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• **Original Paper** •

The Effect of Super Volcanic Eruptions on Ozone Depletion in a Chemistry–Climate Model

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ABSTRACT

With the gradual yet unequivocal phasing out of ozone depleting substances (ODSs), the environmental crisis caused by the discovery of an ozone hole over the Antarctic has lessened in severity and a promising recovery of the ozone layer is predicted in this century. However, strong volcanic activity can also cause ozone depletion that might be severe enough to threaten the existence of life on Earth. In this study, a transport model and a coupled chemistry–climate model were used to simulate the impacts of super volcanoes on ozone depletion. The volcanic eruptions in the experiments were the 1991 Mount Pinatubo eruption and a 100 × Pinatubo size eruption. The results show that the percentage of global mean total column ozone depletion in the 2050 RCP8.5 100 × Pinatubo scenario is approximately 6% compared to two years before the eruption and 6.4% in tropics. An identical simulation, 100 × Pinatubo eruption only with natural source ODSs, produces an ozone depletion of 2.5% compared to two years before the eruption, and with 4.4% loss in the tropics. Based on the model results, the reduced ODSs and stratospheric cooling lighten the ozone depletion after super volcanic eruption.

Key words: stratospheric ozone, volcanic eruptions, stratospheric aerosols, chemistry–climate model

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Article Highlights:

- The global mean total column ozone depletion in the 2050 RCP8.5 100 × Pinatubo scenario is approximately 6% and 6.4% in tropics.
- The 100 × Pinatubo eruption only with natural source ODSs experiment produces an ozone depletion of 2.5%, with 4.4% loss in the tropics.
- The reduced ODSs and stratospheric cooling lighten the ozone depletion after super volcanic eruptions.

1. Introduction

Volcanism has long been considered a strong external force that causes climate and weather variations (Robock, 2000). The most important climatic effect of large volcanic eruptions is caused by their emission of sulfur species into the stratosphere; these sulfur species form sulfur aerosols that change the radiative balance and chemistry in the stratosphere (Coffey, 1996; Robock, 2000; Kremser et al., 2016). The increased stratospheric aerosols reflect more solar radiation, causing decreased shortwave heating in the troposphere and on the surface. Meanwhile, the stratospheric aerosols absorb more solar shortwave radiation and longwave radiation from the surface, leading to a pronounced warming in the tropical stratosphere (Robock, 2000). The adjustment of the vertical and meridional temperature gradients changes the atmospheric circulation and further influences the surface climate (Robock, 2000; LeGrande et al., 2016).

Stratospheric ozone is critical to life on Earth because it screens harmful ultraviolet radiation from the incident solar beam. When the ozone hole over the Antarctic was discov-

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ered in the 1980s (Farman et al., 1985), it caused global concern for its environmental and health effects. Prompt, coordinated, global measures were adopted, such as the Montreal Protocol and its subsequent several amendments, to eliminate the substances that deplete the ozone layer. Meanwhile, more and more research has been conducted to study stratospheric ozone. In addition to anthropogenic chlorofluorocarbons (CFCs), volcanic aerosols were considered a natural external force that could also deplete the ozone layer. Following volcanic eruption, a low ozone concentration has been observed, especially in winter and spring (Bluth et al., 1992; Hofmann et al., 1994; McGee et al., 1994; Randel et al., 1995). The most important impacts of a tropical eruption on stratospheric ozone chemistry can be divided into the following effects: (i) enhanced heterogeneous chemistry from elevated sulfuric acid (H_2SO_4) aerosol surface area density (SAD); (ii) the temperature and aerosol changes modify the occurrence and types of polar stratospheric clouds (PSCs); (iii) the changes of composition and reaction rate induced by the dynamical perturbations in the stratosphere; (iv) the direct injection of halogen species; and (v) coinjected water.

The surfaces of sulfate aerosols provide sites for heterogeneous chemical reactions that activate halogen species to destroy ozone. In high-latitude regions, the heating in the tropics enhances the meridional temperature gradient and strengthens the polar vortex, leading to lower temperatures that form more PSC occurrence (Telford et al., 2009; Oppenheimer et al., 2010; Muthers et al., 2015). Furthermore, the presence of H_2SO_4 in the polar stratosphere within the colder temperatures facilitates the formation of liquid H_2SO_4 ternary solution particles, which increase the SAD and therefore increases ozone depletion in which there is a high background loading of inorganic chlorine (Cl) (Carslaw et al., 1994). Some volcanic eruptions also release a large load of halogen species [i.e., Cl and bromine (Br)], which directly destroy ozone (Oppenheimer et al., 2010; Kutterolf et al., 2013; Cadoux et al., 2015). However, the role of volcanogenic halogens in stratospheric chemistry remains poorly understood, because it is commonly believed that most halogens produced by volcanic eruptions are removed by hydrometeors in the troposphere and therefore do not enter the stratosphere (Tabazadeh and Turco, 1993). For example, Mount Pinatubo, which erupted in June 1991, occurred simultaneously with Typhoon Yunya, leading to the efficient removal of volcanic halogens over a large region. This eruption did not cause measurable accumulation of stratospheric halogens (McCormick et al., 1995; von Glasow et al., 2009; Kutterolf et al., 2013). Atmospheric water has long been considered an important factor in converting SO_2 to sulfate aerosols (Rampino and Self, 1992), and it has been hypothesized to be a limiting factor in volcanic aerosol formation (Bekki, 1995). Water increases the availability of hydroxyl radicals, converting sulfur dioxide (SO_2) more quickly into sulfate aerosols and increasing the rate of aerosol growth (LeGrande et al., 2016). Furthermore, SO_2 is a greenhouse gas that may temper the negative impact of sulfate aerosols (Schmidt et al., 2016), which makes the balance between SO_2 and sulfate aerosols a significant controller of the climate response following an eruption (Joshi and Jones, 2009; LeGrande et al., 2016).

Solomon (1999) noted that the chemical and dynamical effects of volcanic aerosols occur simultaneously, and their effects are not much larger than natural variability. The quasi-biennial oscillation (QBO) and El Niño–Southern Oscillation (ENSO) are the dominant factors that cause the natural variability of ozone. The QBO modulates tropical upwelling and extratropical wave activities, affecting ozone concentrations (Baldwin et al., 2001, Cagnazzo et al., 2009; Xie et al., 2012, 2014). The eruptions of both Mount El Chichón and Mount Pinatubo were followed by the El Niño phase of sea surface temperature (SST). With a positive SST anomaly, El Niño changes circulation patterns, cooling the stratosphere and affecting ozone reaction rates in the tropics. In polar regions, El Niño often features a weaker stratospheric polar vortex (Chen and Wei, 2009; Ren et al., 2012; Graf et al., 2014). When the stratospheric polar vortex is not strong and cold enough, it cannot form many PSCs, which results in fewer sites for heterogeneous reactions and, therefore, less ozone depletion (Solomon, 1999; Solomon et al., 2015).

