THE PHENOMENON OF FORMATION OF PREBIOLOGICAL COMPOUNDS IN VOLCANIC PROCESSES

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Abstract. Organic matter has been found in the juvenile ash of seven volcanoes in Kamchatka, the Kurile Islands and Indonesia. Its amount in one eruption is of the order of 100 000 tons. This matter constitutes a multicomponent mixture (more than 150 components) of, mainly, high-boiling (b.p. over 250°C) organic compounds of a complex structure. These are represented by hydrocarbons of saturated and aromatic nature, and, among them, polycyclic hydrocarbons, amino acids, amino sugars and other heteroatomic molecules, also containing N, O, S and Cl. The formation of the above mentioned organic compounds is associated with volcanic processes – with abiogenous synthesis taking place in ash-gas clouds and, possibly, in the entrails of the Earth (hydrocarbons and their heteroatomic derivatives have also been found in volcanic bombs). On the strength of these facts, volcanic phenomena are regarded as the process which serves as the starting point of the chemical evolution from the inanimate to the animate matter.

1. Introduction

While studying the mechanism of volcanic eruptions, authors noted the similarity of the conditions in ash-gas clouds with those in various biochemical experiments on the abiogenous synthesis of amino acids and other complex organic compounds (Miller, 1953; Harada and Fox, 1965; Grossenbacher and Knight, 1965). Therefore it was considered necessary to study the juvenile volcanic ashes with the aim of ascertaining the presence of complex organic molecules in them.

Such an opportunity presented itself in 1973, when the Tjatja volcano on Kunashir Island in the Kuriles erupted (Markhinin *et al.*, 1974).

The results of the study confirmed the presence of organic compounds in the eruption products.

2. Experiment and Results

The main volcanic material studied was ash and a bomb of the Tjatja volcano. Ash samples were collected directly during the process of eruption on a square grid with the side of each square equal to 2.5 km. Out of 30 samples, an average sample was composed, which served as the basis for quantitative calculations. Data on the chemical composition of organic matter were, mainly, obtained by studying the 10 kg ash sample. Ash was collected in wide-mouthed glass bottles during ash fall, washed with a cleaning mixture and closed with glass stoppers or metal covers. Check experiments (without the analysed substance) were performed in the process of all the laboratory investigations.

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Chemical reagents of the following qualification were used:

(1) Chloroform – manufactured in accordance with the specifications of the U.S.S.R. State Pharmacopeia, that is, tested for the absence of organic compounds.

(2) Ethyl alcohol – 96% rectificate, purified of organic admixtures by oxidizing them with potassium permanganate, and freshly distilled.

(3) Acetone – C. P. (manufactured in the GDR).

(4) Benzene – C. P.

(5) Water – distillate; when analysing amino acids – bidistillate.

(6) Hexane – C. P.

2.1. EXTRACTION OF ASHES WITH WATER–ALCOHOL SOLUTION

Amino acids. 250 g of juvenile ash of the Tjatja volcano were boiled for 5 hours with 300 ml of 80% ethyl alcohol. The solution formed was separated from the ash and concentrated by evaporation to dryness. The sediment obtained was dissolved in 6 ml of water – 1 ml of this solution was taken for the analysis of 'free' amino acids and 1 ml – for the hydrolysis and subsequent determination of 'combined' amino acids.

For hydrolysis, 1 ml of the above solution was evaporated to dryness, 2 ml of 5.7 N HCl were added, the mixture purged with argon and hydrolized in a sealed glass ampule during 20 hours at the temperature of 105 °C, then evaporated to dryness and

