of the gaseous form of chlorine in the atmosphere and (a) the Cl/Na ratio, (b) the SO₄/Na ratio in the atmospheric sea spray particles, and (c) the concentration of sulphates in the atmosphere do not therefore exist.

Analysis of Eriksson's computation of the gaseous form of chlorine in the atmosphere

From the analysis of the experimental data it is clear that chlorine is not released from sea salt in an amount which would be comparable with the great content of gaseous chlorine sometimes occurring in the atmosphere. From the mutual non-dependence of free chlorine and sulphates concentrations in the atmosphere it follows that by action of sulphuric acid only a small (about 10%) proportion of gaseous atmospheric chlorine could originate. As the experiments carried out contradict the opinion that the gaseous form of atmospheric chlorine originates from sea salt the following analysis of Eriksson's calculation is given below as supplement only.

The question has been raised how in the atmosphere sulphuric acid arises which could expel hydrogen chloride from sea salt. Junge & Ryan (1958) who investigated oxidation of SO₂ into SO₃ in clouds have established that this reaction takes place in solution in presence of ammonia. When pH is low this reaction takes place extremely slowly. SO₂ becomes therefore oxidized into sulphate, the original alkalinity (e.g. of sea water) becoming simultaneously lower; or, more exactly said, only after transformation of H₂SO₃ into sulphite the sulphate ions originate. There is, therefore, no doubt that in the atmosphere sulphates arise. The origin of free sulphuric acid which solely can expel hydrogen chloride from sea salt, however, does not follow from Junge & Ryan's ascertainments.

Eriksson quotes Gerhard's (1953) paper (unfortunately not available) according to which in daylight the reaction



takes place with speed 0.1–0.2% in an hour.

In Sweden the amount of the fallout sulphates is 0.9 kg/ha/year; this value corresponds to the sulphur concentration increase in the atmosphere by 1 $\mu\text{g}/\text{m}^3/\text{year}$ or 1 $\mu\text{g}/\text{cm}^3$ in an atmosphere column. On the basis of these data Eriksson (1960, p. 78) calculated the amount of SO₂ which during a year becomes oxidized into SO₃ from the relation $0.1/100 \cdot 24 \cdot 365 = 8.8 \mu\text{g}/\text{cm}^3/\text{year}$. As the value 0.88 kg/ha/year computed in this way agrees with that of the sulphates fallen down from the atmosphere, Eriksson thinks that in the atmosphere sulphuric acid originates in an amount necessary for the release of the atmospheric gaseous form of chlorine.

A shortcoming of the preceding calculation is that it tacitly presumes that in Sweden (a) the sun shines during all the 24 hours and (b) that the total amount of SO₂ remains in the atmosphere on the average during 365 days.

Eriksson (1960) himself says in his reply to Junge's (1960) critical comments: "Both Dr Junge and I agree that the residence time of sulphur in the atmosphere is appreciable, perhaps 2–3 weeks." A. R. Meetham cited by Junge (1960) and by Eriksson thinks that the residence time of the industrial sulphur with respect to absorption by the ground is somewhere between 5 and 16 hours.

Eriksson's computation must, therefore, be rendered more accurate on the basis of a more true assessment of time during which SO_2 can become oxidized into SO_3 . From Eriksson's hypothesis point of view it is advantageous to assume that in Sweden the sun light intensity corresponds to sunshine of 12 hours a day (yearly average) during which the reaction takes place with a speed of 0.15 % in an hour, and that not only the total amount of sulphur, but even SO_2 remains 21 days in the air before it becomes oxidized. Therefore it may be written: $0.15/100 \cdot 12 \cdot 21 = 0.38 \text{ } \mu\text{g}/\text{cm}^2/\text{year}$. In Sweden a fallout of maximum 4 % (or more probably only 1 %) of sulphates, therefore, originates by oxidation of SO_2 into SO_3 ; more than 95 % of sulphates are evidently produced by oxidation of alkali sulphites in the sense of Junge & Ryan's (1958) findings.