The Mount Toba eruption 74 000 years ago was a Volcanic Explosivity Index (VEI)-8 eruption and was approximately 100 times larger than the Mount Pinatubo eruption. After the eruption, the surface temperature of Earth dropped more than 10°C, and a new ice age was triggered (Petraglia et al., 2012; Wu et al., 2012). Some researchers believe that this super volcanic eruption might have killed three-quarters of the plants in the Northern Hemisphere (NH) and that human evolution was at risk (Ambrose, 1998; Rampino, 2002). Though there are still debates about whether this super volcanic eruption caused the subsequent population bottleneck (Oppenheimer, 2002; Delwiche, 2005; Robock et al., 2009; Williams, 2012), all studies have recognized its serious destruction of the global climate.

As a successful result of the Montreal Protocol, both models and observations have shown that the stratospheric abundances of Cl and Br are decreasing slowly, consistent with the long atmospheric lifetimes of the main ozone-depleting substances (ODSs) (SPARC, 2013; WMO, 2014), and the ozone recovery is quite promising (Solomon et al., 2016). However, some scientists have already raised concerns about the possibility that a major volcanic eruption within the near future may enhance ozone depletion, since there are still significant amounts of ODSs in the stratosphere, which may delay the stratospheric ozone recovery (Roscoe, 2001; Tabazadeh et al., 2002). Recently, Klobas et al. (2017) also suggested that, in the coming decades, the stratospheric presence of Br supplied by natural, very short-lived compounds makes the ozone layer more susceptible to loss following volcanic eruptions than if this halogen source were not present. Based on the work of other scientists, and with the Mount Pinatubo eruption as a reference, we use model results to examine ozone depletion under different ODS scenarios of a super volcanic eruption in the future. This study may help us to further understand the potential risks of a super volcanic eruption in the ozone recovery period.

2. Model and data

2.1. *Model description*

Two models were used in this research. One was the highly scalable Massive-Parallel Trajectory Calculations (MPTRAC), in which air parcel trajectories are calculated based on numerical integration using the wind field from global meteorological reanalysis (Hoffmann et al., 2016; Rößler et al., 2018). Diffusion is modeled by uncorrelated Gaussian random displacements of the air parcels with zero mean and standard deviations, $\sigma_x = \sqrt{D_x \Delta t}$ (horizontally) and $\sigma_z = \sqrt{D_z \Delta t}$ (vertically), where D_x and D_z are the horizontal and vertical diffusivities, respectively, and Δt is the time step for the trajectory calculations. Depending on the atmospheric conditions, actual values of D_x and D_z may vary by several orders of magnitude (e.g., Legras et al., 2003, 2005; Pisso et al., 2009). In our simulations, we followed the approach of Stohl et al. (2005) and set D_x and D_z to 50 and 0 $m^2\ s^{-1}$ in the troposphere, and 0 and 0.1 $m^2\ s^{-1}$ in the stratosphere, respectively. A constant half lifetime of seven days was assumed for SO_2 for the stratosphere, and 2.5 days was assumed for the troposphere. More detailed information about the MPTRAC model can be found in Wu et al. (2018) and Wu et al. (2017).

A three-dimensional chemistry–climate model (CCM) developed at the Russian State Hydrometeorological University (RSHMU) was also used in this study. The model includes two important modules: a dynamic module developed at the Institute of Numerical Mathematics of the Russian Academy of Sciences, and a photochemical module developed at the RSHMU. The model resolution is $5^\circ \times 4^\circ$ in longitude and latitude, with 39 sigma levels vertically from the Earth's surface up to 0.003 hPa. The time step is 12 min, and the time integration is conducted by a central-difference scheme combined with a semi-implicit scheme (gravity waves are treated implicitly). In the dynamic module, the equations of atmospheric thermohydrodynamics are solved by the finite-difference method on a C grid. The model also incorporates parametrizations of deep and shallow convection (Betts, 1986) and orographic (Palmer et al., 1986) and nonorographic gravity-wave (Hines, 1997) resistance.

The chemical module incorporates 74 basic atmospheric gas constituents directly or indirectly influencing the rates of photochemical changes in ozone. The model takes into account reactions of the oxygen, hydrogen, nitrogen, Cl, Br, and sulfur cycles, which makes it possible to treat the influence of chemical processes on the formation and evolution of not only ozone and its related gases but also atmospheric sulfate aerosols. The rates of chemical reactions are based on the JPL-2003 (Sander et al., 2003). The photolysis rates are calculated using the modified Delta-Eddington method (Dvortsov et al., 1992). Oxygen, nitrogen, Cl and Br families are considered and hydrogen species are calculated separately. Halogens (especially Cl and Br) play important roles in the destruction of stratospheric ozone (McCormick et al., 1995; Bobrowski et al., 2003; Cadoux et al., 2015). Recent model and observational studies all suggest significantly high ozone depletion with different halogen yields (Hunton et al., 2005; Cadoux et al., 2015; Klobas et al., 2017; Lurton et al., 2018). Therefore, halogens should be carefully considered after volcanic eruptions. All modeled species are transported independently, with a correction at each time step to conserve mass within families. Boundary emissions are taken from the World Meteorological Organization (WMO)/United Nations Environment Programme (WMO, 2007). Water vapor is specified in the troposphere according to its climatological values. Above the tropopause, water vapor is calculated like all other species, with supersaturation control. The model calculates photochemical production and destruction rates based on the adopted scheme of chemical and photolytic reactions, thus facilitating changes in the photochemical mechanisms. Parameterizations of heterogeneous chemistry on the surfaces of stratospheric sulfate aerosol and PSCs are employed in the model, including Br reactions, which can also play a significant role in stratospheric chemistry. Comparisons were made between the model calculations and observations on the ozone content and temperature by Galin et al. (2007), and heterogeneous processes on the surface of PSCs were shown to be important for correct simulation of the spatial and temporal distribution of atmospheric ozone. Smyshlyaev et al. (2010) also conducted model experiments on the evolution of the gas and aerosol compositions of the Arctic and Antarctic atmospheres. A detailed introduction to the parameterization of heterogeneous processes and the model can be found in Smyshlyaev et al. (1998) and Galin et al. (2007).

