POSSIBLE ROLE OF VOLCANIC ASH-GAS CLOUDS IN THE EARTH'S PREBIOTIC CHEMISTRY

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Abstract. Volcanic ash-gas clouds represent versatile local atmospheric environments appropriate for abiotic synthesis of rather complex organic molecules due to the simultaneous presence of various gaseous reagents, catalytically active inorganic particles, electric discharges, pressure and temperature gradients. They are relatively readily attainable for the scientists, contrary to objects or events of space origin (interstellar and planetary dust, meteoritic/cometary impacts, *etc.*), providing excellent opportunities for *in situ* studies and grounded simulating experiments. This paper reviews the available data on this environment, its most important chemical and physical parameters. Based on this analysis, it is suggested in brief experimental conditions for the simulation.

1. Introduction

It is generally accepted that the Earth's interior was very hot, with temperatures essentially at the solidus, immediately after its formation, and that after a period of rapid cooling by vigorous mantle convection lasting several 100 Myr, the interior adjusted to a more gradual cooling by convection lasting most geological time (Schubert *et al.*, 1989). Consequently volcanism was much more intense during the Earth's early history. In addition to the classical mantle-derived volcanism, there was an additional type of volcanism during the late heavy bombardment process (4.5 to 3.8 Gyr) induced by space bodies' impacts. During this period a large number of projectiles (20 km $\leq$ diameter $\leq$ 300 km) collided into Earth accreting a substantial mass, estimated in the range of 1×10^{25} to 4×10^{25} g (Chyba *et al.*, 1994). Such catastrophic events were likely to destroy the incipient crust and trigger volcanism. Evidence for impact-triggered volcanism has been found on Moon at the crater Tsiolkovski and on Earth at the Sudbury Structure in Ontario, Canada, dated at about 2 Gyr old (French, 1970).

Volcanic eruptions must have been common in the Archean and could have played a role in the synthesis of prebiotic molecules. This idea was originally advanced by Fox and Harada (1961) and Harada and Fox (1964). The authors contended that the heat emitted from lava was a plausible source of energy available on the primitive Earth for prebiotic synthesis. A limited number of experiments (Table I) has dealt, however, with the thermal synthesis of simple precursors or biomonomers from simulated primitive atmospheres in contrast to more than hundred experiments done with electric discharge alone. There are several reasons for the

scarcity of the former type of experiments. Some of the most evident are exposed below:

(1) When the field of origins of life began experimentally, about forty years ago, it was believed that the Solar System formed from the collapse of dust cloud at low temperatures (Urey, 1952), and consequently, volcanism should not have been much more intense that at present (Miller and Urey, 1959);

(2) The abundance of volcanic heat on the contemporary Earth is not only small in comparison to other forms of energy (*e.g.*, solar radiation and electric discharges) but its availability is localized. On average about 1 km^3 of new volcanic material in the form of lava and pyroclastic rocks is emitted yearly (Decker and Decker, 1982), at about 1000 °C, corresponding to the energy flux of 0.54 J cm^{-2} yr^{-1} (Miller and Urey, 1959);

(3) Temperatures higher than 600 °C are generally required to activate the atmospheric constituents. Hence, only the surface of molten lava would be effective; once the surface of lava flow became solid, the surface temperature would be nearly that of the atmosphere, even though the lava below the surface was molten (Miller and Orgel, 1974); and

(4) Perhaps the most important drawback for the significance of thermal energy in prebiotic synthesis is low stability of organic molecules at high temperatures. If a simulated atmosphere is heated continuously at 1200 °C, no organic compounds will be produced, and only an equilibrium mixture of the initial gases will be formed. For organic compounds to be synthesized, atmospheric gases must pass slowly over a molten lava bed and then the gas mixture must be rapidly quenched (Miller *et al.*, 1976). Although there are natural mechanisms in analogy to this rapid quenching (*e.g.*, when molten lave flows into lakes, seas or snow), the general point of view has been that the products are not so easily removed from the high temperature zone and consequently are pyrolyzed (see for instance, the discussion followed after the presentation of the paper by Harada and Fox (1965) and published at the end of their paper).

A promising environment for the synthesis of organic molecules and their rapid removal from the reaction zone is volcanic ash-gas clouds (Markhinin and Podkletnov, 1977a,b; Podkletnov and Markhinin, 1981; Lavrentiev *et al.*, 1984; Hill, 1992), where all the gaseous (or vaporous) components necessary for the formation of prebiotic compounds are present under extended pressure gradients. At the same time, ash particles are represented by minerals possessing large surface area and well-expressed catalytic properties. Ash-gas clouds are also characterized by the presence of various temperatures as well as powerful electric discharges, which can serve as an efficient energy source (Schwartz and Henderson-Sellers, 1983; Hill, 1992).

All these factors allow volcanic plumes to serve as natural chemical reactors with a pseudo-fluidized catalyst, like those widely distributed in industry, with variable process parameters, and rapid removal of forming products from the reaction sphere (Podkletnov and Markhinin, 1981). And, what is especially important, they

TABLE I

Prebiotic experiments simulating volcanic environments

Gases	Solid phase	Energy source	Quenched condition	Products [a]	Reference
CH$_4$	Silica gel	1000 °C	0 °C	Several aromatic hydrocarbons	1
CH$_4$, NH$_3$, H$_2$O		1000 °C	?	Gly, **Ala**, β-**Ala**, Thr, Ser, Glu, Leu, **Asp**, Ile, allo-Ile, Phe, Tyr	2
CH$_4$, NH$_3$, H$_2$O	Silica gel and quartz sand	950–1050 °C	3N NH$_4$OH, 25 °C	HCN, Gly, Ala, Asp, Glu, Ser, Leu, Thr, Ile, Pro, Phe, Val, Tyr, allo-Ile, α-aminobutyric acid	3,4
CH$_4$, NH$_3$, H$_2$O	Silica gel	950–1150 °C	20 °C	Aliphatic and aromatic hydrocarbons, ketones, alcohols, carboxylic acids, amides, amines, nitriles, and several amino acids (Gly, β-Ala, Ala, Glu, Ser, Pro, Lys, Val, Leu, aminobutyric acid, Trp, Phe)	5
CH$_4$, NH$_3$, H$_2$O	Quartz sand	900–1060 °C	3N NH$_4$OH in ice bath	**Gly, Ala,** β-**Ala, Asp,** N-CH$_3$-β-**Ala, succinic acid**	6
CH$_4$, CO, NH$_3$, H$_2$O	Basalt	1200 °C	No	**HCN, amines, and aliphatic and aromatic hydrocarbons**	7

TABLE I

Continued.