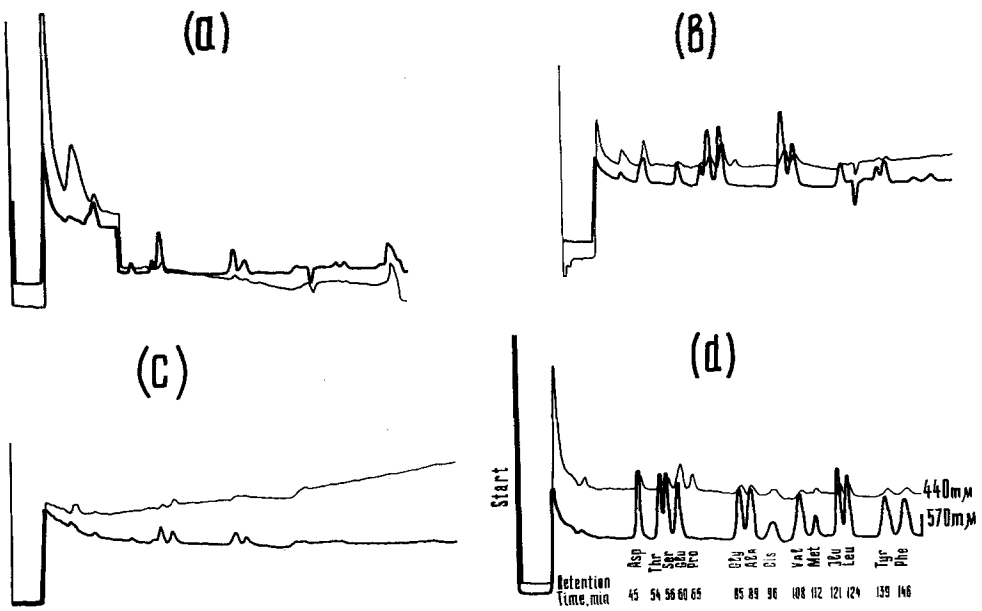

Fig. 1 Chromatograms of neutral and acidic amino acids of volcanic ashes, obtained on amino acid analyser. (a) – Tjatja ash (without hydrolysis). (b) – Tjatja ash (with acid hydrolysis). (c) – Tolbachik ash (with acid hydrolysis). (d) – Standard mixture of amino acids (concentration of each amino acid 12 nM).

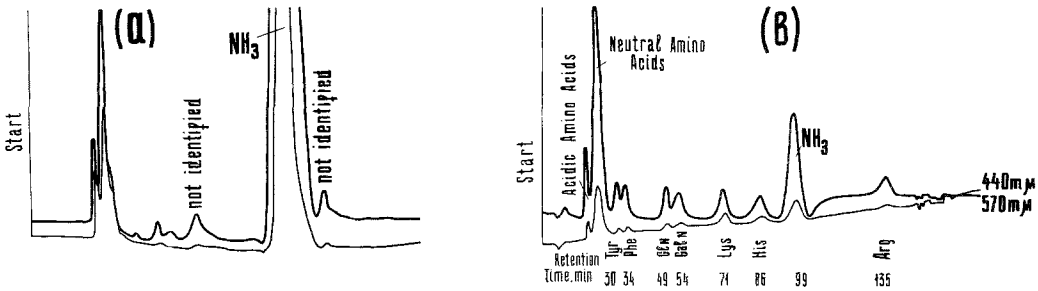

Fig. 2. Chromatogram of basic amino acids and amino sugars of Tjatya ash, obtained on amino acid analyser. (a) – Tjatja ash (with acid hydrolysis). (b) – Standard mixture of amino acids and amino sugars (concentration of each component 12 nM).

dissolved in 2 ml of water. In a similar way was analysed the juvenile ash of the Tolbachik volcano, taken in sterile conditions during the eruptions of 1975–1976.

Qualitative and quantitative determinations of amino acids were performed on the Biotronic LC40/0 amino acid analyzer (FRG). Acidic and neutral amino acids were separated on a column with cationite Aminex A–6 (0.9 x 56 cm), and basic amino acids – on cationite Chromex UA-8 (0.9 x 56 cm). Acidic and neutral amino acids were eluted with Na-citratic muriate buffer solution, pH 3.25 (0.2 N Na) and 4.25 (0.2 N Na). Elution of basic amino acids was conducted with the same buffer, pH 5.28 (0.35 N Na and 0.7 N Na).