The variable describing volcanic aerosols in our model is the SAD taken from the CMIP6 Stratospheric Aerosol Data Set for the historical simulation. For the period of 1979–2014, SAD data were based on satellite data from SAGE, SAM, SAGE II, CALIPSO and OSIRIS. Furthermore, CLAES satellite data were used for gap-filling of missing data for the period several months after the Pinatubo eruption. The data are monthly and zonal means averaged in latitudinal bands of five degrees. Data are provided as three-dimensional (time, altitude and latitude) arrays between 90°S and 90°N and from 5 km to 39.5 km at a resolution of 0.5 km. Figure 1 shows the global mean SAD of the CMIP6 Stratospheric Aerosol Data Set. The two eruptions of Mount El Chichón and Mount Pinatubo are clearly reflected in the SAD. For more detailed information about the SAD data, readers are referred to the CMIP6 website (http://www.wcrp-climate.org/wgcm-cmip/wgcm-cmip6).

2.2. *Data*

The primary dataset used in this study is ERA-Interim, which includes ozone, temperature, wind and SST data (Dee and Uppala, 2009). The ERA-Interim ozone data were used to compare the model's ability to reproduce the variability of ozone after volcanic eruptions. Since ENSO and the QBO have strong influences on ozone, linear regression was applied to remove the ENSO and QBO signals from the reanalysis data (Free and Lanzante, 2009). For the QBO index, the equatorial zonal mean zonal wind at 50 hPa was used, as in previous studies (Holton and Tan, 1980; Hamilton, 1993;

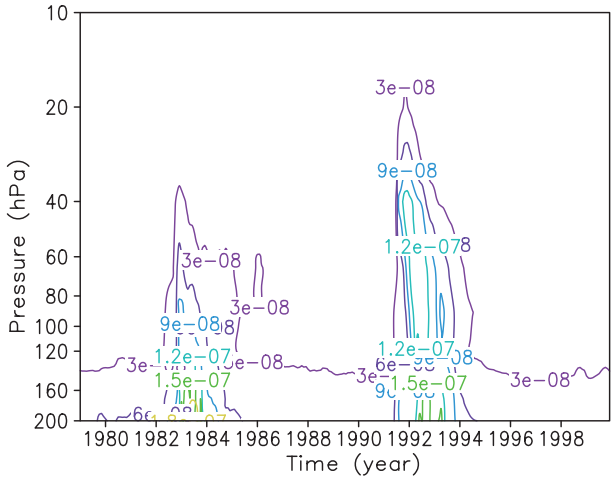

Fig. 1. Time–height sections of the global mean SAD (units: cm^2 cm^{-3}).

Chen and Li, 2007; Wei et al., 2007). For ENSO, the Niño3.4 index was adopted, which is the average SST anomaly in the region bounded by 5°N to 5°S, from 170°W to 120°W. The ENSO index has a four-month lead time, which gives the best correlation for each level (Free and Angell, 2002; Lean and Rind, 2009).

2.3. *Experimental setup and methodology*

Two model runs were conducted using the MPTRAC model: a Pinatubo size run and a 100-times Pinatubo (100 × Pinatubo) size run. For the Pinatubo size experiment, 1.7×10^{11} kg of SO_2 was injected in 100 000 air masses, each containing 170 000 kg of SO_2, ranging from 1.5 to 25 km, centered at (15.13°N, 120.35°E) of Pinatubo's location, and distributed homogeneously within a radius of 30 km. For the 100 × Pinatubo size experiment, 1.7×10^{13} kg of SO_2 was injected, ranging from 1.5 to 50 km, with the same distribution as the Pinatubo size experiment, but up to 50 km. The 100 × Pinatubo experiment could be used to simulate a VEI-8 super volcanic eruption. The two experiments conducted using the MPTRAC model are summarized in Table 1. Based on these model outputs, the global sulfur aerosol distribution under different SO_2 loading scenarios could be analyzed.

In order to build the connections between the sulfur aerosol distribution and SADs, linear regression was adopted to construct the SADs for the 100 × Pinatubo size eruption. The sulfur aerosol distribution at 30 hPa in the Pinatubo size eruption simulated by the MPTRAC model was used to regress the real SADs of the Pinatubo eruption from the CMIP6 datasets (we also used other levels of sulfur aerosol data, and the results did not show large differences). Thus, a linear regression between the SADs and sulfur aerosol was established, and then the SADs of the 100 × Pinatubo eruption could be constructed for the simulations of the CCM. Figure 2 shows the constructed SADs for the 100 × Pinatubo size eruption.

Table 1. Summary of runs made by the MPTRAC model.

Run name	SO_2 amount	SO_2 maximum height
Pinatubo	1.7×10^{11} kg	25 km
100 × Pinatubo	1.7×10^{13} kg	50 km

We then performed four model experiments with the CCM. First, a basic run, utilizing all aspects of the model, with prescribed SAD from 1979 to 1999, was used to simulate the Mount Pinatubo eruption in June 1991. Then, to isolate the effects of volcanic aerosols, a fixed run was carried out with the SAD fixed at the 1979 level, which was considered as a baseline. The fixed run also started in 1979 and ended in 1999. As Klobas et al. (2017) suggested, the response of the stratospheric ozone layer to enhanced aerosol loading is both a function of equivalent effective stratospheric chlorine (EESC) and stratospheric temperature. Meanwhile, model studies show that EESC is likely to decline rapidly (Engel et al., 2018) and the stratospheric temperature is likely to cool (Randel et al., 2016) in the near future. Thus, in order to simulate the stratospheric ozone layer response to a super volcanic eruption, two more model runs were performed with the Community Earth System Model (CESM) SST output of RCP8.5 2040–60 future simulations and future ODSs suggested by WMO (2007). The CESM SST output of RCP8.5 2040–60 was used to reproduce a colder stratosphere, and the 2050 100 × Pinatubo experiment was set to erupt in June 2050 with approximately half the ODSs compared to the 1990s level. The background 100 × Pinatubo experiment was incorporated with all anthropogenic ODSs (such as CFCs, CH_3CCl_3, $CHClF_2$, $C_2H_3FCl_2$, $C_2H_3F_2Cl$, $C_2HF_3Cl_2$, CF_2ClBr and CF_3Br) having disappeared and the remaining ODSs produced by natural processes only [mainly CH_3Br (~7 ppbv) and CH_3Cl (~483 ppbv)]. All the CCM model runs are listed in Table 2.

