Observations of nucleation of new particles in a volcanic plume

Julien Boulon^{a,1}, Karine Sellegri^a, Maxime Hervé^a, and Paolo Laj^b

^aLaboratoire de Météorologie Physique, Observatoire de Physique du Globe de Clermont Ferrand, Centre National de la Recherche Scientifique, Unité Mixte de Recherche 6016, Université Blaise Pascal, 63177 Aubière, France; and ^bLaboratoire de Glaciologie et Géophysique de l'Environnement, Observatoire des Sciences de l'Univers de Grenoble, Centre National de la Recherche Scientifique, Unité Mixte de Recherche 5183, Université Joseph Fourier, BP 53-38041 Grenoble Cedex 9, France

Edited by Mark H. Thieme, University of California, La Jolla, CA, and approved June 21, 2011 (received for review March 29, 2011)

Volcanic eruptions caused major weather and climatic changes on timescales ranging from hours to centuries in the past. Volcanic particles are injected in the atmosphere both as primary particles rapidly deposited due to their large sizes on time scales of minutes to a few weeks in the troposphere, and secondary particles mainly derived from the oxidation of sulfur dioxide. These particles are responsible for the atmospheric cooling observed at both regional and global scales following large volcanic eruptions. However, large condensational sinks due to preexisting particles within the plume, and unknown nucleation mechanisms under these circumstances make the assumption of new secondary particle formation still uncertain because the phenomenon has never been observed in a volcanic plume. In this work, we report the first observation of nucleation and new secondary particle formation events in a volcanic plume. These measurements were performed at the puy de Dôme atmospheric research station in central France during the Eyjafjallajökull volcano eruption in Spring 2010. We show that the nucleation is indeed linked to exceptionally high concentrations of sulfuric acid and present an unusual high particle formation rate. In addition we demonstrate that the binary $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ nucleation scheme, as it is usually considered in modeling studies, underestimates by 7 to 8 orders of magnitude the observed particle formation rate and, therefore, should not be applied in tropospheric conditions. These results may help to revisit all past simulations of the impact of volcanic eruptions on climate.

secondary aerosols | volcanic sulfur | nanoparticles

Volcanic eruptions and their impact on climate have been extensively investigated in geological archives such as sediments (1), ice cores (2–5), and through modeling studies (6, 7) but processes taking place in the volcanic plume have rarely been directly observed. The sulfur dioxide emitted in large amounts during explosive volcanic eruptions (8) can be oxidized to sulfuric acid, thus many authors suspect that the formed sulfuric acid gives rise to the formation of new secondary particle from binary homogeneous nucleation mechanism (1, 9–12). Those new particles can then affect the atmospheric radiative balance both directly and indirectly because they can act as cloud condensation nuclei (CCN) (13). This leads to a cooling effect, which is on a time scale from months to years, depending on the location of the eruption and the height at which volcanic gases were emitted.

The Eyjafjallajökull volcano located in the south of Iceland [63°38' N, 19°36' W, summit 1,660 m above sea level (asl)] erupted on March 20, 2010. A major outbreak of the central crater under the covering ice cap followed on April 14, 2010 (Institute of Earth Sciences, 2010). A large volcanic plume composed of ashes and gases rose up to the tropopause level (approximately 10 km) for days and were observed by satellite and ground-based remote sensing instruments. The volcanic plume reached European altitude stations several times in the following days and until the end of the eruptive period on the May 21, 2010. This event was a unique opportunity to characterize the volcanic ash plume after

it had been photochemically aged for several days, with a sophisticated instrumentation that can only be ground-based.

The puy de Dôme research station is located at 1465 m above sea level in central France (45°46' N, 2°57' E). The station is surrounded mainly by a protected area where fields and forests are predominant, the city of Clermont-Ferrand is located 16 km east of the station. Meteorological parameters, including wind speed and direction, temperature, pressure, relative humidity, and radiation (global, UV, and diffuse), atmospheric trace gases (O_3 , NO_x , SO_2 , CO_2) and particulate black carbon (BC) are monitored continuously throughout the year. In addition to those measurements, the station is equipped with a neutral cluster and air ion spectrometers (NAIS), a nanoparticle size distribution measurement device, which allow the detection of charged and neutral particles from 0.8 to 42 nm, a scanning mobility particle sizer (SMPS; 10–450 nm) and an optical particle counter (Grimm spectrometer, 0.3–20 μm). Atmospheric dynamics and stratification is monitored using a Rayleigh–Mie LIDAR (light detection and ranging) emitting at 355 nm, with parallel and perpendicular polarization channels. LIDAR measurements were conducted from the roof of the laboratory (45°45' N, 3°6' E, 410 m asl) located 11 km east of the puy de Dôme station.