All amino acids, with the exception of proline, were recorded from the optical density at 570 mμ, proline – at 440 mμ. Two standard mixtures were used for identification.

For the results obtained see Figures 1 and 2 and Table I. As is seen from the table, the following seven 'free' amino acids were found in the ash of the Tjatja volcano: asparaginic acid, threonine, serine, glycine, alanine, isoleucine, leucine. In the ash of the Tolbachik volcano, the following four 'free' amino acids were found: threonine, serine, glycine, and alanine. In the extracts studied, the basic amino acids – histidine, arginine and, probably, lysine – were detected as traces in the hydrolysate of the Tjatja ash extract. In other words, amino acids in the investigated ashes are, mainly, of neutral and acidic nature.

It is to be noted, that, next to the regions where trace quantities of the above basic amino acids are recorded on the chromatograms, 6 peaks of unidentified compounds were detected. There is every reason to believe that, along with free amino acids, the ashes of Tjatja and Tolbachik volcanoes contain peptides.

From Table I it is seen that, in the case of the Tjatja volcano, they consist of the following 15 amino acids: Asp, Thr, Ser, Glu, Pro, Gly, Ala, Val, Ilu, Leu, Tyr, Phe, Lys, His, Arg; and in the ash of Tolbachik volcano of the following 8 amino acids: Asp, Thr, Ser, Glu, Gly, Ala, Ilu, Leu.

Amino sugars. These were found in the hydrolysate of the water-alcohol extract of the Tjatja ash during the investigation of its amino acid composition. In other words, amino acids are present in the ash not in their free form. Conditions of the experiment have

TABLE I
Volcanic ash amino acids

Ser. No.	Volcanoes	Content of amino acids, extracted from 250 g of ash, in nano moles													
		Asp	Thr	Ser	Glu	Pro	Gly	Ala	Val	Ilu	Leu	Tyr	Phe	Lys	His	Arg
1.	Tjatja, Kunashir Is. (without hydrolysis)	6.5	7.0	40	–	–	28	17	–	5.5	5.0	–	–	–	–	–
2.	Tjatja (with hydrolysis)	25	19	55	75	30	105	65	30	20	30		traces			
3.	Tolbachik, Kamchatka Pen. (without hydrolysis)	–	4	20	–	–	18	12	–	–	–	–	–	–	–	–
4.	Tolbachik (with hydrolysis)	10	9	40	28	–	31	24	–	traces		–	–	–	–	–

already been described. When determining the composition of this hydrolysate on the amino analyser, two peaks were observed (see Figure 2a): by their retention time they are identified as corresponding to 2-amino-2-desoxy-D-glucose and 2-amino-2-desoxy-D-galactose.

2.2. EXTRACTION OF ASHES WITH ORGANIC SOLVENTS

Hydrocarbons and their hetero-atomic derivatives. 719 g of juvenile ash of the Tjatja volcano were successively extracted in the Soxhlet apparatus with chloroform (50 hr), acetone (20 hr) and alcohol-benzene mixture (1: 1, 30 hr) following the procedure applied in petroleum bituminology. After the removal of the solvents, 3 extracts were obtained.

The yield of the extracts of this ash, as well as that of the ashes of other volcanoes in the Pacific geodynamic belt, obtained by us with the help of the same procedure, is shown in Table II. On a UR-20 spectrophotometer (GDR) the following spectra of the Tjatja ash extracts were obtained (Figure 3): chloroform extract (Figure 3a) – groups CH_2, CH_3, C=C, C=O and $COCH_3$ (1380, 1455, 1600, 1725, 2850, 2940 and 2970 cm^{-1}); acetone extract (Figure 3b) – groups C=C and C=O (1615 and 1720 cm^{-1}); alcohol-benzene extract (Figure 3c) – groups CH_2, CH_3, C=C and C=O (1600, 1650, 1660, 1735, 2860, 2930 and 2965 cm^{-1}).