Two different methods were adopted to analyze the effects of volcanic aerosols on stratospheric ozone: Method A used two years before the eruption as the baseline and determined two years after the eruption minus the baseline as

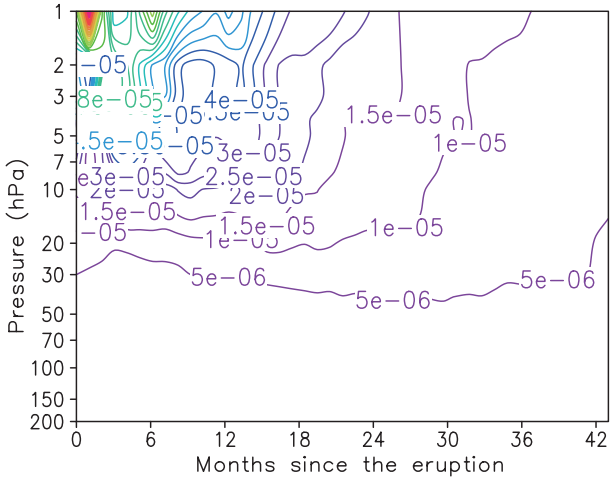

Fig. 2. Constructed SADs for the 100 × Pinatubo size eruption (units: cm^2 cm^{-3}).

Table 2. Summary of runs made by the CCM.

Run name	SAD scenario	ODSs level
Basic run	Real SAD	1979–99
Fixed run	SAD fixed at 1979 level	1979–99
2050 100 × SAD of Pinatubo	100 × Pinatubo SAD	2040–60
Background 100 × SAD of Pinatubo	100 × Pinatubo SAD	Natural source

the effects of volcanic aerosols (Free and Lanzante, 2009). This method was applied to both the model results and the reanalysis data. Stenchikov et al. (2006) used a longer base period (six years for El Chichón and Mount Pinatubo), and Lanzante (2007) used two to four years, while Santer et al. (2001) used just four to twelve months before the eruption as the baseline. We obtained similar results if other time slices were adopted, such as one or four years before and after the eruption (results not shown). Method B used the fixed run as the reference and determined the basic run results minus the fixed run results. Since the fixed run did not contain any SAD variations, it represented normal conditions with no volcanic aerosols. Method B only applied to model runs.

3. Model results of ozone depletion after volcanic eruptions

Laboratory studies have shown that the nitrogen oxides N_2O_5 and $ClONO_2$ react rapidly on the surface of H_2SO_4 solutions (Hanson and Ravishankara, 1993). These reactions decrease NO_x (= NO + NO_2) and increase nitric acid (HNO_3) within the reactive nitrogen reservoir (NO_y). Reduced NO_x decreases inactive Cl reservoir species, $ClONO_2$ and HCl, thereby increasing active chlorine, ClO, and its associated ozone loss cycles (Fahey et al., 1993). A schematic diagram of NO_x and ClO is depicted in Fig. 3. Meanwhile, observations have also revealed large changes in NO_x/NO_y and ClO/Cl_y partitioning, after Mt. Pinatubo erupted, associated with the increase in SADs at midlatitudes (Fahey et al., 1993; Solomon, 1999). Figure 4 shows the modeled changes in chemical partitioning of NO_x/NO_y and ClO/Cl_y at 50 hPa midlatitudes. The decreasing of NO_x/NO_y and increasing of ClO/Cl_y are clearly simulated after the Mt. El Chichón and Pinatubo eruptions. The injected sulfur aerosols provide sites for heterogeneous chemical reactions of N_2O_5 and $ClONO_2$, which consume NO and NO_2, produce active chlorine, ClO and Cl, and finally decrease ozone.

Figure 5 shows the vertical ozone mixing ratio of the ERA-Interim data and model simulations after the Mount Pinatubo eruption in different regions. When a strong volcano erupts, large loads of sulfur aerosols are injected into the stratosphere; the prevailing Brewer–Dobson Circulation then transports the volcanic aerosols around the globe, causing worldwide ozone depletion through heterogeneous reactions (Robock, 2000). For the global mean (Fig. 5a), both the model and ERA-Interim data show negative ozone anomalies after the volcanic eruption between 50 hPa and 10 hPa, as expected, but some differences still exist. First, the ENSO and QBO signals have a strong impact on global ozone content, and distinct differences could be found between the ENSO-and-QBO-removed reanalysis data (purple lines) and the ENSO-and-QBO-unremoved data (blue lines). Table 3 shows the percentage change of ozone at 20 hPa in four different regions after the Mount Pinatubo eruption. ENSO and

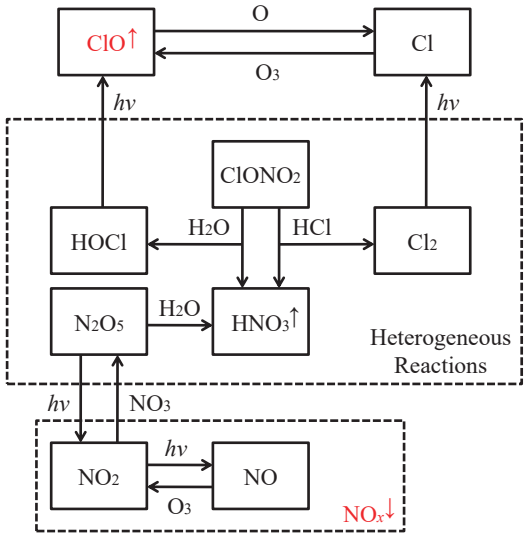

Fig. 3. Schematic diagram of NO_x, ClO and heterogeneous reactions after strong volcanic eruptions.

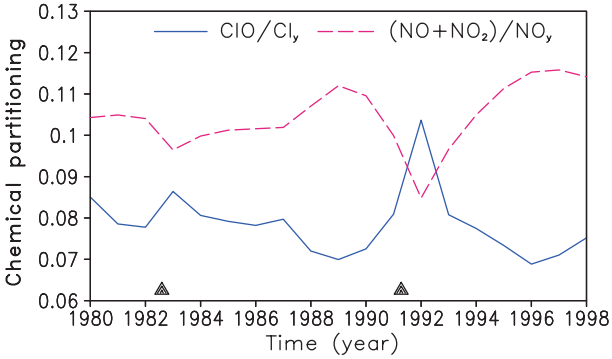

Fig. 4. Modeled changes in chemical partitioning of $(NO+NO_2)/NO_y$ and ClO/Cl_y at 50 hPa midlatitudes (60°S–60°N). The triangles indicate the April 1982 El Chichón and June 1991 Pinatubo eruptions.