The Volcanic Plume Detection

The volcanic plume was first detected over Europe at the high altitude station Zugspitze (2650 m, Germany) on the night from April 17 to April 18, 2010 and a second time in the afternoon on April 19, 2010. Both the SO_2 and the particle number concentrations ($\text{Dp} > 3 \text{ nm}$) were detected with concentrations exceeding the 99th-percentile value (years 2000–2007), and were highly correlated with each other (14). At the puy de Dôme station, a strong depolarization signal indicative of volcanic ash (15) was detected using LIDAR measurements (Fig. 1) on April 18 and April 19, 2010 and from May 18 to May 20, 2010. During April, the volcanic plume was only detected in the free troposphere (between 3,500 and 4,000 m asl) above the puy de Dôme site and neither variations of SO_2 nor particles concentration compared to the mean diurnal variation level could be detected at the puy de Dôme station (1,465 m asl), indicating that the volcanic plume did not reach the lower troposphere and the planetary boundary layer. On the contrary, during the May episodes, the main volcanic ash plume was first detected around 3000 m asl and then mixed into the boundary layer, as witnessed by an increase of the depolarization ratio in the LIDAR signal and a peak of the SO_2 concentration at the puy de Dôme station. Hence, those particular events observed in May 2010 can be analyzed in detail with specific ground-based instrumentation.

Author contributions: K.S. and P.L. designed research; J.B. performed research; M.H. contributed new reagents/analytic tools; J.B. and M.H. analyzed data; and J.B. and K.S. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

¹To whom correspondence should be addressed. E-mail: j.boulon@opgc.univ-bpclermont.fr.

Fig. 1. Depolarization ratio measured by LIDAR, the dotted line illustrates the height of the puy de Dôme research station.

Air masses origins and isobaric backtrajectories were simulated using the Hysplit model and were conducted for each hour of the day for the period between May 18 and May 20, 2010. Results confirm that the volcanic plume arrived during the night between May 18 and May 19, 2010 after 100 h of transportation. At the puy de Dôme station, the plume was first detected between 2,500 and 3,000 m asl on the May 18 at 23:45 when SO_2 concentrations peaked until reaching a maximum value of 2.25 parts per billion by volume (ppbv) around 04:00 exceeding the 99th-percentile value measured at the station from 2005 to present days (Fig. 2). This boundary layer intrusion is also detectable from the LIDAR signal as an increase of the depolarization ratio in the atmospheric lowest layers (Fig. 1). One parameter determining if nucleation of new particles occurs in a given environment is the condensational sink (CS; see *Materials and Methods*). If the condensable vapor/CS ratio is too low prior to the potential onset of the nucleation event then condensable vapors condense onto preexisting particles rather than form new particles by nucleation. The evolution of the CS (Fig. 3, *Lower*) calculated from the pre-existing particulate surface, following the method of Pirjola and coworkers (16), did not increase with the intrusion of the volcanic plume, hence indicating that large particles emitted by the volcano had already settled. This is confirmed by the low number concentration of supermicronic particles detected at the station ($<1 \text{ cm}^{-3}$). As the sun is rising, photochemical reactions lead gas-phase SO_2 to be oxidized to sulfuric acid. This chemical process

was estimated using an indirect approach based on global radiation, SO_2 amount, and CS, following the work of Petäjä et al. (17). The calculation indicates that the production of sulfuric acid reached 3.7 parts per trillion by volume (pptv, exceeding the 09–14:00 90th-percentile determined from long-term measurements (from 2005 to present days) using the same calculation procedure. The sulfuric acid levels that we calculate are in the same order of magnitude as the one directly measured at the Zugspitze in the Eyjafjalla plume in April 2010 (0.65 pptv) (14).

