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Role of Volcanic Factor in Enhancing Springtime Ozone Anomalies over Antarctica

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Abstract

A predominant role of volcanic factor in strengthening the springtime ozone anomalies over Antarctica has been demonstrated. Correlation analysis was performed concerning the average data for September and October with respect to the areas of polar stratospheric clouds and the ozone hole over Antarctica as well as with respect to minimum temperature values in the stratosphere at an altitude of 18 km, during three 11-year period from 1979 to 2011. It is demonstrated that the accelerated growth of the ozone hole in the early 1980s coincided with the maximum gas emissions of the Antarctic volcano Mount Erebus. Within the subsequent 11-year period, increasing the area of the ozone hole was caused by an abrupt increase in the content of sulphuric acid aerosol in the stratosphere over Antarctica associated with powerful volcanic eruptions of Mount Pinatubo and Hudson Cerro in 1991.

Key words: Antarctic ozone hole, volcanoes, Mount Erebus, Volcanic Explosivity Index VEI, sulphuric acid aerosol, chloronitrate, hydrogen chloride, polar vortex, polar stratospheric cloud, condensation nuclei

INTRODUCTION

In 1985, journal "Nature" [1] published the results of observations at the Antarctic station Halley Bay (75°35′ S, 26°34′ W) concerning an abnormal destruction of the stratospheric ozone layer over Antarctica in the spring period, for the first time designated by the term "ozone hole". The authors of the paper connected the process with enhancing the catalytic "chlorine" cycle of stratospheric ozone depletion due to increasing the content of man-caused CFCs in the Earth's atmosphere. This assumption became the base of the "freon" concept of ozone layer destruction.

Modern concepts concerning the catalytic cycle of stratospheric ozone depletion under the conditions of the polar spring associated with heterogeneous reactions on the surfaces of solid particles in the two types of polar stratospheric clouds (PSC Ia and PSC II), resulting from the abnormally low temperature values in the stratosphere (below 195 and 188 K, respectively) [2]. Under the conditions of the polar night with low solar radiation, there is a deficiency of atomic oxygen observed, resulting from which no efficient catalytic "chlorine" cycle can be realized:

$$Cl^{\cdot} + O_3 \rightarrow ClO^{\cdot} + O_2$$
$$ClO^{\cdot} + O \rightarrow Cl^{\cdot} + O_2 \qquad (1)$$

Under these conditions, the reduction of free chlorine atoms from chlorine monoxide radicals ClO is blocked, for example, due to reactions

$$ClO^{\cdot} + ClO^{\cdot} + M \rightarrow Cl_2O_2 + M$$
$$Cl_2O_2 + h\nu \rightarrow Cl^{\cdot} + ClO_2 \qquad (2)$$
$$ClO_2 + M \rightarrow Cl^{\cdot} + O_2 + M$$

where M is any atom or molecule; $h\nu$ is photon energy. As the result of the blocking reaction, reactive chlorine monoxide radical converts into an inert compound such as chloronitrate:

$$ClO^{\cdot} + NO_2 + M \rightarrow ClONO_2 + M \qquad (3)$$

In the case of low solar radiation, this compound is stable under these conditions; the chlorine can be released from the $ClONO_2$ reservoir *via* heterogeneous reactions on the surface of particles in PSC:

$$HCl + ClONO_2\,(g) \rightarrow Cl_2\,(g) + HNO_3 \quad (4)$$

or

$$H_2O + ClONO_2\,(g) \rightarrow HOCl\,(g) + HNO_3$$
$$HOCl\,(g) + HCl \rightarrow Cl_2\,(g) + H_2O \quad (5)$$

Here, (g) means gaseous state, whereas H_2O, HHO_3, HCl are located on the solid particle surface in PSC:

$$Cl_2 + h\nu \rightarrow 2Cl^{\cdot} \quad (6)$$

those are actively involved in the catalytic cycle of ozone destruction.