The yield of chloroform extract, purified of elemental sulphur with metallic sodium, amounts to 0.014%. It contains 76.44% C and 11.90% H. The other elements, according to the data of micro X-ray spectrum analysis, are chlorine, sulphur, oxygen, and nitrogen.

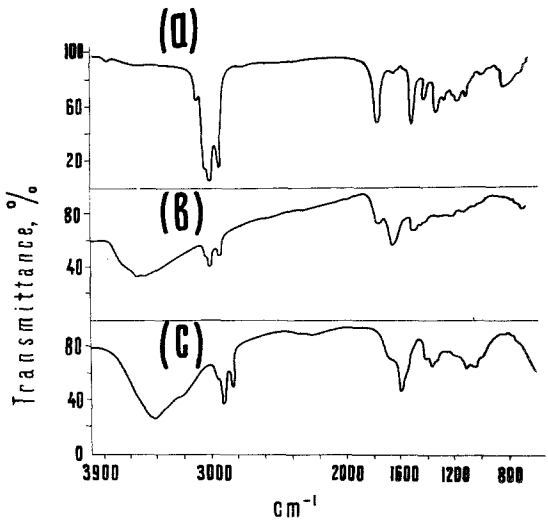

Fig. 3. IR spectra of Tjatja ash extracted with organic solvents. (a) – Chloroform extract. (b) – Acetone extract. (c) – Alcohol-benzene extract.

TABLE II

Content of hydrocarbons and their derivatives [a] in volcanic ash

Ser. No.	Volcanoes	Year of eruption	Content of hydrocarbons and their derivatives, wt. %				Note
			Chloroform extract	Acetone extract	Alchol-benzene extract	Total	
1.	Agung (Bali Is., Indonesia)	1963	0.02	0.01	0.05	0.08	Samples from collection of Institute of Volcanology
2.	Shiveluch, sample 480 (Kamchatka)	1964	0.03	0.03	0.03	0.09	
3.	Shiveluch, sample 481	1964	0.03	traces	0.05	0.08	
4.	Bezymyanny (Kamchatka)	1956	0.02	0.01	0.03	0.06	
5.	Alaid (Alaid Is., Kuriles)	1972	0.010	0.204	0.028	0.242	Average sample of 130 samples taken during eruption
6.	Tjatja (Kunashir Is., Kuriles)	1973	0.03	traces	0.04	0.07	Average sample of 30 samples taken during eruption
7.	Tjatja	1973	0.013	0.014	0.015	0.042	Sample taken during eruption
8.	Klynchevskoy (Kamchatka)	1974	0.03	0.01	0.10	0.14	Sample taken during eruption
9.	Tolbachik (Kamchatka)	1975	0.012	–	–	–	Sample taken during eruption

[a] Data are on the content of tracts unpurified of volcanic elemental sulphur.