Gases	Solid phase	Energy source	Quenched condition	Products[a]	Reference
CO, NH_3, H_2O	Zeolites with Ca^{2+}, NH_4^+ and Fe^{3+}	275–290 °C	No	Gly, Val, Ser, Ala, Asp, urea	8
H_2O	Basalt and P_4O_{10}	1265–1340 °C	–2 °C	**Orthophosphate, pyrophosphate and several polyphosphates**	9
H_2O, CO_2, N_2, NH_3	Volcanic ash	Spark discharge, 350–550 °C	Condenser $T = ?$	Gly, Glu, Ala, Val, Ser, Asp, Tyr, Leu, Lys, Phe, Ile, Pro, Thr, Met, Arg, His, uracil, thymine, adenine and guanine	10

[a] Products are arranged in terms of their abundances. A product is boldfaced when it has been identified by more than one method of analysis or by mass spectrometry or nuclear magnetic resonance technique.
(1) Oró and Han, 1966. (2) Oró, 1965. (3) Harada and Fox, 1964. (4) Harada and Fox, 1965. (5) Taube *et al.*, 1967. (6) Lawless and Boynton, 1973. (7) Mukhin, 1976. (8) Poncelet *et al.*, 1975. (9) Yagamata *et al.*, 1991. (10) Lavrentiev *et al.*, 1984.

are relatively readily attainable for the scientists, contrary to objects or events of space origin (interstellar and planetary dust, meteoritic/cometary impacts, etc.), providing excellent opportunities for *in situ* studies and simulating experiments (Basiuk and Navarro-Gonzalez, 1995). The purpose of this work is to critically analyze the available data on this environment, its most important chemical and physical parameters so that future simulation experiments could be geophysically realistic.

2. Volcanic Plume Environment

Volcanic clouds are characterized by the simultaneous presence of a gas mixture and inorganic fine particles, variable pressures and temperatures, as well as powerful lightning and corona discharges (Figure 1). In general, the following parameters decrease permanently with the distance from crater: concentration of volcanic gases and ash particles, pressure, temperature and electric potential. Lightning is initiated randomly from some point in the volcanic plume and is propagated to another area within the plume or to base of the crater. A detailed analysis of these factors follows below.

2.1. GAS PHASE

Chemical analysis of the gas phase is perhaps one of the best explored aspects of volcanology and geochemistry. This success is due to the utilization of gas chromatographic techniques. *In situ* quantitative analysis of volcanic plumes is relatively difficult (see, *e.g.*, Hobbs *et al.*, 1981; Inn *et al.*, 1981) and, most importantly, it does not reflect accurately the composition of volcanic gases due to the instant dilution with atmospheric gases and subsequent chemical processes taking place within the volcanic plume. For this reason gas probes are taken mainly from fumaroles (Gerlach and Casadevall, 1986; Giggenbach, 1987; Heald *et al.*, 1963; Kodosky *et al.*, 1991; Marty and Giggenbach, 1990; Matsuo *et al.*, 1974; Mizutani and Sugiura, 1982) and underground lava lakes (Gerlach, 1980a,b, 1993; Heald *et al.*, 1963).

The composition of volcanic gases is a subject for considerable variations. From source to source, one can detect in total several tens of volatiles; the most abundant being usually water steam, CO_2, SO_2, N_2, H_2S, H_2, CO, HCl, HF, Ar, CH_4, NH_3, COS, O_2 (N_2, Ar and O_2 are often considered to be air-contaminants). An inventory of the major volatiles is summarized in Table II and was gathered from the data by Gerlach (1980a,b, 1982a,b, 1993), Gerlach and Casadevall (1986), Giggenbach (1987), Giggenbach and Matsuo (1991), Heald *et al.* (1963), Kodosky *et al.* (1991), Le Guern *et al.* (1982a,b), Marty and Giggenbach (1990), Matsuo *et al.* (1974, 1982), Menyailov *et al.* (1982), Mizutani and Sugiura (1982), Ohba *et al.* (1994), Poorter *et al.* (1991), Symonds *et al.* (1990), Taran *et al.* (1991)
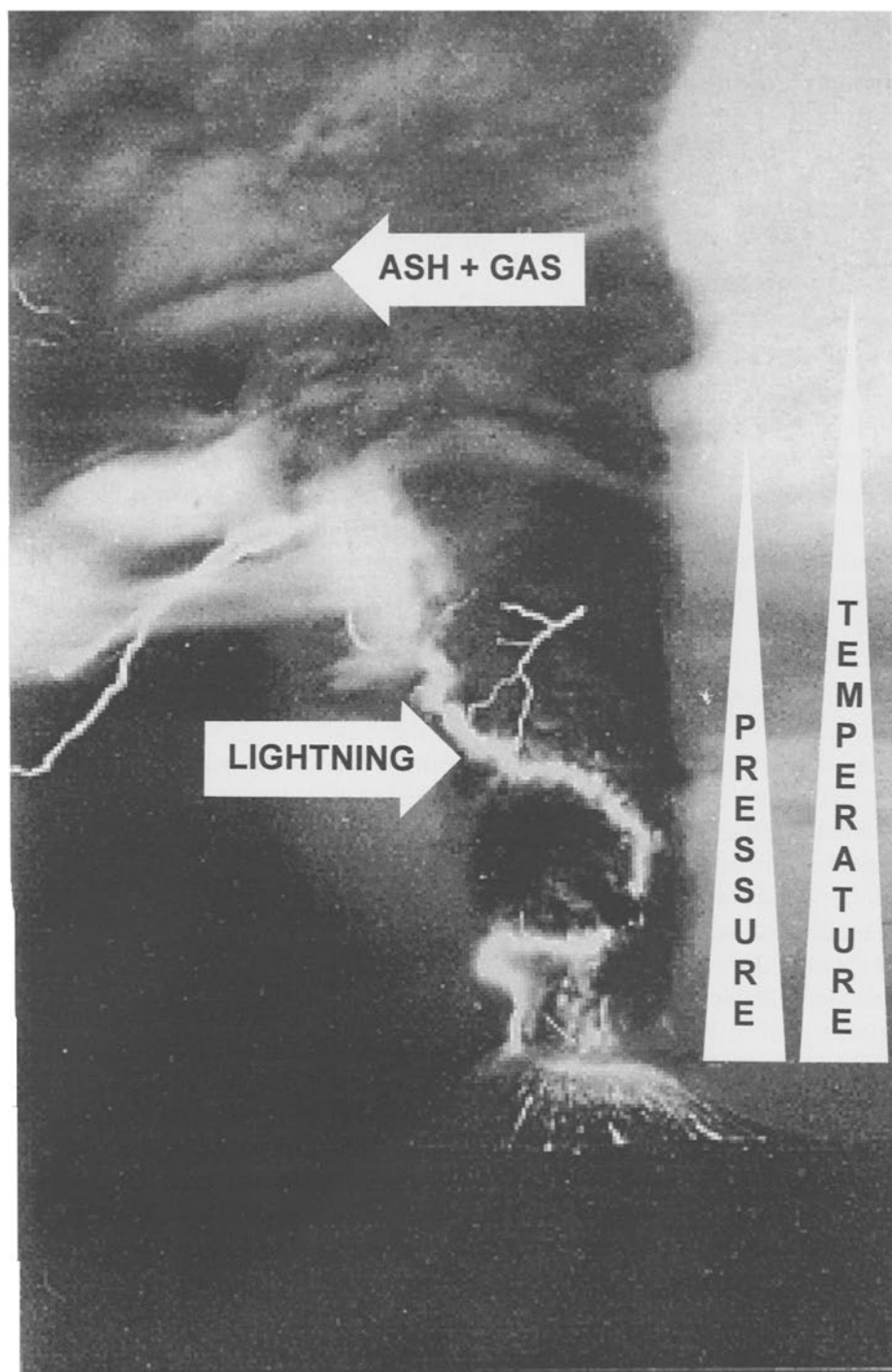
Fig. 1.   The most important factors of a volcanic cloud as a natural chemical reactor are shown in eruption of Tolbachik volcano, Kamchatka Peninsula. Modified from Podkletnov and Markhinin (1981). Reprinted by permission of Kluwer Academic Publishers.

