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Can Magmatic Volcanoes Produce Black Carbon Aerosol at Powerful Explosive Eruptions? †

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Abstract: Volcanoes are not traditionally considered to be significant sources of black carbon particles for the stratosphere. The main reason for this well-established view is the absence of appreciable traces of black carbon in volcanic emissions. Recently, a new hypothesis of the formation and injection of nanodisperse carbon into the stratosphere during explosive volcanic eruptions due to the transformation of carbon-containing volcanic gases into black carbon particles was proposed. Critical analysis of this hypothesis and new observational data have shown that it does not contradict the existing ideas about the principal possibility of the process but can and should be substantially supplemented and corrected. The data on the detection of carbon particles in the stratosphere and in volcanic ash confirm the possibility of the formation of the predicted particles and their identity with particles formed by known technological processes and found after powerful volcanic eruptions in Kamchatka (Russia). The main limiting factors determining both the possibility and the lower boundary of the conditions for the formation of particles of different types of black carbon have been identified: temperature and concentration of carbon-bearing gases in the volcanic column. For Plinian-type eruptions, these parameters appear to be insufficient for the formation of black carbon particles in appreciable amounts and their accumulation in the stratosphere, which contradicts the previously mentioned hypothesis. Virtually, all of the black carbon produced must remain in volcanic ash and volcanic sediments.

Keywords: black carbon; Plinian eruptions; methane; pyrolysis; stratosphere; carbon paragenesis; volcanic ash

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1. Introduction

Soot (black carbon) aerosol plays an important role in the Earth's climate system, being a type of carbon-containing particle with a unique combination of morphological, optical, and thermophysical characteristics. Studies of its climatic role in the atmosphere as a "greenhouse" aerosol have received well-deserved and increasing attention [1]. The results are generally focused on a variety of tropospheric manifestations and effects, since the bulk of soot aerosol is concentrated in this atmospheric layer. At the same time, the presence of soot particles of different natures and origins at different altitudes in the stratosphere cannot be ignored. Modern concepts of high-altitude aerosols traditionally emphasize the predominant role of the Junge sulfate layer and volcanic aerosols, but the presence of soot aerosols from various sources is no longer ignored or not properly taken into account [2]. To date, the main sources of soot particles in the stratosphere are considered to be combustion products from fossil fuels, biofuels, and biomass (including forest fires); emissions from air transport engines ("aviation soot"); and particles of meteoric origin [2].

The authors [3] suggest that the known temperature and ozone anomalies after powerful volcanic eruptions are caused by the long-term residence in the stratosphere of ejected nanodisperse black carbon particles [4], although traditional explanations of these phenomena are without this hypothesis. Estimates of the power of injected black carbon particles into the stratosphere are very significant—tens and hundreds of kilotons after a volcanic eruption similar in characteristics to the eruption of the Pinatubo volcano in 1991.

In the meantime, the absence of direct observational data on the anomalous filling of the stratosphere with particles of highly dispersed black carbon after powerful volcanic eruptions leads to a conclusion about the principal limiting factors that sharply reduce the optimistic estimates of the power of particles injected into the stratosphere. In addition, the analysis of chemical reactions with carbon-containing gases in volcanic columns allows the formation of other types of black carbon particles known from widely used technological processes. Finally, the question of direct detection of predicted black carbon particles in the stratosphere, in the ash particles of volcanic clouds in the troposphere, and in the ash and tephra of volcanic sediment remains open. If black carbon does form in volcanic eruptions of the Plinian type, it must be found necessarily in one form or another.

2. Methods

2.1. Chemistry of Carbon Particle Formation at Powerful Volcanic Eruptions

Abiogenic methane, necessary for the formation of black carbon particles, is found in magma and volcanic gases in very small amounts (on the order of 0.3–0.5%). In an explosive eruption, gases move at very high velocities in the volcanic channel and interact with glowing magma particles (pyroclasts) at high temperatures (1000–1200 °C) in an almost oxygen-free medium. During this, methane can thermally decompose (methane pyrolysis):

$$CH_4 \rightarrow C + 2H_2 \quad (1)$$

Methane can also be additionally produced due to the Fischer–Tropsch catalytic process at lower temperatures (250–350 °C):

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (2)$$

Consequently, the formation of nanodispersed (<0.1–0.01 μm) carbon black particles according to Equation (1) becomes possible. The formed black carbon particles (single particles or those associated with volcanic ash) leave the volcanic column, and they are rapidly cooled by the ambient air and participate in subsequent meteorological processes. During this stage, a part of the soot formed can oxidize to carbon monoxide at a sufficiently high temperature.