New Particle Formation Events

Strongly correlated to the simulated H_2SO_4 concentrations, the particle concentration follow a clear diurnal variation, both on May 19 and May 20, 2010, with number concentrations multiplied by 2.5 at 14 h compared to night time concentrations and by 5 specifically in the size range from 0.8 to 42 nm. The size distributions of aerosol particles measured with the NAIS (Fig. 3, *Upper*) shows that these particles are formed from the nanometric scale by nucleation, and that they subsequently grow in the following hours. Events started respectively around 10:00 and 07:30 on May 19 and May 20, when the CS was respectively of 6.8 and $11.0 \times 10^{-3} \text{ s}^{-1}$. These CS values are slightly higher than the average CS observed on nucleation-event days and no-nucleation-event days calculated from a long-term study conducted at the site (18) (respectively 3.73 ± 0.11 and $5.17 \pm 0.15 \times 10^{-1} \text{ s}^{-1}$),

Fig. 2. Evolution of the SO_2 concentration at the puy de Dôme station (A, *Upper*) and calculated H_2SO_4 (B, *Lower*).

Fig. 3. Evolutions of the total (charged and neutral) particle size distributions (A, Upper) and condensational sink (B, Lower) from May 18 to May 21, 2010.

highlighting that an exceptionally high condensable vapor concentration was needed to onset the nucleation process.

The formation rate for 2-nm particles (J_2) are classically calculated to evaluate the number of particles formed per time unit (see *Materials and Methods*). The nucleation events detected in the volcanic plume are characterized by J_2 that are four times higher ($J_2 = 4.76 \pm 2.63 \text{ s}^{-1}$) than the average values computed from long-term measurements (2007–2011) at the station ($\bar{J}_2 = 1.32 \pm 0.9 \text{ s}^{-1}$ on 34 comparable events) and 10% higher than the J_2 99th-percentile value (3.66 s^{-1} calculated on 34 comparable events). After the observations of the presence of H_2SO_4 and water in volcanic particles during the Pinatubo eruption by Deshler et al. (9), the majority of studies used the $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ binary homogeneous nucleation (BHN) theory (6, 7, 12, 19) to estimate the particle formation rates. In the same manner, we can calculate from our data the $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ binary homogeneous nucleation rate $J_{2,\text{BHN}}$ using Yu's procedure (20), which is the closest to the BHN theory (21). The computed $J_{2,\text{BHN}}$ was found to be seven to eight orders of magnitude below the observed J_2 , suggesting that the volcanic nucleation events could not be adequately described with the $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ binary homogeneous nucleation scheme as it was done in the previous modeling studies. Furthermore, we found that those nucleation events are characterized by an unusual low ion-induced nucleation rate (IIN = 1.2%) compared to the average value computed from long-term measurements [IIN = $12.49 \pm 2.03\%$, calculated on 34 comparable events (18)], indicating that the observed nucleation should be described by a neutral nucleation and growth mechanism.

The average particle growth rate of newly formed particles calculated over the 1.3–20 nm size range, was $5.26 \pm 0.76 \text{ nm}\cdot\text{h}^{-1}$, which is slightly lower than observed growth rates at the puy de Dôme station [$6.20 \pm 0.12 \text{ nm}\cdot\text{h}^{-1}$ (18)]. From this value, the minimal condensable vapor concentration needed to explain the particle growth velocity (22) was estimated to be $2.65 \pm 0.71 \times 10^{+07} \text{ molecules}/\text{cm}^3$. The agreement between the calculated condensable vapor concentration and calculated sulfuric acid concentrations during the nucleation process ($3.67 \pm 0.78 \times 10^{+07} \text{ molecules}/\text{cm}^3$ in average) suggests that the nucleation events observed is likely linked to the H_2SO_4 produced from the atmospheric oxidation of the volcanic emitted SO_2 . As a consequence, this observation may also indicate that condensable

vapors different than sulfuric acid are not needed to explain the observed new particle growth, contrarily to what it is usually observed during nucleation and growth events in the planetary boundary layer under remote conditions (23). When particles grow above a certain limit, between 50 and 100 nm diameter, they can act as CCN. The potential CCN concentration is classically estimated using the two ratios N_{50}/N_{tot} and N_{100}/N_{tot} where N_{50} and N_{100} are respectively the particle concentration with a diameter higher than 50 and 100 nm, N_{tot} is the total concentration. From SMPS data we calculated that freshly formed particle significantly contribute to increase the number of potential CCN. After the nucleation and growth event $38.25 \pm 6.2\%$ of super-10nm particles have reach the 50 nm diameter and $15.2 \pm 3.0\%$ the 100 nm diameter and therefore could act as CCN.

