Evolution of CO_2, SO_2, HCl, and HNO_3 in the volcanic plumes from Etna

C. Voigt[1,2], P. Jessberger[1], T. Jurkat[1], S. Kaufmann[1], R. Baumann[1], H. Schlager[1], N. Bobrowski[3], G. Giuffrida[4], and G. Salerno[5]

[1]Institute of Atmospheric Physics, Deutsches Zentrum für Luft- und Raumfahrt, Oberpfaffenhofen, Germany, [2]Institute of Atmospheric Physics, Johannes Gutenberg University Mainz, Mainz, Germany, [3]Institute for Environmental Physics, Heidelberg University, Heidelberg, Germany, [4]Istituto Nazionale di Geofisica e Vulcanologia, Palermo, Italy, [5]Osservatorio Etneo, Istituto Nazionale di Geofisica e Vulcanologia, Catania, Italy

Abstract The volcanic plumes from degassing Etna (Italy) were extensively probed with instruments onboard the Deutsches Zentrum für Luft- und Raumfahrt research aircraft Falcon during the contrail, volcano, and cirrus experiment CONCERT on 29/30 September 2011. Up to 10.4 ppmv SO_2 and 0.3 ppmv HCl were detected with the atmospheric chemical ionization mass spectrometer AIMS at 3.1 km altitude and 20 km distance to the summit. HNO_3 is the dominant reactive nitrogen component in the plumes. Linking aircraft and ground-based observations by Hybrid Single-Particle Lagrangian Integrated Trajectory dispersion modeling, we identify two crater plumes with different compositions primarily injected by the Bocca Nuova and North East craters. Uniquely, we follow their chemical evolution up to 5 h plume age. Our results show that CO_2/SO_2 and SO_2/HCl molar ratios are stable in the ageing plumes. Hence, conversion of SO_2 to H_2SO_4 and partitioning of HCl in acidic plume particles play a minor role at dry tropospheric conditions. Thus, these trace gases allow monitoring volcanic activity far from the crater.

1. Introduction

Volcanos provide significant natural sources of sulfur and halogen species into the atmosphere [*Oppenheimer et al.*, 2003]. A strong contributor to the worldwide volcanic emission budget is Etna (37.734°N, 15.004°E) on Sicily island [*Allard et al.*, 1991]. Degassing of its four summit craters (Bocca Nuova, Voragine, North East, and South East) provides a permanent supply of gases to the troposphere, punctuated by sporadic small or moderate eruptive events such as paroxysms. The main volcanic emission products are H_2O, CO_2, and SO_2; followed by hydrogen halides e.g., HCl, HF, and HBr [*Aiuppa et al.*, 2008]. In volcanic plumes, enhanced SO_2 and halogen concentrations strongly perturb OH levels and have an impact on ozone concentrations and methane lifetime [*von Glasow et al.*, 2009]. In addition to the volatiles, submicron- to micron-sized liquid sulfate aerosol and acid-coated solid particles are emitted. These emissions mix with ambient air, and hydrogen halides participate in gas, phase and heterogeneous reactions. Although the exact processes are uncertain, HCl may dissolve in sulfate aerosol or in liquid coatings of the solid particles [*Martin et al.*, 2012]. Thereby, the HCl uptake in aerosol depends on acidity, relative humidity, plume dilution, and other parameters.

Here we present new in situ measurements of gas phase CO_2, SO_2, HCl, and HNO_3 in the young Etna plumes. The observations were performed with instruments onboard the Deutsches Zentrum für Luft- und Raumfahrt (DLR) research aircraft Falcon during the CONCERT (contrail, volcano, and cirrus experiment) campaign on 29 and 30 September 2011. We use the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) dispersion model to link ground-based crater plume to distant aircraft observations. For the first time, we investigate the chemical evolution of the volcanic plumes up to ~5 h plume age. Molar CO_2/SO_2 and SO_2/HCl ratios are sensitive markers of the volcanic crater origin [*Burton et al.*, 2003] and volcanic activity [*Burton et al.*, 2007] and can be used for the prediction of volcanic eruptions [*Shinohara et al.*, 2008].

2. Aircraft Mission and Instrumentation

A suite of CONCERT missions [*Voigt et al.*, 2010, 2011] was conducted in 2008 and 2011 to investigate the impact of clouds and volcanic plumes on atmospheric composition and climate. Below, we describe the Falcon instrumentation, which is most relevant for our study.