TABLE II

Major components of volcanic gases

Gas	Concentration range (mol%)	
H_2O	2.73	– 99.88
CO_2	0.022	– 64.0
SO_2	0.00057	– 33.54
N_2^a	0.00116	– 4.23
H_2S	0.00002	– 3.21
H_2	0.00000084	– 4.63
CO	0.00001	– 2.7
HCl	0.001	– 9.27
HF	0.0002	– 1.12
Ar^a	0.000012	– 0.000494
CH_4	0.000000285	– 0.49
NH_3	0.00001	– 0.027
COS	0.00049	– 0.04
O_2^a	0.0000005	– 0.00056

[a] Often considered as air contaminant.

and Vakin *et al.* (1982). Large discrepancies, within several (up to 8) orders of magnitude, are observed in the concentrations of volatiles. Steam is in average the most abundant and has a relatively constant content. These fluctuations are attributed to a heterogeneous mantle from which the volatiles were released, namely from the deep (less altered) and the upper (more recycled) mantle.

From the stand point of prebiotic chemistry, it is especially interesting to know what organic compounds have been detected in volcanic gases. The first is methane, found in the concentration range from about 3×10^{-7} to 5×10^{-1} mol% (Table I). Tedesco and Sabroux (1987) has considered methane to form *via* the catalytic Fischer-Tropsch hydrogenation of carbon dioxide. Muenow (1973) has reported mass spectra patterns suggesting also the presence of C_2H_2, C_2H_4, C_2H_6, C_3H_8, CH_2O, CH_3OH, C_2H_5OH and C_4H_{10}. Additionally Graeber *et al.* (1979) has observed a number of hydrocarbons adding up to 1% in total (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{10}, C_6H_6 and $C_6H_5CH_3$). Capaccioni *et al.* (1993) has recently identified fifteen hydrocarbons pertaining to five homologous series (linear and iso-alkanes, cycloalkanes, alkenes, and benzenes). Halomethanes have also been reported in volcanic gases, *e.g.*, by Stoiber *et al.* (1971), Naughton *et al.* (1974), and Inn *et al.* (1981). According to Gerlach (1980a) these data may not be attributed to any abiotic syntheses (except for methane) and must be considered only as evidences of contamination by organic materials as a result of pyrolysis of plant materials and sediments. Capaccioni *et al.* (1993) still admit the influence of Fischer-Tropsch synthesis.

Analyses of the isotopic composition of He, Ne, Ar and Xe in a suite of glasses from the mid-ocean ridges and from the island of Hawaii show that the Hawaiian samples have systematically lower $^4He/^3He$, $^{40}Ar/^{36}Ar$ and $^{129}Xe/^{130}Xe$ ratios than the mid-ocean ridge basalts indicating that the mantle source for the Hawaiian samples is less degassed than that from the mid-ocean ridge (Allègre et al., 1983). This has been interpreted to imply the existence of a primordial, undegassed reservoir deep in the Earth's mantle (Allègre et al., 1983, 1993). Nevertheless, Anderson (1993) argues that the ^3He measured in mantle-derived rocks should not in all cases be considered of primordial origin, and could derive from the subduction of ancient sediments (probably 1.5 to 2 Gyr old) containing ^3He-rich interplanetary dust particles. Regardless of whether ^3He in the Hawaiian samples is of primordial or cosmic origin, the volatiles emitted by Hawaiian volcanoes have been less recycled and could, perhaps exemplify more accurately the nature of gases emitted by Archean volcanoes.