Table 3. Ozone percentage changes at 20 hPa after Pinatubo eruption.

	North Pole	Tropics	South Pole	Global mean
ENSO and QBO removed	−0.84%	−3.51%	2.28%	−2.10%
ENSO and QBO unremoved	0.74%	−4.74%	3.79%	−2.44%

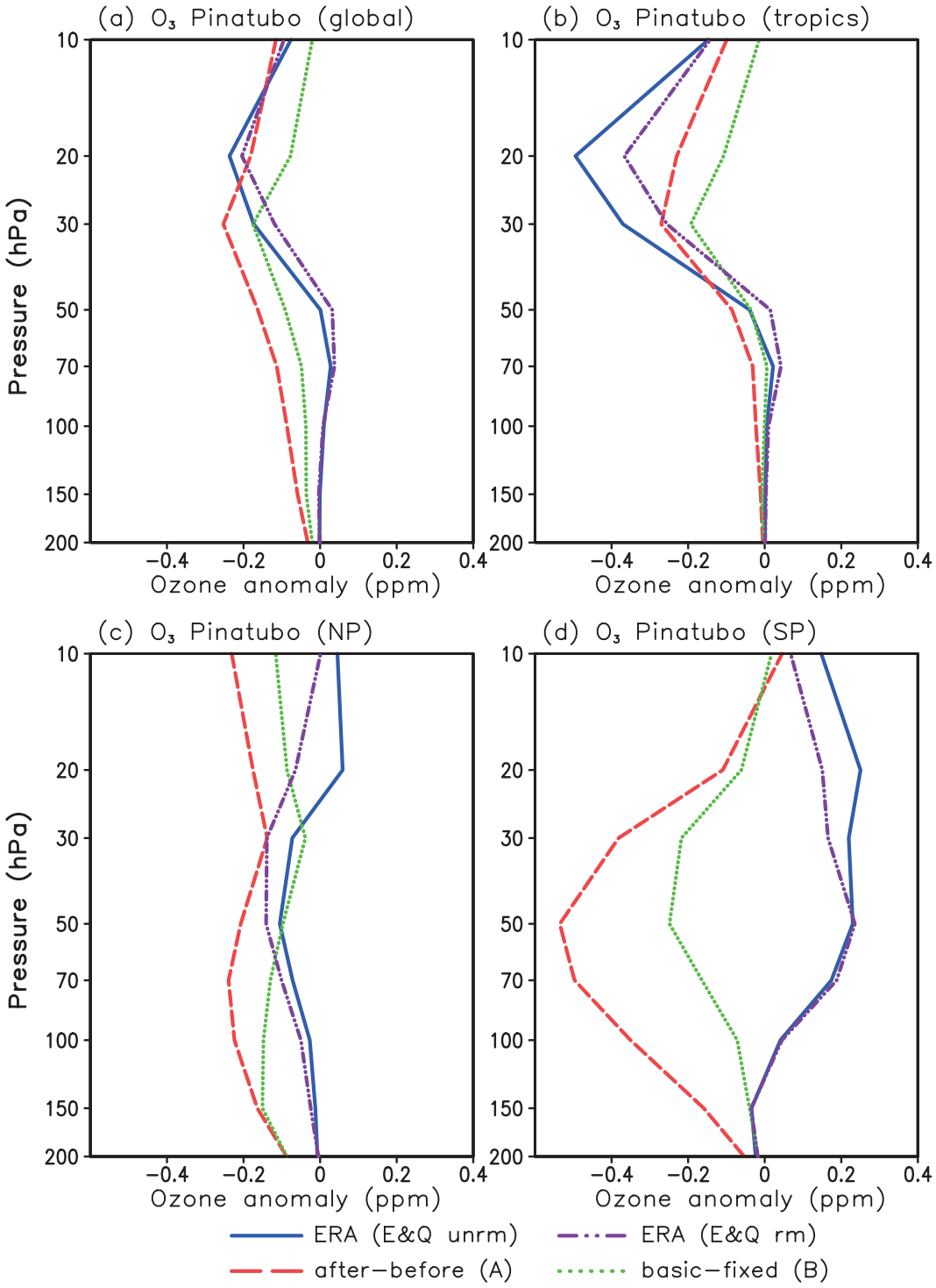

Fig. 5. Comparison of the vertical ozone mixing ratio between the model runs and ERA-Interim reanalysis data after the Mount Pinatubo eruption in terms of the (a) global mean, (b) tropical mean (30°S–30°N), (c) north polar mean (60°–90°N), and (d) south polar mean (60°–90°S). Units: ppm (10^{-6} kg kg^{-1}).

the QBO make opposite contributions to ozone variations. Thus, to analyze the effect of volcanic aerosols on ozone, ENSO and the QBO must be carefully treated. Although linear signals of ENSO and the QBO have been removed from the reanalysis data, the interaction of atmospheric circulation is quite nonlinear. Nonlinear signals of ENSO and the QBO may still remain in the data and are mixed with the volcanic influences. Meanwhile, the two methods of identifying volcanic effects also have inconsistencies. The ozone content of Method B (basic run minus fixed run) decreases less than that of Method A (after minus before). As mentioned above, Method B determines the basic-run-minus-fixed-run results,

and the chemical effect of the eruption on ozone is caused by the changes in SAD; while Method A uses two years before the eruption as the baseline and determines two years after the eruption minus the baseline as the effects of volcanic aerosols. Thus, Method B only demonstrates the chemical influences of volcanic aerosols (Telford et al., 2009). However, the model is coupled with chemistry, radiation and dynamics; there must be interactions between these modules, and some dynamic and radiative signals must remain in the chemistry part of the model. Therefore, Method B mainly contains the chemical effect of volcanic aerosols, but some other factors also exist.

As Mt. Pinatubo (15°N) erupted in the tropics, the direct injection of sulfur aerosols caused ozone depletion simultaneously and significantly. The tropical mean (Fig. 5b) shows that the ENSO-and-QBO-unremoved reanalysis data (blue line) depict more ozone depletion than the ENSO-and-QBO-removed data (purple line), which means that the impact of ENSO and the QBO in the tropics is completely contrary to that in the north polar regions (Fig. 5c). The difference between them is also quite large, indicating that ENSO and the QBO have a very strong or even controlling impact on the ozone content at low latitudes, despite these two volcanoes both erupting in equatorial regions.