Conclusions

The observational data and analysis presented here demonstrate that nucleation and subsequently growth can derived from volcanic eruption gaseous released and that this new secondary particle formation event could occur within the lower troposphere at a large distance from the eruptive activity. The analysis of such events reveals that the binary $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ homogeneous nucleation scheme implemented in modeling studies is not adapted to describe the processes observed in the low troposphere, even at high sulfuric acid concentrations. The underestimation of the formation rate of new secondary particles in volcanic plumes by seven to eight orders of magnitude when performed from calculations based on this nucleation scheme could lead to an underestimation of the CCN and the subsequent potential formation of low-level clouds. As a consequence, such results may help to revisit nucleation schemes implemented in all past simulations of the impact of volcanic eruptions on climate. Schemes involving a third species such as ammonium [ternary nucleation theory (24)] or the nano-Köhler theory of cluster activation (25) are examples of paths to explore to improve the representation of nucleation and particles growth to climate relevant sizes in global models.

In addition to volcanic explosive eruptions, large SO_2 amounts are released in the low troposphere by a continuous volcanic degassing activity. Such geological activities represent an unused laboratory and offer a new field of experimentation for testing

hypothesis and models to describe the tropospheric nucleation in volcanic plumes.

Materials and Methods

Growth rate, Nucleation Rate, and Condensational Sink Calculation. Growth rate calculations were performed from the NAIS size distribution. The procedure involves fitting the size distribution with a log-normal structure and calculating the temporal change in the modal diameter (26). The condensational sink is classically estimated using sulfuric acid as a condensing molecule on the surface available from the total aerosol population (27). The formation rate of 2 nm particles was calculated from the aerosol size distribution (from 0.8 to 42 nm) obtained from the NAIS (27)

$$J_2 = \frac{dN_{2-3}}{dt} + \text{CoagS}_2 \times N_{2-3} + GR_{1.3-3}N_{2-3}, \quad [1]$$

where N_{2-3} is the particle concentration in the size range from 2–3 nm, $GR_{1.3-3}$ is the growth rate (GR) between 1.3 and 3 nm (assumed to be equal to the GR of 2 nm particle), and CoagS_2 is the loss of particles by coagulation scavenging of 2 nm particles (27).

The aerosol condensation sink determines how rapidly molecules will condense onto preexisting particles and depends strongly on the shape of the size distribution and can be calculated using the following formula (27):

$$CS = 4\pi D_{\text{vapor}} \times \sum_i \beta_{Mi} r_i N_i, \quad [2]$$

where D_{vapor} is the diffusion coefficient of the condensing vapor (here sulfuric acid), β_{Mi} is the transitional correction factor, r_i and N_i are respectively the radius of the particle and its number concentration.

Gap-Filling the CS Data. When SMPS data were not available, we estimated the CS from TEOM (Tapered Element Oscillating Microbalance, FDMS 8500C) and condensation particle counter (TSI CPC 3010). Those two instruments provide the mass and the number concentration of particles, from which we can infer a mean single particle volume. Using this average volume and size, we reconstruct an equivalent particle size distribution from which the CS is computed. This method was tested on TEOM/CPC data for which SMPS measurements were available and an agreement of more than 90% between the estimated and real CS was achieved.

ACKNOWLEDGMENTS. We thank E. Freney and S. Valade for reading the manuscript. We also thank the Observatoire de Physique du Globe de Clermont-Ferrand for contributing to maintaining instrumentation at the puy de Dôme research station. This work has been partly funded by the European Commission program project EUSAAR, Contract n°026140 (EUSAAR).