Considerable data have been collected over the years during the different active phases of the Kilauea volcano in Hawaii (Gerlach, 1993), from a group of basaltic volcanos (see Section 2.2). The volatile content varied in the course of two principal types of outgassing processes, which were described by Gerlach (1993) as follows. When magma ascends continuously to the surface to sustain lava lake eruptions, relatively CO_2-rich volcanic gases (Type I) are released in a one-stage degassing process (Figure 2a). A more complex two-stage degassing process (Figure 2b) occurs when magma injected into the summit chamber remains there long enough to equilibrate to chamber conditions. The first stage consists of the quiescent degassing of CO_2, SO_2 and H_2O in excess of melt solubilities from the summit chamber in a chamber gas that is more CO_2-rich than the Type I volcanic gases and estimated to contain up to 80 mol% CO_2. The second stage of degassing is the emission of CO_2-poor (<10 mol%) Type II gases during subaerial eruptions of reservoir-equilibrated magma. Table III collects the data of volatiles emitted in these two different types of outgassing processes with emphasis on H_2O, CO_2, CO and H_2, the most important starting materials for prebiotic synthesis of organic compounds in the atmosphere. For comparison Table III contains the volatiles emitted by Usu (Matsuo et al., 1982), a dacitic volcano characterized by discharging abundant ash during violent eruptions. The values under the subheading Kilauea-1 correspond to the one-stage degassing process (Figure 2) emitting Type I gases; and Kilauea-2, to the two-stage degassing process emitting CO_2-depleted Type II gases. For the both types, H_2O content appears much lower, whereas CO_2 and H_2 contents are much higher than for Usu volcano. CO concentrations vary in even wider range, more than 2 orders of magnitude, down to trace amounts in the case of Usu (Matsuo et al., 1982). Nitrogen was not included for the case of Kilauea since Gerlach (1993) considered N_2 content to be influenced by atmospheric contamination; for Usu volcano, N_2 concentration is typically less than 0.1 mol%.
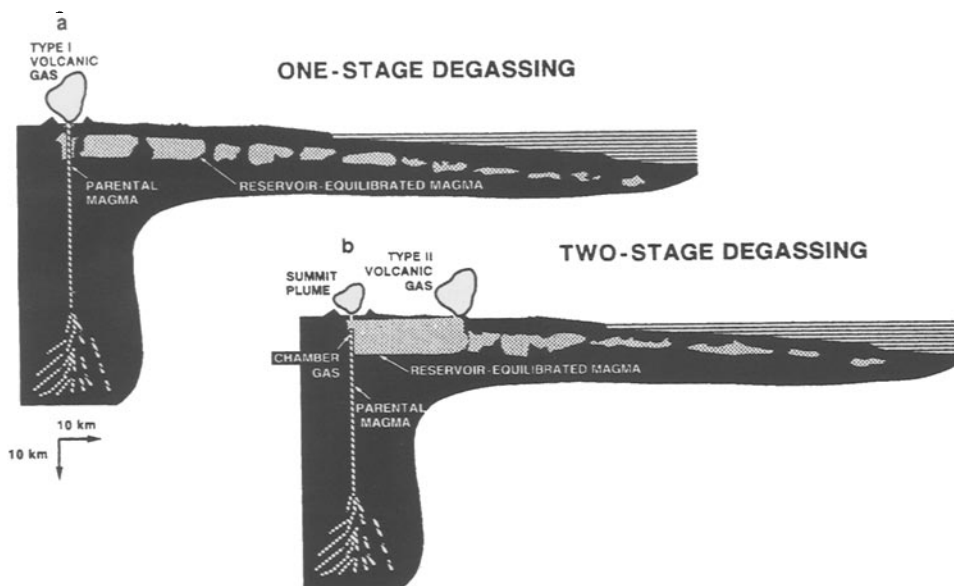
Fig. 2. Schematic cross section of the magma supply and degassing of Kilauea volcano. (a) A one-stage degassing process during a continuously supplied summit lava lake eruption emitting Type I volcanic gases; (b) a two-stage degassing process involving CO_2-rich chamber gas venting from magma in the summit chamber and an eruption emitting CO_2-depleted Type II volcanic gases derived from reservoir-equilibrated magma (Gerlach, 1993). Reprinted with kind permission from Elsevier Science Ltd. ©1993.

TABLE III

Calculated mean composition of major gases from the volcanos Kilauea (Gerlach, 1993) and Usu (Matsuo et al., 1982). $\bar{x}$, mean values (mol%); sx, sample standard deviation. Dash, not analyzed or traces

Gas	Kilauea-1[a]		Kilauea-2[b]		Usu	
	$\bar{x}$	sx	$\bar{x}$	sx	$\bar{x}$	sx
H_2O	52.30	14.44	79.72	1.78	97.30	1.60
CO_2	30.87	13.27	3.48	0.30	1.84	1.23
SO_2	14.59	3.68	13.66	1.83	0.12	0.10
N_2	–	–	–	–	0.08	0.23
H_2S	0.16	0.09	1.17	0.81	0.35	0.26
H_2	0.79	0.25	0.93	0.08	0.15	0.14
CO	1.00	0.39	0.06	0.01	<0.01	<0.01
HCl	0.14	0.12	0.16	0.02	0.12	0.10
HF	–	–	0.18	0.03	0.02	0.02

[a] One-stage degassing process (Figure 2) emitting Type I gases.
[b] Two-stage degassing process emitting CO_2-depleted Type II gases.

2.2. ASH

Volcanic ash is fine-grained magmatic material (Kearey *et al.*, 1993). There are three basic mechanisms for its formation (Heiken and Wohletz, 1985):

(1) The release of gases from solution due to decompression within the magma as it reaches the planetary surface (magmatic eruptions);

(2) Chilling and explosive fragmentation of magma during contact with ground and surface water or ice and snow (phreatomagmatic eruptions); and

(3) The communication and ejection of particles from vent walls or crater debris during eruptions of steam and hot water (phreatic eruptions).

Since the atmosphere and hydrosphere were formed by the early degassing process occurred contemporaneously with the accretion process (which could also contribute to their formation due to the inventory of cometary and asteroid volatiles) or shortly thereafter by vigorous mantle overturning (Schubert, 1989), it seems plausible that the three mechanisms of ash formation took place in the Archean.

The amounts and rates of ash production sometimes reach enormous scales (Walker, 1981a). For instance, the amount of ash fall during the Mount St. Helens eruption on May 18, 1980, was estimated to be about 5.1×10^{11} kg (Carey and Sigurdsson, 1982; Rose *et al.*, 1983); total mass of ash fall deposits resulting from the eruption of Tambora volcano in 1815, 4.33×10^{12} kg (Sigurdsson and Carey, 1989); total volume of ash deposits from the Roseau eruption (the age of 31,000 yr B.P.), 25.4 km^3 (Carey and Sigurdsson, 1980). During the 1979 explosive activity of Soufriere volcano, the volume of ejected ash particles was 5×10^5 m^3 with the discharge rate of 1350 m^3 s^{-1} (Brazier *et al.*, 1982).