The formation of the ozone hole requires for the three conditions: 1) low stratospheric temperature values (<195 K); 2) the presence of condensation nuclei (sulphuric acid mist); 3) the presence of chlorine reservoirs (HCl and $ClONO_2$). Large-scale circulation processes (polar vortices) determine low stratospheric temperature values over Antarctica, these phenomena are regularly observed in the winter-spring period over the South Pole. The formation of the latter two conditions is determined to a considerable extent by the volcanogenic factor that is of sporadic character.

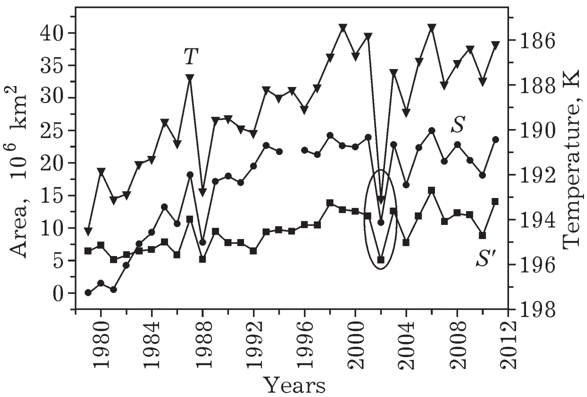

Fig. 1. Interannual changes in the minimum temperature averaged for September–October (T) at an altitude of 18 km within in the latitudinal range (50–90° S) and the areas of ozone hole (S) and PSC of Ia type (S') in the Antarctic stratosphere. 2002 is the year of abnormally abrupt (>2σ) increasing the stratospheric temperature values.

ANALYZING THE TEMPERATURE MODULATION OZONE HOLE AREA AND PSC

Appearing the ozone hole over Antarctica in the spring is caused by cooling the stratosphere down to the temperature values whereat the formation of particles in PSC becomes possible (<195 K). Figure 1 demonstrates the values of minimum temperature (T) averaged for September–October at an altitude of 18 km within the latitudinal range of 50–90° S as well as the ozone hole area (S) and the area of PSC Ia (S') for the period 1979–2011 years [3]. It should be noted that the area of PSC Ia (S') is almost an order of magnitude greater than that that of PSC II, whereas the changes thereof are identical, so only the changes in S' were taken into account.

It is obvious that the main regulator of changing the area values of S and S' is presented by temperature. On the one hand, the temperature effects on the extent of the PSC formation, whereas on the other hand it influences upon the rate of chemical reactions responsible for the depletion of stratospheric ozone. The correlation coefficients (R) of S–T and S'–T series for the entire period (from 1979 to 2011) reach statistically higher values equal to −0.91 and −0.92, respectively. At relatively high temperature values (190 K < T <195 K) in the stratosphere over the Antarctic spring period 1979–1983 as well as in 1988 and 2002 the size of the ozone hole area and PSC were minimal. Warming the stratosphere in 2002 was of anomalous character (deviation $\Delta T > 2\sigma$), wherewith we did not considered data concerning the parameters analyzed for this period.

On the curves in Fig. 1 demonstrate three distinct periods with the duration of about 11 years each (1979–1989, 1990–2000 and 2001–

TABLE 1

Correlation coefficients (R) for interannual changing the averaged data (September–October) concerning the area of ozone hole (S), PSC Ia (S') and the minimum temperature (T) at the altitude of 18 km within the latitudinal range of (50–90° S) over Antarctica

Series	1979–1989	1990–2000	2001–2011
S'–T	−0.82	−0.91	−0.85
S–T	−0.92	−0.77	−0.86

2011). To all appearance, this could be caused by the 11-year solar activity cycle. Table 1 presents the correlation coefficients (R) of the series (see. Fig. 1) within the framework of the periods under consideration.

It is obvious that the correlation between the parameters under consideration is statistically significant to a great extent. However, though for the period of 2001–2011 it remains still high, including the reducing of the time interval down to 7–8 years, however, within the periods of 1979–1989 and 1990–2000 decreasing the time interval results in considerable weakening the relationship between the parameters. Thus, within the period of 1979–1986 the correlation becomes statistically insignificant for $S'-T$ series, whereas within the period of 1993–2000 the correlation is insignificant $S-T$ series. The absence of correlation within these periods of time indicates the presence of an additional significant factor influencing the formation of the areas of PSC and the ozone hole. This factor is presented by a volcanogenic disturbance of Antarctic stratosphere.