- Bao H, Yu S, Tong DQ (2010) Massive volcanic SO_2 oxidation and sulfate aerosol deposition in Cenozoic North America. *Nature* 465:909–912.
- Legrand M, Delmas JR (1987) A 220-year continuous record of volcanic H_2SO_4 in the Antarctic ice sheet. *Nature* 327:671–676.
- Zielinski GA, et al. (1994) Record of volcanism since 7000 B.C. from the GISP2 Greenland ice core and implications for the volcano-climate system. *Science* 264:948–952.
- Zielinski GA, et al. (1997) Volcanic aerosol records and tephrochronology of the Summit, Greenland ice cores. *J Geophys Res* 102:26625–25540.
- Dunbar NW, McIntosh WC, Esser RP (2008) Physical setting and tephrochronology of the summit caldera ice record at Mount Moulton. *West Antarctica, GSA Bulletin* 120:796–812.
- Ramaswamy V, Ramachandran S, Stenchikov G, Robock A (2006) A model study of the effect of Pinatubo volcanic aerosols on stratospheric temperature. *Frontiers of Climate Modeling* (Cambridge University Press, New York).
- Schmidt A, et al. (2010) The impact of the 1783–1784 Laki eruption on global aerosol formation processes and cloud condensation nuclei. *Atmos Chem Phys* 10:6025–6041.
- Self S, Widdowson M, Thordarson T, Jay AE (2006) Volatile fluxes during flood basalt eruptions and potential effects on the global environment: A Deccan perspective. *Earth Planet Sc Lett* 248:518–532.
- Deshler T, Hofmann DJ, Johnson BJ, Rozier WBR (1992) Balloonborne measurements of the Pinatubo aerosol size distribution and volatility at Laramie, Wyoming, during the summer of 1991. *Geophys Res Lett* 19:199–202.
- Sheridan PJ, Schnell RC, Hofmann DJ, Deshler T (1992) Electron microscope studies of Mt. Pinatubo aerosol layers over Laramie, Wyoming during summer 1991. *Geophys Res Lett* 19:203–206.
- Robock A (2000) Volcanic eruptions and climate. *Rev Geophys* 38(2):191–219.
- Highwood EJ, Stevenson DS (2003) Atmospheric impact of the 1783–1784 Laki Eruption: Part II Climatic effect of sulphate aerosol. *Atmos Chem Phys* 3:1177–1189.
- Merikanto J, Spracklen DV, Mann GW, Pickering SJ, Carslaw KS (2009) Impact of nucleation on global CCN. *Atmos Chem Phys* 9:8601–8616.
- Flentje H, et al. (2010) The Eyjafjallajökull eruption in April 2010—detection of volcanic plume using in-situ measurements, ozone sondes and lidar-ceilometer profiles. *Atmos Chem Phys* 10:10085–10092.
- Sassen K, Zhu J, Webley P, Dean K, Cobb P (2007) Volcanic ash plume identification using polarization lidar: Augustine eruption, Alaska. *Geophys Res Lett* 34:L08803.
- Pirjola L, et al. (1999) Formation of sulphuric acid aerosols and cloud condensation nuclei: An expression for significant nucleation and model comparison. *J Aerosol Sci* 30:1079–1094.
- Petäjä T, et al. (2008) Sulfuric acid and OH concentrations in a boreal forest site. *Atmos Chem Phys* 9:7435–7448.
- Boulon J, et al. (2011) Investigation of nucleation events vertical extent: a long term study at two different altitude sites. *Atmos Chem Phys Discuss* 11:8249–8290.
- Zhao J, Turco R, Toon O (1995) A model simulation of Pinatubo volcanic aerosols in the stratosphere. *J Geophys Res* 100:7315–7328.
- Yu F (2007) Improved quasi-unary nucleation model for binary H_2SO_4 – H_2O homogeneous nucleation. *J Chem Phys* 127:054301.
- Zhang Y, McMurry PH, Yu F, Jacobson MZ (2010) A comparative study of nucleation parametrizations: 1. Examination and evaluation of the formulations. *J Geophys Res* 115:D20212.
- Dal Maso M, et al. (2002) Condensation and coagulation sinks and formation of nucleation mode particles in coastal and boreal forest boundary layer. *J Geophys Res* 107:8097.
- Paasonen P, et al. (2010) On the roles of sulfuric acid and low-volatility organic vapors in the initial steps of atmospheric new particle formation. *Atmos Chem Phys* 10:11223–11224.
- Korhonen P, et al. (1999) Ternary nucleation of the H_2SO_4 and H_2O in the atmosphere. *J Geophys Res* 104:26349–26353.
- Kulmala M, Kerminen V-M, Anttila T, Laaksonen A, O'Dowd CD (2004) Organic aerosol formation via sulfate cluster activation. *J Geophys Res* 109:D04205.
- Dal Maso M, et al. (2005) Formation and growth of fresh atmospheric aerosols: Eight years of aerosol size distribution data from SMEAR II, Hyytiälä, Finland. *Boreal Env Res* 10:323–336.
- Kulmala M, et al. (2001) On the formation, growth and composition of nucleation mode particles. *Tellus B* 53:479–490.