Shape and size of the particles vary significantly depending on the mechanism of their formation and magma composition (Heiken and Wohletz, 1985). Separated rounded or elongated droplets can be found, as well as aggregates (clusters) of fragments shaped quite irregularly; the size extends from several and several tens centimeters to microns or even less (Sorem, 1982; Dawson et al, 1992; Sigurdsson and Carey, 1989; Carey and Sigurdsson, 1980, 1982; Smith *et al.*, 1982; Fruchter *et al.*, 1980; Hooper *et al.*, 1980; Rose *et al.*, 1983; Brazier *et al.*, 1982; Murrow *et al.*, 1980; Walker, 1981a,b; Schumacher, 1994; Hobbs *et al.*, 1981). The bigger-size fragments are typically sedimented within several kilometers from the eruption plume; whereas the fine particles may travel far distances vertically (*e.g.*, they have been detected at stratospheric and tropospheric altitudes, higher than 20 km (Shepherd *et al.*, 1979; Ackerman *et al.*, 1980; Christiansen, 1980; Hobbs *et al.*, 1981; Danielsen, 1981; Vossler *et al.*, 1981; Farlow *et al.*, 1981; Carey and Sigurdsson, 1982; Carey *et al.*, 1990; Riehle *et al.*, 1994)) and horizontally (*e.g.*, over 8000 km (Riehle *et al.*, 1994)).

Volcanic ash, like parent magma, is a composite of oxides of the major rock-forming elements where silica dominates. It is formed by disordered Si-O tetrahedra with inclusions of the ions of Mg, Fe, Ca, Na, and K. Depending on the composition,

magmatic materials may be classified under the following types (Kearey *et al.*, 1993):

(1) dacite;

(2) basalt;

(3) andesite;

(4) rhyolite; and

(5) komatiite.

Any of them is composed of several individual minerals (Heiken and Wohletz, 1985; Kearey *et al.*, 1993; Dawson *et al.*, 1992). Andesite contains mainly plagioclases (feldspar minerals) $NaAlSi_3O_8$ to $CaAl_2Si_2O_8$, biotite $K(Mg,Fe)_3(AlSi_3O_{10})$ $(OH)_2$, hornblende $(Ca,Na)_{2-3}(Mg,Fe,Al)_5Si_6(Si,Al)_2O_{22}(OH)_2$, quartz SiO_2, and pyroxene $A_{1-p}(B,C)_{1+p}T_2O_6$ where $A = Na,Ca$; $B = Mg,Fe^{2+}$; $C = Al,Fe^{3+}$; $T = Si,Al$. Basalt contains Ca-plagioclase, pyroxene, quartz, nepheline $(Na,K)AlSiO_4$, olivine M_2SiO_4 $(M = Mg,Fe,Mn,Ca)$ and accessory Fe-Ti oxides. Rhyolite is composed of quartz ($>20\%$), plagioclase, and alkali feldspar; hornblende, titano-magnetite and some other minerals can be found as minor components (Carey and Sigurdsson, 1980). Komatiite contains mainly olivine and pyroxene with especially high MgO content, typically $>18\%$ (Viljoen and Viljoen, 1977; Gelinas *et al.*, 1977). Dacite occupies an intermediate position between andesite and rhyolite (see, *e.g.*, Fruchter *et al.*, 1980; Hooper *et al.*, 1980).

The type which is most relevant to the primordial Earth is komatiite, since such eruptions occurred mainly in the Archean due to enhanced geothermal gradients in the mantle (Nesbitt *et al.*, 1982; Kearey *et al.*, 1993). At the same time, so far it is difficult to explain what volatiles were present in the komatiitic magma to drive eruptions (Heiken and Wohletz, 1985). Water (in significant amounts) is unlikely to be such volatile (Heiken and Wohletz, 1985); instead, another interpretation has been suggested. The pyroclastic rocks from Moon, especially those collected at the Apollo 15 landing site, appear to have compositions similar to the Spinifex Ridge komatiites (Table IV). It was suggested that water is not necessary for the explosive dispersion to form the particles; in the lunar case CO has been accepted to be such principal volatile phase (Meyer *et al.*, 1975; Sato, 1977). Most likely it was also the case for the primitive Earth.

To characterize volcanic samples in detail, usually it is more convenient to operate with element compositions. For the five principal ashes the data are exemplified in Table IV. In contrast to volcanic gases, concentration ranges for all the major oxides vary insignificantly, typically within 1–2 orders of magnitude. Silica (not free) dominates in each case. The second most abundant oxide is alumina, except for komatiitic materials where MgO content can exceed 30%. Besides, numerous trace elements are also found, such as, B, Ba, Br, Cd, Cl, Co, Cr, Cu, F, Ga, Hg, Li, Mo, Nb, Ni, Pb, Rb, S, Se, Sr, U, V, Y, Zn, and Zr (Fruchter *et al.*, 1980; Smith *et al.*, 1982). An important source of them is the condensation of volatile compounds (*e.g.*, MoS_2, $FeWO_4$, $NaCl$, KCl, CdS, PbS, $Pb_3Bi_2S_6$) under cooling

TABLE IV

Major oxide constituents of principal volcanic ashes

Constituent	Ash				
	Dacitic[a]	Basaltic[b]	Andesitic[c]	Rhyolitic[d]	Komatiitic[e]
SiO_2	65.0	50.60	54.57	73.70	48.58
Al_2O_3	16.9	19.20	19.14	12.10	6.28
Fe_2O_3	4.81[f]	10.60[f]			
FeO			6.05[g]	1.44[g]	11.22[g]
CaO	4.94	8.90	4.23	1.67	5.66
Na_2O	4.57	3.70	3.75	3.78	0.08
MgO	2.21	4.11	1.42	0.21	30.77
K_2O	1.47	0.86	5.83	2.61	0.02
TiO_2	0.69	1.13	0.64	0.18	0.33
P_2O_5	0.37	–[h]	0.42	–	–
MnO	0.077	–	0.20	–	–

[a] The Mount St. Helens ash (Fruchter et al., 1980; Table 1, Average).
[b] The Pacaya ash (Smith et al., 1982; Table I, Pacaya 1974: mean).
[c] The Tambora ash (Sigurdsson and Carey, 1989; Table 6, 6 Falls: Whole rock).
[d] The Roseau ash (Carey and Sigurdsson, 1980; Table 1, Column 3).
[e] The Spinifex Ridge deposit (Gelinas et al., 1977).
[f] Total Fe calculated as Fe_2O_3.
[g] Total Fe calculated as FeO.
[h] Dash = not analyzed or traces.

of high-temperature volcanic gases (Bernard and Le Guern, 1986; Varekamp et al., 1986).