2.1. The Atmospheric Chemical Ionization Mass Spectrometer

In 2011, the Atmospheric chemical Ionization Mass Spectrometer (AIMS) was for the first time deployed on the DLR Falcon. The mass spectrometer [*Huey*, 2007] was equipped with an inlet system and a gas discharge ion source. Ambient air is drawn into the backward-facing perfluoroalkoxy (PFA) inlet line heated to 40°C. In the high-voltage gas discharge ion source, SF_5^- ions are produced from a flow of 50 ppm SCF_8 in N_2 at pressures controlled to 40 hPa. Here SF_5^- ions react selectively with trace species X such as SO_2, HCl, and HNO_3 to form product ions via a fluoride transfer reaction [*Jurkat et al.*, 2011]

$$X + SF_5^- \rightarrow XF^- + SF_4.$$
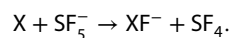
The ions pass the differentially pumped vacuum chambers of the mass spectrometer system, consisting of a collision dissociation chamber, an ion focusing octopole chamber, and the quadrupole chamber for mass separation before they are detected with a channeltron. By adding a permanent flux of isotopically labeled $^{34}SO_2$ to the inlet line, we monitor the instrument's stability and permanently calibrate SO_2 in flight. We use an isotopic composition of 0.0454 of $^{34}S/^{32}S$ [*Allard*, 1986] to derive volcanic SO_2 mixing ratios. In addition, HNO_3 and HCl were calibrated in the laboratory after the flights. During the flights, we diluted the inlet flow by factors of 3–8 to avoid saturation effects, yielding accuracies of 17–36% for SO_2, 33–35% for HCl, and 18–36% for HNO_3. While ambient SO_2 and HCl are below the detection limit above Sicily, we subtract the ambient HNO_3 background to derive HNO_3 concentrations in the volcanic plume. In order to minimize inlet effects, plume encounters with sampling times between 49 and 460 s are selected for further trace gas analysis and trace gas ratios are derived by integration over the total encounter time within individual plumes.

2.2. CO_2, NO_y, and H_2O Instruments

Carbon dioxide was measured using cavity ring-down spectroscopy (PICARRO, model G2301). Here the exponential decay of light intensity leaking from an optical cavity including the gas sample is used to quantify the CO_2 volume mixing ratio. The precision and accuracy of 5 s data are 0.2 and 0.4 ppmv. To derive volcanic CO_2 concentrations in the plume, we subtract the 30 s mean of the background concentrations detected before and after each plume encounter.

Gas-phase reactive nitrogen species (NO_y = NO, NO_2, HONO, HNO_3, N_2O_5, PAN,...) and nitric oxide (NO) were detected with a chemiluminescence instrument from Ecophysics [*Schlager et al.*, 1999]. In the instrument, gaseous NO_y is reduced to NO using CO in a heated gold converter and the chemiluminescence reaction of NO with ozone is detected in the infrared [*Voigt et al.*, 2007]. The NO_y instrument has a detection limit < 10 pptv and an accuracy of ± 8–12% for 1 s data [*Voigt et al.*, 2008].

Water vapor was measured with the tunable diode laser hygrometer Water Vapor Sensing System version II from SpectraSensors [*Kaufmann et al.*, 2014]. In the measurement cell, a laser is tuned over the water vapor absorption line at 1.37 μm and the water vapor mixing ratio is determined from the absorption signal. The passive sample flow through the system is realized using a Rosemount inlet. The water vapor mixing ratio is measured with an accuracy < 6% at 2.4 s time resolution. The instrument is calibrated before and after the campaign using a frost point hygrometer (MBW373LX) as reference. Including the uncertainty of 0.5 K for the temperature measurements, the relative humidity with respect to water (RH_l) is determined with a relative uncertainty of 10%.