Sulphuric acid arising in a small amount in the atmosphere will react not only with sea salt but also the calcium and other salts and especially with organic substances (bacteria, etc.) dispersed in the atmosphere or with matter on the earth's surface (trees, soil, etc.). A fairly great part of the acidity of a small amount of atmospheric sulphuric acid coming into contact with sea salt solutions contained in the atmosphere will at last be balanced by buffer equilibria occurring in these solutions.

In the atmosphere amount of sulphate is by an order of magnitude more than that of chlorine (Table 6). The ratio of the gaseous form of chlorine to chlorine in the shape of particles (sea salt) being equal to those given in Tables 1 or 6, the hydrogen chloride amount released by action of sulphuric acid will representant at the maximum about one tenth of the total amount of the gaseous chlorine.

The more accurate recalculation on the basis of Eriksson's consideration therefore leads to the same conclusion as the above analysis of the experimental results. The amount of the atmospheric gaseous chlorine released by action of

sulphuric acid upon sea salt will not exceed (at least in the case of higher proportions of atmospheric gaseous chlorine) 10 % of its total amount in the atmosphere. The amount of HCl released by action of sulphuric acid is therefore approximately the same as that of Cl_2 set free by action of ozone, etc.

Note: In the introduction of Eriksson's (1959 and 1960) meritorious study it is stated that in 1877 the origin of chlorides in river water and some salt deposits has been explained by the Hungarian geologist Posephny who maintained on the basis of geological evidence that chlorides are transported by the atmosphere from the sea to the continent. František Posephny (= Pošepný), born on 30 March, 1836, in Jilemnice, Bohemia, professor of the Mining Academy, Příbram, was a Czech. This many-sided geologist introduced for instance, the term "vadose water", which is used up to the present and is one of the basic terms of hydrogeology.

The theses of the new interpretation

When the natural gaseous atmospheric chlorine does not come from the sea, its origin can only be sought in the second great natural source of chlorine, i.e. volcanic activity. This action really produces gaseous chlorides: for instance, the Valley of Ten Thousand Smokes in Alaska exhales chlorine in the form of HCl in amount of $1.2 \cdot 10^6 \text{ ton}/\text{Cl}/\text{year}$; the same source releases $0.2 \cdot 10^6 \text{ ton}/\text{year}$ fluorine in the form of HF. With regard to the amount of chlorine in the sea (which could not be washed from the rocks of the earth's crust) it can be assumed that the average yearly volcanic production of chlorine amounts to $9 \cdot 10^6 \text{ ton}/\text{year}$ (Eriksson, 1959 and 1960).

In the sea the value of the Cl/F ratio equals 10^4 (according to Rankama & Sahma's data, 1952), in the Valley of Ten Thousand Smokes it equals 6 (Koritnik, 1951). In the precipitations sampled in the Prague area during February and March, 1965—according to the present author's establishments—the ratio Cl/F is about 11 (at 3.9 mg Cl/litre and precipitation 2.2 mm/day). It has been found that the value of the Cl/F ratio most probably was not influenced to a considerable extent by artificial sources. The value of the Cl/F ratio in the precipitations of the Prague area approaches the value of this ratio in volcanic exhalations to which about

50 % of chlorides of marine origin were added. The origin of the Cl/Na ratio value in the summer season of the year 1960 (Table 6) can be interpreted in the same way. It can be concluded, that in the summer of 1960 in the atmosphere of Hradec Králové there existed 50 % of chlorine not bound to sea salt; approximately the same amount of gaseous chlorine has been found in the atmosphere of Florida (Table 2). It is, therefore, probable that the volcanic action is the source of gaseous chlorine in the atmosphere.