2.2. Analogies of Particle Formation of Different Types of Black Carbon in Technological Processes and in Powerful Volcanic Eruptions

The structure and properties of the formed carbon particles are diverse and depend on the process conditions. The black carbon formed is traditionally divided into three structural classes [5]: layered or lustrous carbon, called pyrocarbon; fibrous or filamentous carbon; carbon in a highly dispersed state; or technical carbon black (soot). Pyrocarbon is a monolithic carbon body that follows the geometric shape of the surface on which it is formed as a layer. Carbon filaments, or fibers, have the form of cylindrical needles or fibers whose length is several orders of magnitude greater than their diameter. Soot is a substance consisting of an aggregate of submicroscopic primary carbon particles of spherical (or close to spherical) shape. The structure of pyrocarbon formed from the gas phase contains only elements of the graphite structure and, in general, is much less ordered than crystalline graphite. Carbon filaments are produced on catalytically active surface sites, which are either sites containing metal atoms or dislocation sites. The graphite mesh packets in carbon filaments are arranged parallel to the long axis of the filament. In contrast to the formation of pyrocarbon and carbon filaments, the formation of nanodispersed carbon black is a volumetric process of homogeneous nucleation of carbon vapor [5,6]. This type of black carbon particle injected into the stratosphere is what is implied in the hypothesis [3].

In thermal decomposition (pyrolisys) of methane, the formation of pyrocarbon at atmospheric pressure becomes visible at 850–900 °C, and soot appears only at temperatures above 1100 °C. The size distribution curves of carbon nanoparticles formed during the pyrolysis of hydrocarbons strongly depend on temperature. With increasing temperature, a narrowing of the distribution is observed, which can be explained by the different nucleation rates of soot particles [7]. Thermal (technical) soot (unlike all other types of soot) has the least pronounced secondary chain structure and consists mainly of individual, unbound particles. The main regularities of the influence of various factors on the formation of highly dispersed soot are:

1. In the thermal decomposition of hydrocarbons, the dispersity of the resulting soot should be higher when the heating rate of the hydrocarbon is higher.
2. Increasing the temperature leads to a certain increase in the yield and specific surface area of soot, as well as the yield of soot particles. When some temperature is reached, the change in yield and specific surface area stops due to the almost complete decomposition of the hydrocarbon.
3. With increasing hydrocarbon concentrations in the hydrocarbon-nitrogen mixture, soot yield increases, and specific surface area and soot particle yield decrease.
4. For the formation of soot particles, it is necessary to reach some critical, or threshold, concentration of hydrocarbon.
5. Dilution of hydrocarbons with nitrogen or hydrogen leads to a decrease in soot yield. However, up to a known limit, dilution leads to an increase in the number of particles forming rather than a decrease.

3. Results and Discussion

3.1. Detection of Black Carbon in Stratospheric Samplings

Hypothetical black carbon particles from volcanoes can be recorded by high-altitude aircraft, gliders, and stratospheric balloon flights with direct sampling and subsequent analysis on board or in a ground laboratory. Non-contact particle detection by optical methods is less favored, although it does provide useful information on particle size and composition [8,9]. High-altitude flights in the stratosphere of the famous ER-2, M-55 "Geofizika" aircraft with a flight ceiling of 23–24 km have long been implemented in various scientific programs. Stratospheric balloons can ascend to altitudes up to 35–40 km. "Heavy" stratospheric balloons perform mainly vertical flights (e.g., balloons with STAC optical counters [8]), while the flight trajectories of "light" stratospheric balloons with LOAC optical counters are determined by the wind field [9]. The use of the second type of balloon is much cheaper than the first, and about 150 stratospheric flights of these balloons have been made to date. Electron microscopy (SEM, TEM, and HRTEM) is widely used to analyze the morphology and structure of particles in impactor samples during high-altitude flights. Elemental analysis of particles is based on mass spectrometry (direct analysis on board the aircraft is now possible) and energy-dispersive X-ray spectroscopy in EDX, EDRS, and EDS variants. Optical counters with a lower limit of 150–200 nm are commonly used to estimate particle sizes. In "light" stratospheric balloons, a two-angle optical counter (LOAC) is used [9]. This instrument allows estimating the size of particles detected (the lower limit is 200 nm) and their concentration, as well as determining the typology of particles of different origins. The chemical (elemental) composition of particles in this case is not directly determined, but the particles are divided into characteristic types by the value of so-called speciation index [9], which is based on the high sensitivity of the light-scattering signal to the complex refractive index of particles at certain scattering angles (the higher the speciation index, the stronger the particles absorb radiation). Calibration of the LOAC counter with well-certified particles of different compositions and the creation of an extensive database allow us to match the recorded particles with real stratospheric aerosol types and reliably identify particles with high elemental carbon content (black carbon). Methods for detecting black carbon particles in the stratosphere are discussed in more detail in [10]. Some summary data on the detection and characteristics of black carbon particles in the stratosphere are presented in Table 1.

Table 1. Detection of highly dispersed black carbon particles in the stratosphere.