An exciting problem, from the view point of chemical evolution, is the detection of organic compounds in ash samples. Markhinin and Podkletnov (1977a,b), Podkletnov and Markhinin (1981), Kolesnikov and Egorov (1977, 1979), and Florovskaya et al. (1978) have collected juvenile ashes and bombs of Tolbachik, Tjatja and Alaid volcanos (Kamchatka and Kurile Islands, Russia) and analyzed the composition of organic constituents. Normal (C_{15}-C_{36}) and isoalkanes (C_{18}-C_{26}), polycyclic aromatic hydrocarbons, and many important biological compounds have been identified, particularly some amino acids (aspartic and glutamic acids, threonine, serine, proline, alanine, glycine, valine, isoleucine, leucine, phenylalanine, histidine, lysine, tyrosine, and arginine) and carbohydrates (glucose and arabinose); some other amino acids, amino sugars, nucleic acid bases, and porphyrins have been tentatively detected. The authors support the abiogenic origin of these compounds by the absence of chlorines (naturally accompanying porphyrins in soils and sediments). Regretfully, they did not analyze enantiomeric composition of the amino acids, that would provide more insight into the problem.

The presence of various alkanes, fatty acids, dicarboxylic acids, benzene ring-containing acids, polycyclic aromatic acids, ketones, alcohols, phenols and aldehydes, aromatic and polycyclic aromatic hydrocarbons, as well as chlorinated aromatics in volcanic (Mount St. Helens) ashes has been also detected by Pereira *et al.* (1980). However, these authors believe that such compounds originated from pyrolysis of plants and soil organic matter. The evidences are, for instance, as follows:

(1) The occurrence of alkanes (C_{15}-C_{32}) with an odd/even ratio greater than 1;
(2) The oxygenated derivatives (fatty, dicarboxylic and aromatic acids as well as aldehydes) are similar to those reported as degradation products of humic material; and
(3) Pyrolysis of plant materials is known to produce polycyclic aromatic hydrocarbons.

The presence of carbonaceous matter in basalts and related materials was reported by Mathez (1987) and Tingle *et al.* (1990,1991), though again it was not possible to unambiguously determine its origin. Thus, the origin of organic matter in volcanic ash samples is a subject for further discussions.

2.3. TEMPERATURE

The range of initial temperatures at which magmatic materials rich the planetary surface and the plume formation begins depend on the melt composition, though it appears rather narrow (Sabroux, 1983). For instance, basaltic andesite magma of the 1979 eruption of Soufriere volcano was at 1000 °C (Brazier *et al.*, 1982); basaltic lava of the 1980 eruption of Large Tolbachik volcano was at 980 to 1070 °C (Fedotov *et al.*, 1980); for Hawaiian basalts, 980 to 1200 °C (Peck *et al.*, 1979); lava of Niragongo 1977 eruption, 1100 °C (Tazieff, 1977). The temperature of the Mount St. Helens dacitic/andesitic melt varied from 920 to 990 °C (Casadevall *et al.*, 1983); the heat content of this lava was estimated at 1344 to 1553 J g^{-1} (Friedman *et al.*, 1980). Nisbet (1985) has pointed out that in the Archean time the temperatures of primary igneous melts rising up from the mantle were probably much higher than today (1700 °C or more). However, the temperature of erupted materials rapidly drops with altitude. In the case of Mount St. Helens, Lawrence *et al.* (1980) reported plume temperature 100 m above the crater to be only slightly higher than the ambient temperature. Obviously, for the plume parts reaching tropospheric and stratospheric levels (Shepherd *et al.*, 1979; Ackerman *et al.*, 1980; Christiansen, 1980; Hobbs *et al.*, 1981; Danielsen, 1981; Vossler *et al.*, 1981; Farlow *et al.*, 1981; Carey and Sigurdsson, 1982; Carey *et al.*, 1990) temperatures should be far below 0 °C.

2.4. PRESSURE

Magma and gases are compressed at very high pressures prior to eruption, *e.g.* 2200±500 bar for Mt. Pinatubo's eruption on June 15, 1991 (Rutherford, 1991).

However, it is very difficult to estimate the pressures at which volcanic matter is erupted from the crater. According to Sabroux (1983) they cannot exceed a few hundred atmospheres. But after the eruption, the pressure equilibrates with the atmospheric one even faster than the temperature does. Therefore, this plume parameter is generally defined by the altitude. The densest part of the Mount St. Helens plume on May 18, 1980, was reported to reach the upper tropospheric and lower stratospheric levels, which are characterized by the pressure of about 300 and 200 mbar, respectively (Carey and Sigurdsson, 1982). Thus one may accept the pressure range for present-day volcanic ash-gas clouds to be 200 to 1000 mbar.

2.5. ELECTRIC DISCHARGES

Lightning discharges are frequently generated during volcanic eruptions, in which steam and tephra are emitted simultaneously into the atmosphere; for instance, they have been detected in the clouds produced by the following volcanoes: Paricutin (Green, 1944), Surtsey (Anderson *et al.*, 1965), Heimaey (Brook *et al.*, 1974), Large Tolbachik (Fedotov *et al.*, 1980), Soufriere (Shepherd *et al.*, 1979), Mount St. Helens (Cobb, 1980), Galunggung (Allard, 1983), and Redoubt (Hoblitt, 1994). These lightning discharges are hundreds of meters in length, *e.g.*, about 500 m at Surtsey (Anderson *et al.*, 1965) and 200–500 m at the Westmann island of Heimaey (Brook *et al.*, 1974).