These theses of the present author are dealt with in greater detail in his other communications. Only some data concerning chlorine exclusively should be here also quoted. Eriksson writes that authors during their aviatic examination of chloride content in various heights found the maximal chloride concentration in the height of about 500 m above sea and 3000 m above the continent. Czechoslovakian precipitations usually contain c. 3 mg Cl/l, on Lomnický Štít (2634 m/m); however, it was determined during IGY 8.8 mg Cl/l as a mean, and 344 mg Cl/l maximally (Macků *et al.*, 1960). The individual values are varying very quickly (Table 7). I found 70 mg Cl/l and 0.5 mg Na/l in a snow sample from Lomnický Štít (March, 1965). In U.S.A., precipitations mean content of chlorides is 0.3 mg Cl/l; however, in the precipitations from Mount Vernon it was found 0–120 mg Cl/l (Rankama & Sahama, 1952).

The chloride concentration increase (probably chlorine only, not NaCl) in higher level and the very quick changes of its content in the precipitations on the Lomnický Štít (independent on the year seasons) are explainable by the idea that chlorine, mainly in higher levels, was generated by volcanic exhalations. (Similar observations were made in the case of sulphates as well, namely in precipitations on Mount Vernon and Lomnický Štít as compared with those from lower levels.)

After great volcanic outbursts volcanic ash is transported over the whole globe; before it is laid down and washed out from the atmosphere it may, even for a fairly long time, distinctly lower the intensity of sunshine (explosion of the volcano Krakatoa). After the explosion of the French experimental atomic bomb a radioactive cloud was observed to migrate round the whole globe; after explosions of bombs a small proportion of radioactive ash is transported during several years by air currents from place to place. If after

Table 7. *Chlorine contents in precipitations from Lomnický Štít, 1958 (according to Macků *et al.*, 1960)*

Month	mg Cl/l		g Cl/m ²	
I and II	9.2	8.0	1.25	1.49
III	38.5		3.37	
IV–VII	4.1–	7.8	0.45, 1.07–1.50	
VIII and IX	20.0	28.7	3.00	3.13
X and XI	5.2	6.9	0.88	1.26
XII	11.5		1.94	

great volcanic outbursts the volcanic ash travels in observable amount round the whole globe and if after atomic explosions the relatively easily identifiable radioactive particles fallen down can be observed in places considerably distant from the place of experiment, obviously it cannot be excluded that after weak volcanic outbursts a small unobservable amount of ash also travels round the earth. In *gaseous* volcanic exhalations which themselves cannot be deposited, their transportation over the whole surface of the earth (or with regard to the character of air currents in the stratosphere over the whole half of the earth's surface) is still more probable.

About 90-years-old, F. Pošepný's opinion that chlorides (their particles capable to be deposited) are transported by the atmosphere from the sea for great distances should be supplemented in the sense that the gaseous portion of the atmospheric chlorine derives from volcanoes and is transported for still greater distances than chlorides of marine origin.

Meteorological application

Junge (1960) emphasizes that the material which is contained in rain water comes from two predominant sources: Collection of material within the cloud, during the formation process of the cloud and rain drops, and secondly, from the interception of aerosol particles by falling rain drops *below* the cloud. Unless the original air concentration of the aerosol is much larger *below* the cloud than *within* the cloud (i.e., sea salt particles over the ocean along the coasts), the first source is the predominant one.

It cannot, therefore, be excluded in the precipitation samples taken on the earth that in spite of the relation of chlorides of marine

origin to those of volcanic origin >1 , the influence of halogenes of volcanic origin upon the origin of precipitations may be of the same extent, if not greater, than the influence of chlorides of marine origin.

Recently, the development of weather in the uppermost layers of the atmosphere can be better predicted than that in the lower ones. This is due to the fact that in the uppermost layers of the atmosphere the weather practically depends on processes taking place on the Sun only—and these are thoroughly investigated. The difficulties met in predicting weather in the layers close to the earth's surface may be in relation with the circumstance that the processes taking place at depth in the earth, producing volcanic activity and in this way seriously influencing the meteorological conditions of the lower layers of the atmosphere have not so far been studied in greater detail.