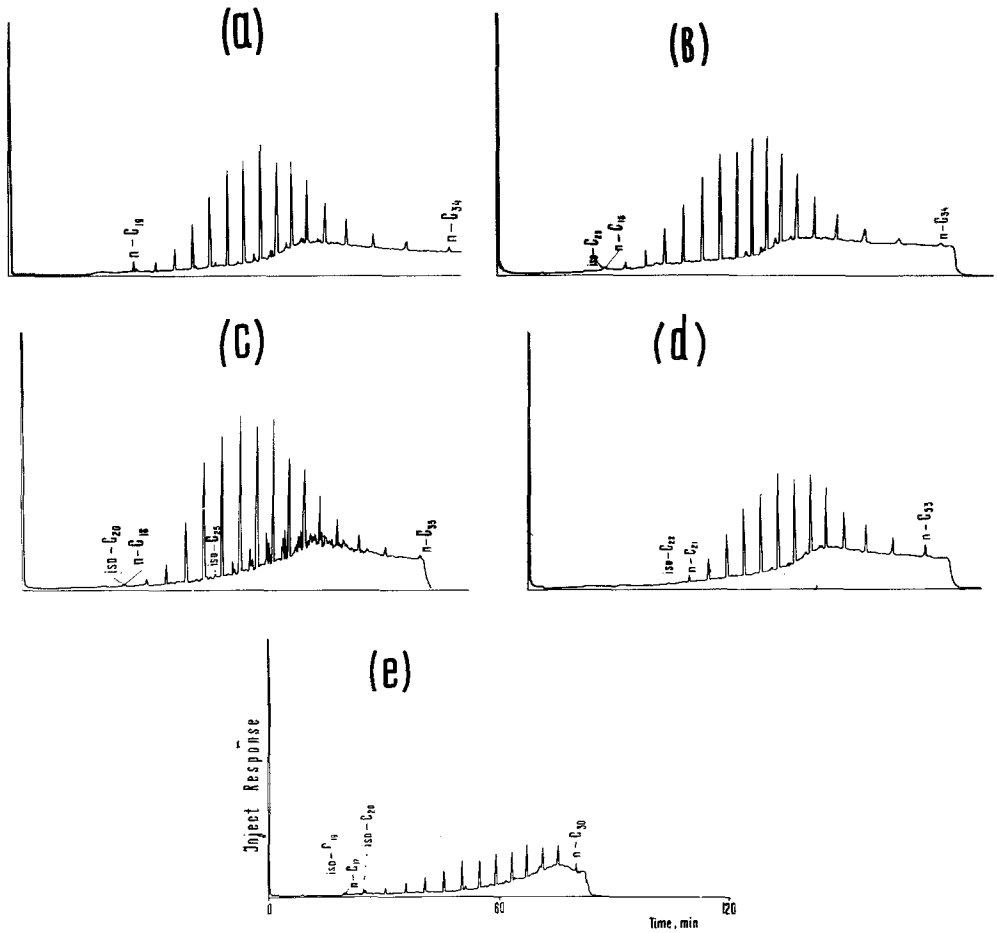

Fig. 4 GLC chromatograms of saturated hydrocarbons of volcanic ashes. (a) – Agung (Indonesia, 1963). (b) – Shiveluch, Sample 481 (Kamchatka, 1964). (c) – Bezymyanny (Kamchatka, 1956). (d) – Alaid (Kuriles, 1972). (e) – Tjatja (Kuriles, 1973). GLC conditions: column – 30 m x 0.25 mm, stationary phase – Apiezon L, carrier gas – H_2, initial temperature – 150 °C, heating rate – 2 °C per min., recording rate – 200 mm hr^{-1}.

With the help of capillary GLC, the composition of the portion of chloroform extract, dissolving in hot normal-hexane, was studied (Figure 4). The number of peaks on GLC chromatograms (minimum number of individual compounds) reaches 76. From Figure 4 it is seen that saturated hydrocarbons of volcanic ashes are, mainly, represented by normal paraffins of C_{17}–C_{34} composition with a small quantity of paraffins of C_{19}–C_{25} composition.

The yield of alcohol-benzene extract, purified of elemental sulphur, amounted to 0.009%. The total yield of hydrocarbons and their derivatives, purified of elemental sulphur amounted to 0.023% of the weight of the ash.

Among the aromatic polycyclic hydrocarbons in the benzene extract of Tjatja ash, with the help of thin-layer chromatography and fluorescence spectroscopy, A.P. Il'nitsky detected benzopyrene to the extent of 4×10^{-5}%.