EFFECT OF VOLCANOGENIC DISTURBANCE IN ANTARCTIC STRATOSPHERE ON THE BEHAVIOR OF PSC AND OZONE HOLE

A major role in the formation of PSC particles is played by sulphuric acid aerosol those present the condensation nuclei. The most significant source of stratospheric sulphuric acid aerosol is presented by volcanic eruptions capable with breaking through the tropopause, to throw products into the stratosphere, first of all, sulphur dioxide SO_2. Such eruptions are explosive to be, as a rule, generally measured by the value of Volcanic Explosivity Index VEI ≥ 4 (the Volcanic Explosivity Index characterizes the volume of thrown product according to 8-point scale). The gaseous and aerosol products of volcanic eruption ingress into the stratosphere reach the South Pole within 1?2 months, with a maximum meridianal transport during the winter period. Within a few weeks almost all the SO_2 is oxidized to be hydrated, and transformed into sulphuric acid mist (H_2SO_4/H_2O) that is able to remain in the strato-

TABLE 2

List of volcanic eruptions in the tropical belt and in the middle latitudes of the Southern Hemisphere, whose products were registered in the stratosphere [6]

Point No.	Years (months) of eruption	Volcanoes	Terrain	VEI	Eruption height, km above sea level
1	1979 (04)	Soufriere	St. Vincent	3	18
2	1981 (05)	Pagan	Mariana Islands	4	18
3	1982 (03)	El Chichon	Mexico	4+	17
3′	1982 (04)	El Chichon	Mexico	5	18
4	1982 (05)	Galangung	Indonesia	4	16
5	1983 (07)	Kolo (Uno Uno)	Indonesia	4	16
6	1990 (02)	Kelut	Indonesia	4	20
7	1991 (06)	Mount Pinatubo	Philippines	6	40
8	1991 (08)	Cerro Hudson	Southern Chile	5+	14
9	1993 (04)	Laskar	Northern Chile	4	25
10	1994 (09)	Rabaul	Papua New Guinea	4	18
11	2002 (09)	Ulaun	Papua New Guinea	4	17
12	2002 (09)	Ruang	Indonesia	4	18
13	2002 (10)	Reventador	Ecuador	4	17
14	2004 (11)	Manam	Papua New Guinea	4	18
14′	2005 (01)	Manam	Papua New Guinea	4	20
14″	2005 (02)	Manam	Papua New Guinea	4	19
15	2006 (10)	Rabaul	Papua New Guinea	4	16
16	2008 (05)	Chayten	Southern Chile	4	30
17	2010 (11)	Mount Merapi	Indonesia	4	20

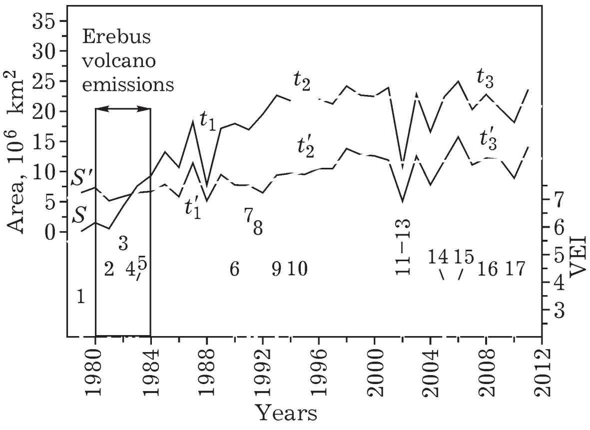

Fig. 2. Interannual changes in the Antarctic stratosphere within the spring period (September–October), the areas of ozone hole (S) and PSC Ia (S') and linear trends thereof (t_i and t'_i) within the periods of 1979–1989, 1990–2000 and 2001–2011. For designations of points 1–17 see Table 2.

sphere for several years. In the Antarctic stratosphere, sulphuric acid aerosol can repeatedly participate in the formation of PSC, serving as condensation nuclei [4, 5]. Table 2 presents data concerning the volcanic eruptions of the tropical belt and the middle latitudes of the Southern Hemisphere [6], the gaseous and aerosol emissions thereof were thrown into the stratosphere.