If the assumption is confirmed that volcanic

exhalations seriously influence the weather (in the current sense of the term), the study of at least some of the processes occurring at depth in the earth will become obligatory also from the point of view of meteorology and thus also agriculture, transportation, etc.

The meteoric matter fallen down to earth amounts according to new assessments (Fedinskij, 1964) to 10 million tons/year; the earlier data gave only 700–1800 tons/year (Watson, 1947). The amount of chlorine separated out from the mantle of the earth into the atmosphere is therefore comparable with the present-day estimate of the amount of the matter fallen down. If the influence of the meteoric dust on meteorological phenomena is studied, it would be useful to also investigate in the same way—already on the basis of the above-mentioned comparison—the chlorine derived from volcanic activity.

REFERENCES

- Eriksson, E. 1959 and 1960. The early circulation of chloride and sulfur, in nature, meteorological, geochemical and pedological implications. *Tellus* 11, 375–403; 12, 63–109.
- Eriksson, E. 1960. Reply. *Tellus* 12, 465–467.
- Fedinskij, V. V. 1964. *Nekotorye kompleksnyje problemy v naukach o zemle i kosmose*, in *Zemlja vo vselej. Izdat. Mysl, Moscow*, 1964, pp. 145–155.
- Gerhard, E. R. 1953. *The photochemical oxidation of sulfur dioxide to sulfur trioxide and its effect on fog formation*. Thesis Engineering Exp., Sta. Univ. of Ill., Urbana, Ill.
- Junge, C. E. 1956. Recent investigations in air chemistry. *Tellus* 8, 127–139.
- Junge, C. E. & Ryan, T. G. 1958. Study of the SO_2 in solution and its role in atmospheric chemistry. *Quart. J. Roy. Met. Soc.* 84, 46–55.
- Junge, C. E. 1960. Letter to "The yearly circulation of chloride and sulfur, etc." by E. Eriksson. *Tellus* 12, 463–465.
- Koritnik, S. 1951. Ein Beitrag zur Geochemie des Fluors. *Geochim. et Cosmochim. Acta* 1, 89–116.
- Macků, M., Podzimek, J. & Šrámek, L. 1960. Results of chemical analyses of precipitation collected on territory of Czechoslovak republic in IGY. *Travaux Inst. Géophys. Acad. Tschécosl. Sci. No. 99–125*. Geofyzikální sborník, 1959; Prague, 1960, pp. 441–520.
- Podzimek, J., Šrámek, L. & Volfová, E. 1964. Chemical analyses of precipitation collected around Hradec Králové. *Travaux Inst. Géophys. Acad. Tschécosl. Sci. No 195*. Geofyzikální sborník, 1963; Prague, 1964, pp. 493–520.
- Rankama, K. & Sahama, Th. G. 1952. *Geochemistry*. The University of Chicago Press, p. 295.
- Valach, R. 1967. Fluoride und Chloride in Niederschlägen von Böhmen. *Studia geoph. et geod.* 11, 349–251.
- Vatson, F. 1947. *Mezdu planetami, Ogiz. Moscow–Leningrad*.

ПРОИСХОЖДЕНИЕ ГАЗООБРАЗНОЙ ФОРМЫ ЕСТЕСТВЕННОГО ХЛОРА В АТМОСФЕРЕ

Из рассмотрения экспериментальных данных Юнге по Флориде было сделано заключение, что газообразная форма естественного хлора в атмосфере не может производиться из частичек морской соли. Согласно данным Подзимека и его сотрудников по области Градек Кралове (Чехословакия) кажется особенно невероятным, чтобы гидрат хлорида появлялся из морской соли под действием серной кислоты; более точный пересчет первоначальных вычислений, на которых были

основаны приведенные выше гипотезы, приводит к тому же самому заключению. Приведены основные причины, обосновывающие идею, что газообразная форма атмосферного хлора является результатом вулканической деятельности. Если принять эту новую гипотезу, то изучение процессов, вызывающих глубоководные извержения вулканов также станет важным с точки зрения метеорологии, сельского хозяйства, транспорта и т. д.