2.3. EXTRACTION OF VOLCANIC BOMB WITH ORGANIC SOLVENTS

Hydrocarbons and their hetero-atomic derivatives. Before analysis, the volcanic bomb, constituting a lump of molten lava ejected during the eruption of the Tjatja volcano in July 1973, was crushed into pieces of the size of a nut. These were then treated with chloroform in the Soxhlet apparatus for 100 hours (up to the absence of luminescence) to remove possible impurities both of the surface type and those which penetrated through the cracks.

Pieces of the bomb, purified in this way, were ground into fine powder. 480 g of this powder were extracted in the Soxhlet apparatus, first with chloroform and then with alcohol-benzene mixture, similar to ash extraction. The yield of organic matter, extracted with chloroform and purified of elemental sulphur, amounted to 0.04 g or 0.009%. Elemental composition: 77.24% C; 11.19% H.

Figure 5 shows a GLC chromatogram of the portion of this matter dissolving in hot normal-hexane. As it is seen from the chromatogram, saturated hydrocarbons of the investigated volcanic bomb consist, mainly, of normal paraffins of C_{15}–C_{35} composition and a small quantity of branched paraffins of C_{18}–C_{26} composition. The total number of peaks on the chromatogram in Figure 5 is 146.

The yield of alcohol-benzene extract, with the initial amount of the bomb powder equal to 192 g, after sulphur removal, amounted to 0.0136 g or 0.007%. The total amount of hydrocarbons and their derivatives, isolated from the bomb, after their purification of elemental sulphur, was 0.016 wt. %.

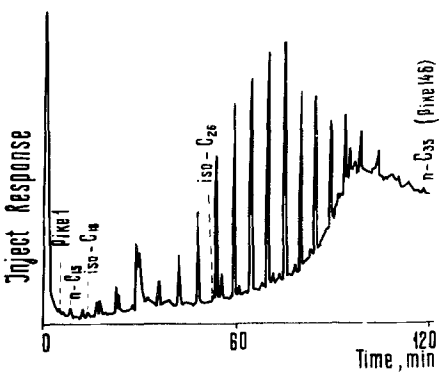

Fig. 5. GLC chromatogram of saturated hydrocarbons of Tjatja volcanic bomb. GLC conditions: column – 30 m x 0.25 mm, stationary phase – Apiezon L, carrier gas – H_2, initial temperature – 150 °C, heating rate – 2 °C per min., recording rate – 100 mm hr^{-1}.

2.4. ON THE POSSIBLE SOURCES OF IMPURITIES

To ascertain the possible sources of organic impurities in the analysed volcanic ash and, first of all, those of amino acids (due to the microbial activity in the volcanic ash, adsorption of microorganisms from the air, admixtures of the organic substances of the soil, contaminated during the collection of samples and their analysis), a series of experimental investigations were performed, as a result of which it can be regarded as an established fact that the organic compounds, found by us in the ash, are of volcanic origin.

As regards the hydrocarbons and their derivatives found in the Tjatja volcano bomb, we, naturally, cannot consider in this case the above possible sources of impurities (adsorption from the atmosphere, etc.), there being no doubt whatsoever that these compounds are associated with volcanic processes.

Since 1972 systematic microbiological studies have been conducted in volcanic areas of Kamchatka and the Kurile Islands. One of the aims of these studies was to determine the extent to which the atmosphere and the products of volcanic eruptions were contaminated with microflora. Microbiological analysis was conducted by inoculating various solid nutrient media (plain agar (PA), starch-ammonia agar, Capek medium, nitrite agar, PA + wort agar, potato agar) with ash suspension or pellets, and by direct microscopic observation using optical, luminescent and electronic microscopes. In the analysed freshly-deposited volcanic ashes from Alaid (Alaid Is., 1972), Tjatja (Kunashir Is., 1973) and Tolbachik (Kamchatka, 1975) no microorganisms were found.

The qualitative and quantitative composition of air microflora was determined by exposing Petri cups for 1 hour (repeated 3 and 5 times) with subsequent calculation of the number of microorganisms per 1 m^3. Microorganisms were incubated at the temperatures of 27° and 60°C.