In the north polar regions, besides the volcanic aerosols, the PSCs in the NH winter also decrease ozone (Schoeberl and Hartmann, 1991; Peter, 1997; Zhu et al., 2018). ENSO and the QBO also play important roles in ozone natural variability (Baldwin et al., 2001; Yu et al., 2011; Son et al., 2017; Xie et al., 2018), and the winter following Pinatubo's eruption featured an El Niño cycle. Usually, the stratospheric polar vortex is weaker than normal during ENSO years (Chen and Wei, 2009; Ren et al., 2012; Graf et al., 2014), which is unfavorable for the formation of PSCs and thus leads to fewer heterogeneous reactions and less ozone depletion (Solomon, 1999; Solomon et al., 2015). Therefore, when the ENSO and QBO signals were removed from the reanalysis data, the ozone depletion was less severe than that of the data without those signals removed (Fig. 5c).

The same as in the NH, the abundant PSCs and volcanic aerosols both decrease ozone in the south polar winters. However, the stratospheric vortex in the Southern Hemisphere (SH) is usually colder and more isolated than in the NH, leading to the formation of more PSCs, and severer ozone depletion (Crutzen and Arnold, 1986; Schoeberl and Hartmann, 1991; Zhu et al., 2018). For the south polar regions (Fig. 5d), however, the ERA-Interim data and model simulation show opposite results: the ozone decreases in the model simulation but increases in the ERA-Interim data. Poberaj et al. (2011) suggested that the increased ozone in the SH was caused by the enhanced ozone transport in late 1991 and early 1992, which compensated for the aerosol-induced chemical ozone depletion. This enhanced transport was related to the enhanced wave activities of the SH stratosphere. Aquila et al. (2013) used a set of CCM simulations to show that aerosol-induced longwave radiation heating in the lower stratosphere would increase tropical upwelling, leading to increased Brewer-Dobson circulation (BDC), which transported more ozone to the SH. These two mechanisms likely acted together to explain the ozone increase in the SH, despite the eruption of Mount Pinatubo. Meanwhile, it is worth noting that the CCM may overestimate ozone loss due to heterogeneous processes in the polar regions, as Galin et al. (2007) suggested. On the one hand, the CCM failed to represent the anomalous transport of ozone from the tropics to the south polar regions, while on the other hand it tends to overestimate ozone loss in the polar regions. These two reasons lead to the large inconsistencies between the simulations and reanalysis data in Fig. 5d.

4. Ozone depletion caused by a super eruption

As the Mount Pinatubo eruption led to severe ozone depletion in the stratosphere, it is natural to wonder about the effects caused by super volcanoes, which might be much stronger than the 1991 Pinatubo eruption. The true effect of such eruptions on the global scale might be very complicated and uncertain, and the volcanic products should be more complex than simple sulfate aerosols. For instance, the 1257 Samalas eruption released a very large load of gases into the atmosphere, including approximately 158 ± 12 Tg of SO_2, 227 ± 18 Tg of Cl and 1.3 ± 0.3 Tg of Br. These emissions represent the greatest volcanogenic gas injection of the Common Era (Vidal et al., 2016). The Mount Toba eruption 74 000 years ago was a VEI-8 level event and approximately 100 times larger than the Mount Pinatubo eruption. The Toba catastrophe theory has illustrated its destructive power on global climate (Rampino and Self, 1992; Petraglia et al., 2012; Williams, 2012). However, from the perspective of stratospheric ozone, we considered sulfate aerosols as a major point to simply study the ozone changes after a super volcanic eruption. This could give us some references and precautions if such an eruption truly happens.

Figure 6 shows the vertical ozone depletion of the 2050 $100 \times$ Pinatubo and background $100 \times$ Pinatubo scenarios in terms of the global mean, tropical mean, north polar mean, and south polar mean. The anomalies were calculated by the two-year mean after the eruption minus that before the eruption. The ODS level in the 2050 $100 \times$ Pinatubo scenarios is approximately half of the 1990s level, and in the background $100 \times$ Pinatubo scenario is only naturally produced. For the global mean ozone depletion (Fig. 6a), the 2050 $100 \times$ Pinatubo scenario (blue line) shows strong ozone depletion under half the ODSs of the 1990s level. The ozone depletion peaks at 5 hPa (approximately 1.3 ppm), which is higher than that of the Pinatubo eruption (Fig. 5b) at 20 hPa. This is due to the SO_2 maximum height set in the model simulations; the injected SO_2 reached 50 km (approximately 1 hPa) in the $100 \times$ Pinatubo scenarios. The higher volcanic aerosol caused higher ozone depletion. The background $100 \times$ Pinatubo scenario (red line) also shows strong ozone depletion, but less than the 2050 $100 \times$ Pinatubo scenario. The depletion also peaks at 5 hPa, at approximately