Methodology	Date, Area, and Detection Altitudes	Particle Characterization	Comments
High-altitude airplanes	ER-2 high-altitude aircraft, 1979–1983, North America, up to 21 km	Compact black carbon particles up to 1 µm	After the eruptions of St. Helens and El Chichon
	ER-2, 1993, California, up to 19 km	Submicron aggregates of primary particles 20–30 nm; internal or external inclusions in sulfuric acid droplets	2 years after the eruption of Pinatubo
	ER-2, January–March 2000, polar vortex region, Kiruna, 17–20 km	Submicron black carbon particles, inclusions in sulfuric acid droplets	Analysis of particle origins, including volcanism
Stratospheric balloons	Stratospheric STAC balloons, 1994–2003, polar vortex region, Kiruna, up to 33 km [8]	Submicron particles with high elemental carbon content, pronounced layers, and islands of soot	The method does not involve chemical analysis of particle matter
	"Light" LOAC wind balloons, 2013–2019, wide geography, up to 35 km [9]	Submicron particles with high elemental carbon content and the correlation of their detection with volcanic eruptions	Detection of smaller particles, large number of runs

3.2. *Carbon Particles of Different Nature in Ash and Tephra Samples after Explosive Volcanic Eruptions*

The organic compounds detected in the products of modern Kamchatka volcanism are represented by variously colored filaments, angular "amber-shaped" particles of yellow and orange color, and rounded particles varying in color from colorless and yellowish-green to brownish and dark gray. The data testify to the significant prevalence of graphite in volcanic ashes, which probably indicates the deep nature of these inclusions. In this connection, the question arises about the possibility of the presence of diamonds in ashes, which are known to be found in basalts. Graphite has been observed in pyroclastic products of volcanism in Kamchatka repeatedly [11].

Based on the results of isotopic studies, it was concluded that the paragenesis of carbon minerals, phases, and organic compounds revealed in the explosive products of Kamchatka and Kuril volcano eruptions first, had a single carbon source; second, this source was hydrocarbon gas (predominantly methane); and third, the primary carbon source was deep [11]. The mantle origin of the carbon source for the explosive mineralizations may be the reason for the revealed homogeneity of the carbon isotopic composition in volcanites, volcanic gases, carbon minerals, phases, and condensed organocompounds. It follows from all this that the volcanic-carbon phenomenon, including diamond formation, detected in Kamchatka and the Kuril Islands may have not a local but quite a global scale. Thus, black carbon nanoparticles, ash with fibrous and compact ("encapsulated") particles, as well as graphite-like particles, can potentially be formed during eruptions. Table 2 shows examples of finding carbon particles of different kinds in volcanic sediment samples.

Table 2. Carbon particles of different types in volcanic sediment samples.

Volcano	Area, Date, and Type of Eruption	Comments
Koryaksky	Kamchatka, Avacha group, 2008–2009, phreatic eruption [11,12]	Particles of carbon paragenesis in volcanic ash and tephra (microdiamonds, graphite plates, shungite-like particles, and fibrous abiogenic particles)
Tolbachik	Kamchatka, 2012–2013 [12]	Particles of carbon paragenesis in volcanic ash and tephra (nano- and microcrystalline diamonds)

Table 2. *Cont.*

Volcano	Area, Date, and Type of Eruption	Comments
Alaid	Kuril Islands, Atlas Island, 2012 [11,12]	Combination of carbon phases into multiphase carbon paragenesis (microdiamonds, graphite, bitumoids, and filamentous fibers)
Almazny	Kamchatka, 2012–2013 [11,12]	Multiphase carbon paragenesis, including microdiamond particles, graphite, diocarbon allotropes, and abiogenic condensed organoids
Kliuchevskoi	Kamchatka, 1988 [12]	Particles of carbon paragenesis in particles of pyroclastic material (diamond microcrystals)

4. Conclusions

Analysis of physicochemical processes in a volcanic gas-thermal column showed the possibility of the formation of the following types of black carbon particles: single highly dispersed particles or their small aggregates; fiber-type particles associated with pyroclasts; and graphite-like pyrocarbon particles. The formation of particles of the first type by homogeneous nucleation in carbon vapor is energetically the most costly, and the probability of their formation is minimal for all three types of particles. The data on the detection of carbon-containing particles in the stratosphere and volcanic ash confirm the possibility of the formation of all types of predicted particles and their identity with particles produced in technological processes. Of particular interest are the data on the detection of nano- or highly dispersed black carbon particles in the stratosphere. The most informative are sample collections with high-altitude ER-2 airplanes with subsequent laboratory analysis (Table 1). These reveal either single submicron particles of fractal-like structure or particles as external or internal inclusions in sulfuric acid droplets of the Junge layer. These may be the discussed evidence of recent volcanic eruptions, or they may be particles of aircraft soot. A final conclusion about their nature requires further analysis [12]. The main limiting factors determining the possibility and the lower boundary of the conditions for the formation of particles of different types are identified as temperature and the concentration of carbon-containing gases in the volcanic column. For eruptions of the Plinian type, these parameters are apparently insufficient for the formation of black carbon particles in appreciable quantities. As a consequence, the injection of a large mass of black carbon particles into the stratosphere is unlikely, even during the most powerful volcanic eruptions.

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