When determining the air contamination in the area of the Tjatja volcano the highest number of microbial cells – 756 per 1 m^3 – was found 2 metres from the summit of the crater Otvazhny.

The qualitative composition of air microflora is quite uniform, with sporogenous bacteria predominating. With the above degree of contamination, according to our calculation (with full adsorption of microflora from the volume of air equal to 160×10^{12} m^3), not more than 27 kg of microbial carbon deposited with ash from the air during the time of eruption.

As regards the question of the possibility of the ash being contaminated with the organic matter of the soil, it should be noted that the material, filling the craters and orifices in the area of the Tjatja volcano, was ejected during the initial period of the eruption and fell in large masses in close vicinity to the craters. In the process of eruption (360 hours) these masses were buried under a layer of fresh juvenile ashes, i.e., practically isolated.

The content of amino acids in the atmosphere in the Tjatja and the Klyuchevskoy volcano areas was also determined in 1974 and 1975. Determinations were made by suction of 1 m^3 of air through a Drexel bottle with bidistilled water and analysis of

amino acids with the help of paper chromatography. Only traces of two unidentified amino acids were detected in the lower portion of the ascending chromatogram.

Isopiestic determinations of the adsorptive ability of Tjatja ash, with respect to water and benzene, showed the sorption capacity of the ash to be insignificantly small, amounting only to 0.006–0.008 $cm^3\ g^{-1}$. From this it follows that the ash does not, practically, constitute a sorbent, at any rate as compared with the known natural sorbents. The results of determining the specific surface of ash also confirm the fact of this ash having a low absorption capacity – its specific surface was equal to only 0.1 $m^2\ g^{-1}$.

3. Conclusion

In the products of volcanism investigated, a multicomponent (more than 150 components) mixture of, mainly, high-boiling (b.p. above 250 °C) organic compounds with a complex structure has been found. These are represented by saturated and aromatic hydrocarbons, among them – polycyclic hydrocarbons, amino acids (free and combined) amino sugars and other hetero-atomic compounds, containing also sulphur, chlorine, oxygen and nitrogen (in the order of decreasing concentration).

Formation of prebiological compounds during volcanic processes is a natural phenomenon occurring on a large, possibly, global scale. The amount of organic matter, unpurified of sulphur, ejected into the environment during one eruption was, e.g. for the Tjatja volcano (1973), 2×10^8 tons (ash mass) $\times\ 7 \times 10^{-4}$ (concentration of organic matter, see Table I) $\approx$ 140 000 tons.

For the Alaid (1972) and Tolbachik (1975) eruptions, this amount is several times greater. The mass of amino acids, that had been formed in the ash of the Tjatja volcano during the 1973 eruption amounted to 26 tons (calculated from Table II).

From calculations, the annual influx of volcanogenic organic matter into the Earth's environment is estimated at 10^6 tons. In our opinion, amino acids, amino sugars and some other, as yet unidentified compounds of a relatively low molecular weight, are formed in the ash-gas clouds produced by volcano eruptions. That such synthesis is, in principle, possible has been confirmed by the above-mentioned biochemical laboratory experiments on the abiogenous synthesis of complex organic compounds. These experiments were conducted under conditions resembling those of ash-gas clouds. In volcanic clouds, however, such factors as the composition of initial gas mixture, catalysts, temperature, electric discharges, are even more effective.

The formation of relatively high molecular weight hydrocarbons and their hetero-atomic derivatives, found both in the ash and the volcanic bomb, is, probably, associated with the processes taking place deep in the entrails of the Earth.

We regard the present work as a further development of A. I. Oparin's theory of the origin of life. The investigation described shows that a number of prebiological compounds, and among them, first of all, amino acids are formed in the Earth in great amounts in the areas of active volcanism as a result of volcanic processes.

It is here that the process of chemical evolution from the inanimate to the animate starts.

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