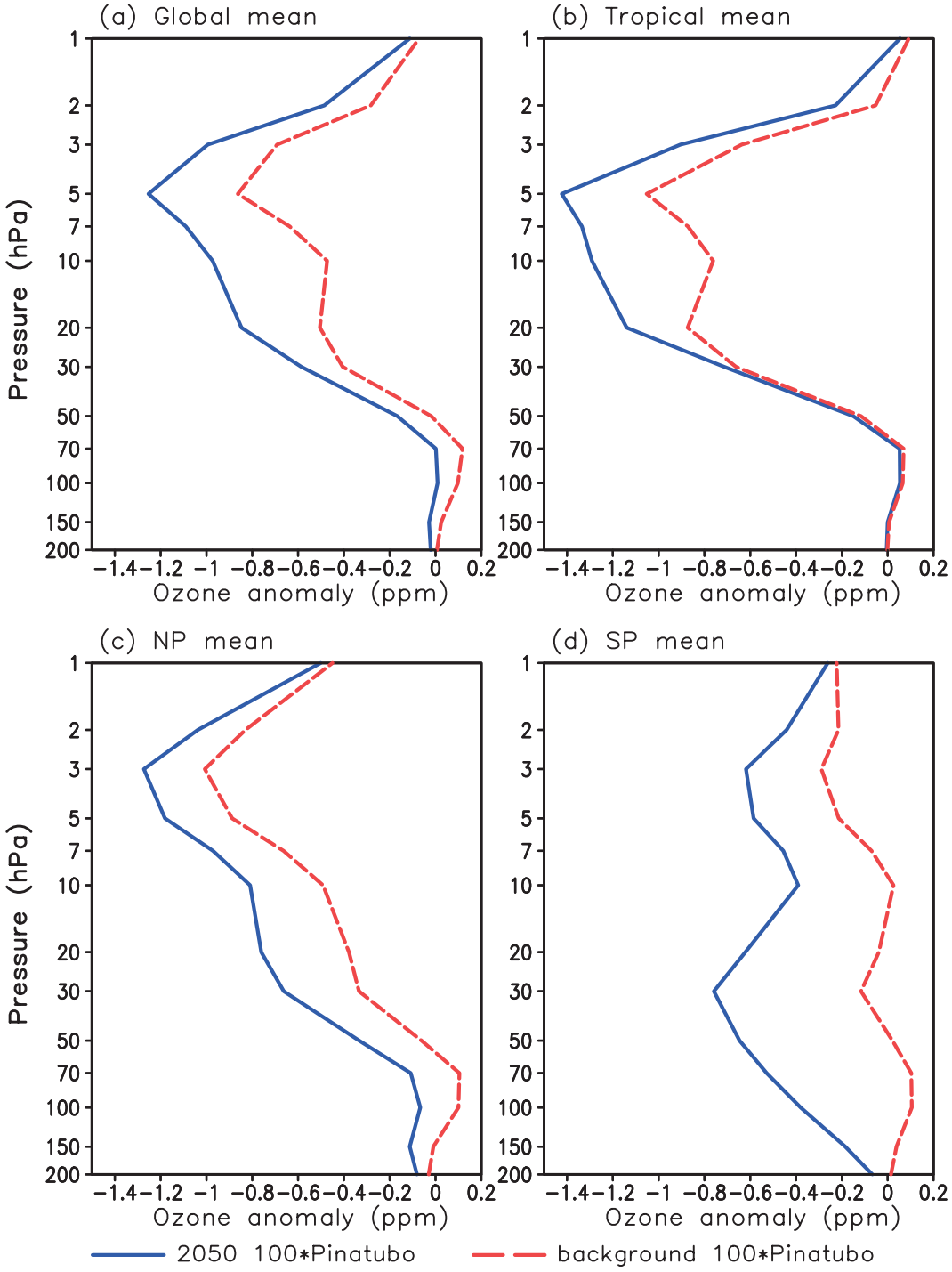

Fig. 6. Ozone depletion of the 2050 100 × Pinatubo and background 100 × Pinatubo scenarios in terms of the (a) global mean, (b) tropical mean (30°S–30°N), (c) north polar mean (60°–90°N), and (d) south polar mean (60°–90°S). The anomalies were calculated by Method A: two-year mean after the eruption minus that before the eruption. Units: ppm (10^{-6} kg kg^{-1}).

0.9 ppm. As the anthropogenic ODSs all disappear from the stratosphere, the naturally produced ODSs also cause serious ozone depletion when a VEI-8 level volcano erupts. For the tropical mean ozone depletion (Fig. 6b), it shows worse ozone reduction than the global mean (Fig. 6a). In the 2050 100 × Pinatubo scenario, the worst ozone depletion reaches approximately 1.4 ppm at 5 hPa and 1 ppm in the background 100 × Pinatubo scenario.

For the north polar mean (Fig. 6c), the 2050 100 × Pinatubo scenario (blue line) shows a worst ozone depletion of approximately 1.3 ppm at 3 hPa, while the background 100 × Pinatubo scenario (red line) shows a worst ozone de-

pletion of approximately 1 ppm at 3 hPa. However, for the south polar mean (Fig. 6d), the ozone depletion is not as serious as in other regions. In the 2050 100 × Pinatubo scenario (blue line), the worst ozone depletion is at 30 hPa, at approximately 0.8 ppm, which is less than that of the north polar region and tropics. In the background 100 × Pinatubo scenario (red line), a VEI-8 volcano does not cause serious ozone depletion in the south polar regions when all anthropogenic ODSs are removed. Ozone only shows a slight depletion at 30 hPa and above; the worst reduction is around 3 hPa, at approximately 0.2 ppm.

The most recent ozone assessment report (WMO, 2018) suggested that, outside the polar regions, upper-stratospheric ozone has increased by 1%–3% (10 yr)$^{-1}$ since 2000, while total column ozone declined across most of the globe during the 1990s and early 2000s by approximately 2.5%, averaged over 60°S to 60°N (WMO, 2014). Figure 7 shows total column ozone depletion as a function of time in the

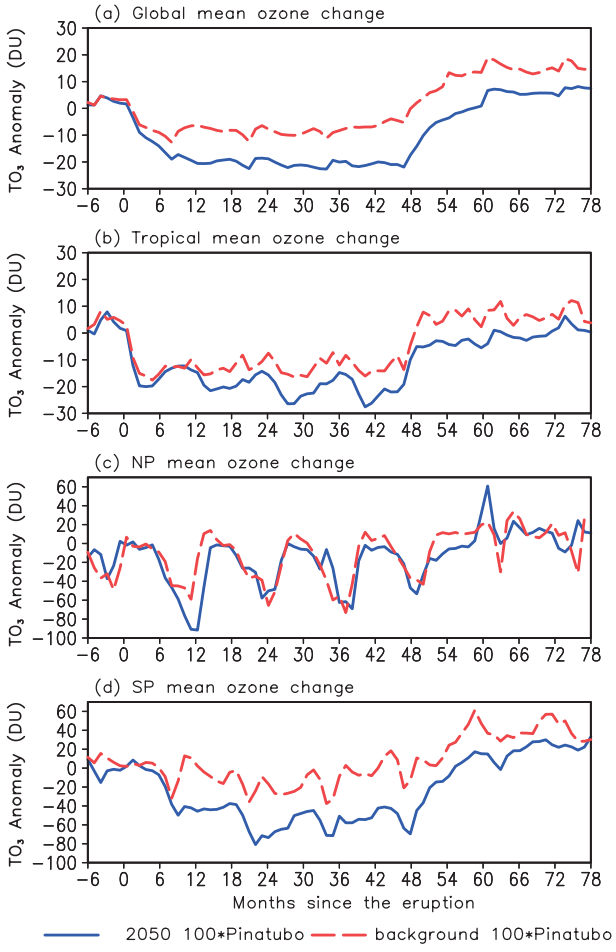

Fig. 7. Global mean total column ozone depletion as a function of time in the 2050 100 × Pinatubo and background 100 × Pinatubo scenarios of the model runs in terms of the (a) global mean, (b) tropical mean (30°S–30°N), (c) north polar mean (60°–90°N), and (d) south polar mean (60°–90°S). The ozone anomalies were calculated by subtracting two years before the eruption. Units: DU.