Nevertheless, there has been little opportunity for investigators of thunderstorm electricity to study such a phenomenon. Some measurements of atmospheric electricity have been made in several volcanic eruptions. Injection of steam and/or volcanic ash into the atmosphere results in an abnormal positive electrostatic field, *i.e.* it differs from the regular fine-weather field of $+100$–130 V m^{-1} by several orders of magnitude. Anderson *et al.* (1965) recorded electric field potentials in the range of 7.8 to 30 kV m^{-1} during the formation of Surtsey volcano. Brook *et al.* (1974) detected potential gradients sometimes exceeding 7 kV m^{-1} in the Westmann island of Heimaey's eruption. Kikuchi and Endoh (1982) measured 15 kV m^{-1} about 5 km away from Mount Usu volcano. Cobb (1980) measured 20 kV m^{-1} at the ground whereas Hobbs and Lyons (1983) registered in an aircraft 10 kV m^{-1} at 175 km from Mount St. Helens on May 18, 1980. The data gathered in Surtsey by Anderson *et al.* (1965) enable us to obtain some insights into the characteristics of electric disturbances associated with volcanic eruptions.

On November 14, 1963, volcanic eruptions were observed in Atlantic Ocean at the southern coast of Iceland in waters 130 m deep (Anderson *et al.*, 1965). Within 10 days an island formed that was nearly 1 km long and about 100 m above the sea level. This island was named Surtsey. The first scientific observations near the volcano were made during February by aircraft and boat. The eruption cloud rose almost vertically to the maximum altitude of about 9 km. The cloud was positively charged and had an electric potential as high as 30 kV m^{-1} in the upper regions. The net positive charge decreased rapidly as the cloud was carried

away from the crater by wind. At sea level the electric potential was recorded to be about 8 kV m^{-1} and point discharge currents were measured in the microampere magnitude during the expedition to the island. As the boat approached the volcano, a vivid display of lightning occurred when large black clouds were rising rapidly (see Figure 1). Because of high concentration of fine, black tephra particles, the volcano cloud was far more opaque than ordinary thunderstorm clouds. For this reason the appearance of lightning over the volcano at night did not provide much illumination. Undoubtedly there were many undetected strokes, and it was not possible to conclude whether the discharges were intracloud or cloud-to-ground. The maximum lightning frequency was about ten discharges per minute. In the average, about 20 discharges per hour were produced. The longest period in which no lightning occurred was about 20 minutes. It is estimated that between 0.1 to 0.5 C of positive charge was neutralized in these discharges. The energy released by each of these discharges is about 10^6 J; this is about 10^2 times lower than the typical lightning discharges in thunderstorms.

Table V summarizes the relevant electric parameters available for volcanic clouds. For comparison, this table contains equivalent data derived under different environmental conditions: clear fair weather and thunderstorms. It is estimated that the energy flux for corona and lightning discharges in volcanic clouds is roughly two orders of magnitude lower than in thunderstorms. The total energy expended in volcanic lightning is about 3.2×10^{11} J yr^{-1} whereas thunderstorms expend about 10^{18} J yr^{-1} (Hill, 1992). Nevertheless, thunderstorms are relatively short-lived (average duration of about 40 min) in contrast to volcanic eruptions that can extent from hours up to days or even weeks.

3. Rational Approaches to Simulate Abiotic Syntheses in Volcanic Ash-Gas Clouds

The development of rational approaches to simulate precambrian volcanic plumes seems complicated because we do not have a precise knowledge of the primordial conditions in this environment (as well as others of the early Earth). It is possible that modern and primordial volcanoes could differ significantly in any of the five general parameters previously described: composition of volcanic gases and the surrounding atmosphere, ash composition, temperatures, pressures, and properties of electric discharges. In general, the eruptions themselves should have been much more abundant and violent in the Archean, resulting in higher intensities of heating and electric discharges as compared to the present.

The ash composition is known in great detail (Table IV). One could accept as an approximation that the volcanic gas components have not changed significantly and may include the major species detected presently (Table II); the exact molar composition could had been subject to significant variations.

TABLE V

Comparison of electric parameters between clear fair weather, volcanic clouds and thunderclouds

Parameter	Fair weather[a]	Volcanic cloud[b]	Thunder cloud[c]
Storm duration (min)		Continuous	40
Storm area (km^2)		1	10^2
Cloud height (km)		9	≈ 1
Charge of cloud		Positive	Positive: upper part; negative: lower part
Electric field (V m^{-1})	1.2×10^2	$(0.8\text{--}3) \times 10^4$	$(1\text{--}2) \times 10^5$
Corona discharge:			
current (A)		μA range	μA range
current density (A m^{-2})	3×10^{-12}	$\approx 10^{-9}$ [d]	$\approx 10^{-9}$ [e]
energy flux (J km^{-2} min^{-1})		$10^5\text{-}10^{6}$[d]	10^7[e]
Lightning discharge:			
intracloud flashes (%)		?	$\approx 60\%$
cloud-to-ground flashes (%)		?	$\approx 40\%$
flash frequency (min^{-1})		0.3	4.5
flash density (km^{-2} min^{-1})		0.3	0.04
flash length (km)		0.2--0.5[b,f]	>1
flash energy (J flash^{-1})		10^6	4×10^8[e]
energy flux (J km^{-2} min^{-1})		10^5	5×10^7 [e]

[a] Lide and Frederikse, 1993.
[b] Anderson *et al.*, 1965.
[c] Uman, 1987.
[d] This value was estimated considering that a cylindrical plume flowing at 150 m s^{-1} from the cone, carried a charge of about 0.01 C per kilometer and that the electric potential within the cloud was $(0.8\text{--}3) \times 10^4$ V m^{-1}.
[e] Chyba and Sagan, 1991.
[f] Brook *et al.*, 1974.

Right after a volcanic eruption, the gases are diluted with atmospheric gases to some extent. Geophysical evidences for oxidation state of the primordial atmosphere can be interpreted in different ways, making unequivocal conclusions impossible (Henderson-Sellers, 1983). It is believed that the early Earth possessed a nearly neutral or mildly reducing atmosphere composed of the volatiles CO_2, H_2O, N_2 and CO (see, *e.g.*, Walker, 1977; Owen *et al.*, 1979, Henderson-Sellers, 1983; Kasting and Toon, 1989). Since these are also the major components of volcanic gases, in the first approach one may neglect the dilution.

Coming from the two most important energetic effects in volcanic plumes, *i.e.* temperature and electric discharges, one could formulate two extreme experimental approaches to simulate a volcanic ash-gas cloud. In the first one, the syntheses

driven by heating are considered (Fischer-Tropsch-type reactions); in the second approach, those driven by electric discharges (plasma chemistry) are examined. Despite these phenomena may not be separated in the case of real plume environment, such division still seems expedient in order to elucidate effects on the abiotic syntheses of temperature and electric discharges separately. Besides, in some cases it is difficult to combine them under laboratory conditions.