Figure 2 for the spring period (September–October) demonstrates the interannual changes in the Antarctic stratosphere: the ozone hole area (S) and PSC Ia (S') [3], linear trends thereof (t_i and t'_i) for the periods of 1979–1989, 1990–2000 and 2001–2011, as well as the moments of explosive volcanic eruptions (see Table 2).

Table 3 demonstrates the numerical values for the rate of changing the area S' and S within the periods under analysis. In the course of assessing the trends we excluded the critical points of 2002 from consideration.

TABLE 3

Rates of changing the values of S' and S for the periods under analysis

Trends	Rate of changing S' and S, km^2/year		
	1979–1989	1990–2000	2001–2011
t'	0.24	0.63	0.06
t	1.66	0.52	−0.13

Against the general background of deceasing the temperature (see Fig. 1), the positive PSC trend (t'_1) within the period of 1979–1989 (see Fig. 2) was negligible, to all appearance, due to the deficiency of PSC condensation nuclei (sulphuric acid aerosol) in the Antarctic stratosphere. The transport of volcanic sulphuric acid aerosol after volcanic eruptions of Soufriere (St. Vincent), Pagan, El Chichon, and Galangung Kelut occurred mainly in the stratosphere towards the Northern Hemisphere, and only a small part thereof appeared in the Antarctic stratosphere. On the contrary, after the volcanic eruptions of Galangung and Kolo (Uno Uno) in July of 1983 the sulphuric acid aerosol formed was transferred mainly to the Antarctic stratosphere.

The positive trend of changing the ozone hole area (t_1) in 1979–1989, on the contrary, is characterized by a maximum rate (see Table 3). In fact, within this period there occurred a major increase in the size of the ozone hole. At this stage, a key role in the advancing growth of the area of the ozone hole (S) with respect to S' was played by Antarctic volcano Mount Erebus (77° S; crater height 3794 m), activity was renewed in 1972 to continue up to this day. The Erebus acts as a major supplier of HCl, SO_2 and steam into the Antarctic stratosphere, which determine the process of PSC particle formation having the surface enriched with HCl. At the time of the Erebus eruption, gas jets shoot therefrom up under high pressure, the minimum initial speed thereof exceeds 700 km/h even for a relatively weak eruption [7], whereas the height of the gas emissions can reach 2–3.5 km with respect to the top. In the course of acting the polar vortex (June–October) there is a decrease in the temperature gradient between the troposphere and the stratosphere observed. In the lower layers of the atmosphere, there occurs a motion from the periphery to the centre of the cyclone. As the result, a vertical upward movement of air is observed in the centre, which further contributes to ascending the gases erupted by Erebus directly into the stratosphere.

Tables 4 and 5 present the dynamics of SO_2 and HCl emissions. It can be seen that within the period from 1980 to 1984, there was a maxi-

TABLE 4

Average SO_2 emissions from Erebus volcano

Year/Month	SO_2, t/day	Reference	Year/Month	SO_2, t/day	Reference
1978/11	1.69	[8]	1993/12	42	[12]
1980/11	158.02	[8]	1994/12	95	[12]
1983/12	230.90	[9]	1995/12	50	[12]
1984/9	230	[6]	1996/12	39	[12]
1985/12	16.70	[10]	1997/12	46	[12]
1986/12	21.09	[10]	2000/12	57	[12]
1987/12	48	[10]	2001/12	54	[12]
1988/12	27.90	[10]	2002/12	75	[12]
1989/12	72.11	[10]	2003/12	79.5	[12]
1990/1	100	[6]	2004/12	74.3	[14]
1991	71.08	[10, 11]	2005/12	68.24	[12, 13]
1992/12	52	[12]	2006/12	45.8	[13]