2050 100 × Pinatubo and background 100 × Pinatubo scenarios of the model runs in terms of the global mean, tropical mean, north polar mean, and south polar mean. The ozone anomalies were calculated by subtracting two years before the eruption. For the 2050 100 × Pinatubo scenario, the global mean ozone shows a strong decline (Fig. 7a), with the worst global mean depletion being about 6% compared to two years before the eruption, and the ozone has fallen to approximately 289 DU. For the background 100 × Pinatubo scenario (red line), the ozone content also shows depletion, but less than the 2050 100 × Pinatubo scenario (blue line). The worst global mean depletion is about 2.5% compared to two years before the eruption. For the tropical mean (Fig. 7b), the 2050 100 × Pinatubo scenario shows a worst depletion of approximately 6.4%, and the background 100 × Pinatubo scenario is approximately 4.4%, both worse than the global mean ozone depletion. For the north polar mean (Fig. 7c) and the south polar mean (Fig. 7d), the ozone depletion depicts large variations, especially in the north polar regions. After a strong volcanic eruption in the tropics, large loads of sulfur aerosols are injected into the tropical stratosphere, and then transported to the poles by BDC (Robock, 2000). Besides the volcanic aerosols that destroy polar ozone, PSCs forming in winter also decrease ozone. Sulfur aerosols and PSCs together cause ozone depletion in winter with ODSs. However, when winter passes, the cold and strong polar vortex that forms PSCs breaks down, along with PSCs, and thus the rate of ozone decline slows down, causing large ozone variations in polar regions.

5. Conclusions and discussion

A transport model and a coupled CCM were used to study the effect of volcanic aerosols on stratospheric ozone. The MPTRAC model was used to simulate the aerosol particle distribution of a Pinatubo eruption and 100 × Pinatubo size eruption. Linear regression was adopted to build the correlation between the volcanic aerosol distribution and the SADs. The CCM was then used to simulate the ozone depletion after the Pinatubo size and 100 × Pinatubo size eruption scenarios. The Pinatubo scenario was analyzed to verify the ozone depletion simulated by the CCM and ERA-Interim datasets. The impacts of volcanic eruptions on ozone may not be larger than its natural variability (Solomon, 1999), so the method of Free and Lanzante (2009) was used to remove the ENSO and QBO signals from the reanalysis data. Two different methods were adopted to calculate the impacts of volcanic aerosols on ozone. Furthermore, two more model runs were conducted with CESM RCP8.5 SST from 2040 to 2060 and future ODSs of WMO (2007) to simulate 2050 100 × Pinatubo and background 100 × Pinatubo scenarios, respectively. The ODS level in the 2050 100 × Pinatubo experiment was approximately half that of the 1990s, while in the background 100 × Pinatubo scenario the anthropogenic ODSs all disappeared and only natural products remained.

For the reanalysis data, the ENSO and QBO signals

should be carefully treated because the data with removed and unremoved signals have distinct differences. The two methods used to analyze the volcanic effects indicated that Method A (mean of two years after the eruption minus two years before) reflects more comprehensive effects on ozone, including the chemistry, radiation and dynamics, while Method B (basic run minus fixed run) mainly shows the chemical effect.

The 2050 $100\times$ Pinatubo scenario showed that the worst global mean total column ozone depletion is approximately 6% compared to the two years before the eruption, and the tropical mean ozone depletion is approximately 6.4%, while the ozone depletion of the background $100\times$ Pinatubo scenario is approximately 2.5% in terms of the global mean and 4.4% in terms of the tropical mean. The decreased ODSs and stratospheric cooling indeed lighten the ozone depletion after a super volcanic eruption.

However, it should be pointed out that, even if the aerosol transport has been explicitly calculated with the MPTRAC model, as in our research, the aerosol particle growth processes, which will significantly affect the SAD (LeGrande et al., 2016; Marshall et al., 2018) and aerosol effective radius (Ansmann et al., 1997; Wyser, 1998) relative to the Pinatubo eruption, were not included in the simulations. This needs to be improved in future studies.

As discussed, the total impacts of volcanic eruptions on stratospheric ozone should be more complicated than the single effect of volcanic aerosols, although the enhanced SAD caused by volcanic sulfate is the most prominent effect. The Mount Pinatubo eruption occurred simultaneously with Typhoon Yunya, probably leading to efficient removal of volcanic halogens over a large region, and thus that eruption caused no measurable injections of stratospheric halogens (Rosi et al., 2001). Therefore, the impacts of the Mount Pinatubo eruption on ozone were mostly equal to the effect of volcanic aerosols. For the other effects, we mentioned the composition and reaction rate changes induced by dynamic perturbations in the stratosphere; the direct injection of halogen species and coinjected water might have important impacts on ozone, according to the different types of volcanic eruptions. The abundant halogens, which are directly injected by volcanic eruptions, may be an uncertain factor involved in the impacts of volcanic aerosols on ozone depletion (Cadoux et al., 2015; LeGrande et al., 2016). Water also plays an important role in stratospheric ozone (Joshi and Jones, 2009; LeGrande et al., 2016), but a large load of water injection is strongly dependent on the location of the volcanic eruption; specifically, whether it is in the vicinity of a large body of water (Joshi and Jones, 2009).

The volcanically injected halogens have the largest uncertainties for the ozone depletion caused by strong volcanic eruptions. Although the 1991 Pinatubo eruption resulted in stratospheric ozone loss, it was due to heterogeneous chemistry on volcanic sulfate aerosols involving Cl of anthropogenic rather than volcanogenic origin (Cadoux et al., 2015). Until now, it is a common recognition that the volcanically produced halogens indeed play an important role in decreasing ozone, and many researchers have suggested to take volcanic halogens into account when simulating ozone depletion caused by volcanic eruptions in the future or in the past (Cadoux et al., 2015, Mather, 2015). However, there are still few observations or references able to estimate the quantities of volcanic halogens that enter the stratosphere. As Cadoux et al. (2015) suggested, even if only 2% of these halogens reach the stratosphere, it will result in strong global ozone depletion. Models should be sensitive to the volcanic halogens that enter the stratosphere: the more volcanic halogens in the stratosphere, the greater the level of ozone depletion. Thus, there are still uncertainties in simulating the effects of strong volcanic eruptions on ozone depletion, especially volcanic halogens.

For paleoclimatology and paleobiology, however, the surface temperature features strong centennial and decadal oscillation (Lisiecki and Raymo, 2005; Jouzel et al., 2007; Hansen et al., 2013), which also makes the stratospheric temperature quite uncertain during the Toba eruption. Furthermore, due to the absence of anthropogenic CFCs, the sources of ODSs also include volcanic injection, which makes the ozone depletion caused by the ancient Toba eruption more uncertain.

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