3.1. THERMAL APPROACH

The heating in volcanic clouds can induce noticeable chemical processes only in proximity to the eruption site, for plume temperature several tens/hundreds m above the crater appears only slightly higher than ambient temperature (Lawrence *et al.*, 1980). Here, one may completely neglect the dilution by atmospheric gases. The thermal approach has been used in several experiments (see Table I). However, only those of Lavrentiev *et al.* (1984) and Yagamata *et al.* (1991) seem more appropriate to model the volcanic plume environment. Of particular interest for the synthesis of biomolecules is the experiment of Lavrentiev *et al.* (1984), who studied the formation of amino acids, pyrimidines and purines from simple gases H_2O, CO_2, N_2, and NH_3 (4:1:1:0.1), using pulverized volcanic bombs as a catalyst, under the temperatures of 350 and 530 °C and the action of spark discharges. The vapor-gas mixture was supplied to the reactor at a flow rate sufficient to sustain the microparticulate catalyst in pseudo-fluidized state. As a whole, the described experimental design itself mimics the real environment quite well. As to the vapor-gas mixture, it is a subject for some (maybe even significant) modification. No matter the early or present Earth is under discussion, the used NH_3 concentration is inferred too high. To our knowledge, the CO_2/NH_3 ratio in present-day volcanic gases is never found below 100, *e.g.* 178 (Giggenbach, 1987). On the other hand, CO and H_2 should not be disregarded. The CO_2/CO ratio is typically >20, though sometimes is found to drop below 2 (see, *e.g.*, Gerlach, 1980a). The CO_2/H_2 ratio can appear lower, for instance about 1 (Giggenbach and Matsuo, 1991; Kodosky *et al.*, 1991) or even <0.1 (Mizutani and Sugiura, 1982; Taran *et al.*, 1991), typically, however, varying at about 2–20. Since such CO- and H_2-containing atmospheres would possess certain reducing properties, the ash-gas environment must be quite favorable for the thermal-induced abiotic syntheses *via* Fischer-Tropsch processes.

For simulating experiments, one may use the available data on gas composition for the present-day volcanic sources, which are exemplified by the volcanos Kilauea and Usu (see Table III). Of course, the gas ratio may be modified within a wide range. Nitrogen should be necessarily included since even in a close proximity from an eruption site, instant atmospheric dilution of the volcanic cloud must occur (to what extent, it is subject for a separate discussion). Some constituents may be even excluded in the first approximation, *e.g.* SO_2, H_2S, HCl and HF. However, despite for CHNO-organic syntheses (in common sense), presence of the latter

compounds is not crucial; they can drastically change properties of ash catalyst upon adsorption/chemisorption; thus, to create a realistic picture of ash-catalyzed reactions, these components still should be finally included in the gas mixtures. The pressure recommended is 1 to 10 bar, reflecting the assumed value for the early Earth (Kasting and Toon, 1989).

As was said above, in contrast to volcanic gases, concentration ranges for all the major constituents of volcanic ash vary insignificantly, typically within 1–2 orders of magnitude (Table IV). Therefore, one can expect that any type of the ash will exhibit certain catalytic activity in Fischer-Tropsch processes and can be successfully used in the simulating experiments. There is another problem (common for heterogeneous catalysis by complex catalysts) associated with understanding the roles of various surface active sites. Obviously, it is just the case, since any of the ash oxide constituents itself exhibits catalytic properties in respect to one or another chemical conversion. The only way to solve this problem is to use in the simulations, besides natural ash samples, their oxide constituents separately, other conditions being kept equal experiment to experiment.

3.2. ELECTRIC DISCHARGE APPROACH

The electric discharge technique is widely used to drive abiotic syntheses of organic compounds under conditions simulating different planetary atmospheres (Gupta *et al.*, 1981; Hirose *et al.*, 1991; Honda *et al.*, 1989; McDonald *et al.*, 1994; Miller, 1953; Navarro-Gonzalez *et al.*, 1994; Sanchez *et al.*, 1966; Thompson *et al.*, 1991; Toupance *et al.*, 1975).

To simulate the influence of discharge phenomena during volcanic eruptions, along with heating effects, the design proposed by Lavrentiev *et al.* (1984) can be utilized. Under the rather high pressures (of the order of 1 bar), spark discharges are produced. The use of the pressures of tens mbar and below results in glow discharge. The latter type is most appropriate to simulate the chemistry of the upper parts of volcanic plumes reaching tropospheric and stratospheric levels, where no considerable heating is observed; that should be reflected by performing the simulating experiments under temperatures close to the ambient ones. In any case, the design ensuring continuous-flow conditions is desirable, for instance, like those described by Lavrentiev *et al.* (1984) and Thompson *et al.* (1991).

Regarding the chemical parameters, *i.e.* the gas and ash composition, here the considerations presented in Section 3.1 are also valid. Necessary modifications to be made are due to the dilution with primordial atmospheric gases: the gas mixtures should contain lesser amounts of the reductive volcanic gases and water vapor, and correspondingly higher CO_2 and N_2 contents. The higher layers of volcanic plumes are simulated, the higher amounts of these gases should be provided. Regretfully, more or less reliable information on their content for the primordial Earth's atmosphere is not available. According to Lewis and Prinn (1984) N_2 was dominating component, with small amounts of CO_2 and H_2O, and H_2 mole

fractions of 10^{-2} or less; Kasting and Toon (1989) admit CO_2 to dominate, by up to an order of magnitude.

4. Conclusions

A detailed information is available on the present-day composition of volcanic gases and ash, as well as the most important physical conditions for volcanic clouds, *i.e.* temperature, pressure and electric discharges. These parameters (particularly outgassing patterns of the Hawaiian volcanoes) can reflect those for volcanic events on the early Earth, and thus may be used to simulate the primordial abiotic syntheses of organic compounds under laboratory conditions. The separation of thermal and electric effects into different simulating experiments is expedient to elucidate their effects on the syntheses, as well as the use of pure oxide constituents of volcanic ash along with the natural samples seems reasonable to study mechanisms of the catalytic conversions.

Acknowledgements

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