mum volume of gas emissions from the volcano observed, those were an order of magnitude greater than all the data of the following years. An intense filling of the Antarctic stratosphere with HCl in the early 1980s had stimulated rapid increasing the ozone hole area due to enriching the surface of PSC particles by HCl and the corresponding enhancement of heterogeneous reactions (4) and (5) required for restoring the reactive Cl, which led to achieving the first significant maximum of the ozone hole in 1985 (see Fig. 2). The situation was quite different within the period of 1990–2000. The most powerful volcanic eruption of Mount Pinatubo (VEI 6) and Hudson Cerro (VEI 5+) in 1991 provided a significant increase in the content of the sulphuric acid aerosol in the Antarctic stratosphere. Volcanoes Laskar (1993) and Rabaul (1994) reinforced the effect of the eruption of 1991, which led to a long-term aerosol perturbation of the stratosphere over Antarctica.

TABLE 5

Average HCl emissions from Erebus volcano [11], t/day

Year/Month	Emissions	Year/Month	Emissions
1983/12	166.85	1988/12	14.39
1984/12	18.08	1989/12	39.45
1985/12	10.96	1991/12	36.44
1986/12	15.34	2004/12	20.74*
1987/12	32.05		

* According to [14].

This period is characterized by almost the same trend in changing the area values S and S' at the rates of 0.52 and 0.63 km^2/year, respectively (see Table 3). Increasing the number of condensation nuclei, *i. e.* the amount of sulphuric acid mist, resulted in increasing the area of reactive surface in PSC those provide the reduction of active chlorine through heterogeneous reactions (4) and (5). The trend in changing the ozone hole (t_2) is slightly inferior with respect to the trend of PSC (t_2'). To all appearance, this could be caused by a gradual decrease in the amount of HCl in the Antarctic stratosphere. The “washout” of HCl from the stratosphere could occur on the surfaces of heavy-weight aerosols (the same particles of PSC) having lost buoyancy.

Within the period of 2001–2011, there was observed a strong correlation between the area variability of PSC, ozone hole and the temperature of the stratosphere (see Fig. 1). Regular stratospheric perturbations after volcanic eruptions of the Ulaun, Ruang, Reventador, Manam, Rabaul, Chayten and Merapi resulted in the spikes of increasing the area of PSC and subsequent decreasing thereof as the result purifying the stratosphere *via* the sedimentation of aerosols. These fluctuations can be generally characterized by a slightly positive trend t_3'. At the same time, the trend of changing the ozone hole (t_3) is of low-negative value, most likely resulting from HCl deficiency appeared in the Antarctic stratosphere due to weakening the gas emissions from the Erebus.

CONCLUSION

During the entire period under analysis (1979–2011), in the stratosphere over Antarctica (in the spring period, September–October), there began conditions to occur necessary for the formation of large-scale ozone holes. Low stratospheric temperature values (<195 K) promoted the formation of PSC. At the same time, the powerful explosive volcanic eruptions in the tropical belt and in the middle latitudes in the Southern Hemisphere resulted in increasing the number of the condensation nuclei of PSC particles (sulphuric acid mist) in the Antarctic stratosphere, whereas the gas emissions of Antarctic volcano Erebus enriched the surface of these particles with HCl to provide efficient chemical reactions responsible for the depletion of stratospheric ozone.

An intense growth of the area of the ozone hole registered in the early 1980s of the last century, became a result of the maximum (within the period of observation) gas emissions into the stratosphere from volcano Erebus. The greatest impact on the Antarctic stratosphere caused by a long-term and intensive decrease in the amount of stratospheric ozone was exerted by powerful volcanic eruptions from the Pinatubo and Hudson Cerro in 1991 and the Lascar volcano in 1993. As the result, in the spring of 1993 almost all the Antarctic stations observed maximum ozone depletion [5]. In particular, October 21, 1993 the station at Halley Bay registered the ozone content equal to 99.6 DU, the minimum value for this station within the period from 1979 to 2011 [15].

Thus, the fundamental factor determining, alongside with the temperature, the increase in the area of PSC and ozone anomaly over Antarctica within 33 years (1979–2011), is presented by a long-term volcanogenic disturbance of the Antarctic stratosphere.

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