2.3. Ground-Based CO_2, SO_2, and HCl Instruments

SO_2 flux measurements from the bulk plume of Etna were carried out by the ultraviolet scanning spectrometers of the Flux Automatic Measurement (FLAME) network. Each of the ten automated stations scans the sky every 5 min and collects open-path ultraviolet spectra. We determine SO_2 slant column densities using the differential optical absorption spectroscopy method [*Platt and Stutz*, 2008] and derive the SO_2 emission rate by integration over the scanning surface and multiplication with the plume velocity. The uncertainty of SO_2 fluxes ranges between −22 and +36% [*Salerno et al.*, 2009]. A Multi-Component Gas Analyzer System (Multi-Gas) and Drechsler bottle were used to determine the composition of the Bocca Nuova crater plume. The Multi-Gas uses a LICOR non-dispersive infrared CO_2 spectrometer and an electrochemical sensor specific to SO_2 [*Aiuppa et al.*, 2008; *Shinohara et al.*, 2008], allowing real-time detection of CO_2 and SO_2
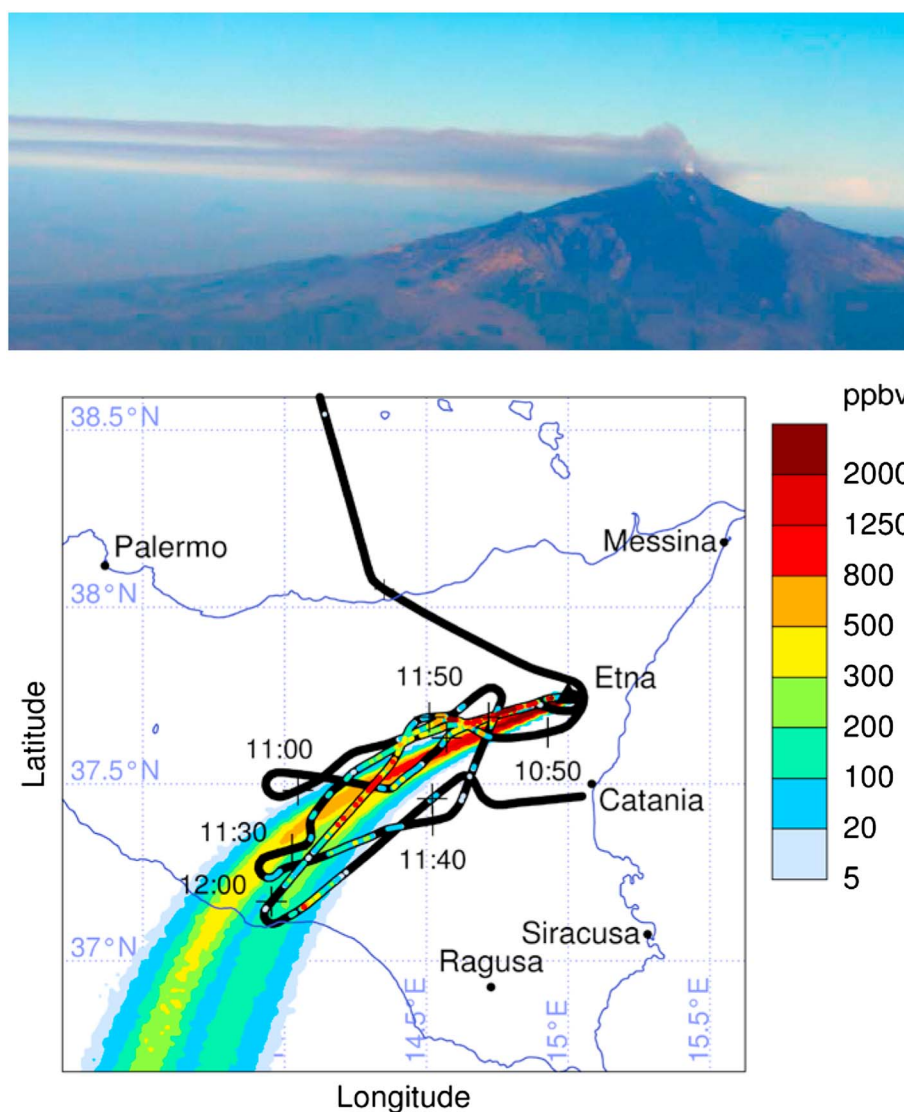
Figure 1. (top) Degassing Etna, photo taken from the DLR-Falcon research aircraft on 30 September 2011. (bottom) SO_2 mixing ratios (color coded) measured along the Falcon flight track on 29 September 2011 and HYSPLIT model results of the dilution and spreading of the SO_2 plume (same color coding).

concentrations in the plume with 2 s acquisition frequency. A flow of 1 L/min of air was pumped through a Drechsler bottle filled with a 1 M NaOH solution. The concentrations of the acidic gases SO_2 and HCl are determined from the amounts of S and Cl solved in the solution measured by ion chromatography.

3. Trace Gas Observations in the Etna Plume

In the evening of 28 September 2011, Etna showed increased activity and a paroxysm with lava fountains took place. In the early morning of 29 September, Etna had returned to quiescent degassing and two volcanic plumes were visible above a shallow cloud deck. The Falcon descended into the plumes at 10:45 UT and performed measurements inside the plumes at altitudes between 3.1 and 3.7 km for ~1.4 h (Figure 1). On 30 September, after the Falcon take off at 6:30 UT, the Etna plume was again probed for ~2 h at similar altitudes. The plume profile clearly consisted of two layers, see Figure 1, suggesting at least two crater plume origins. Visual observations at the craters suggest Bocca Nuova and North East craters as major emitters on that day.
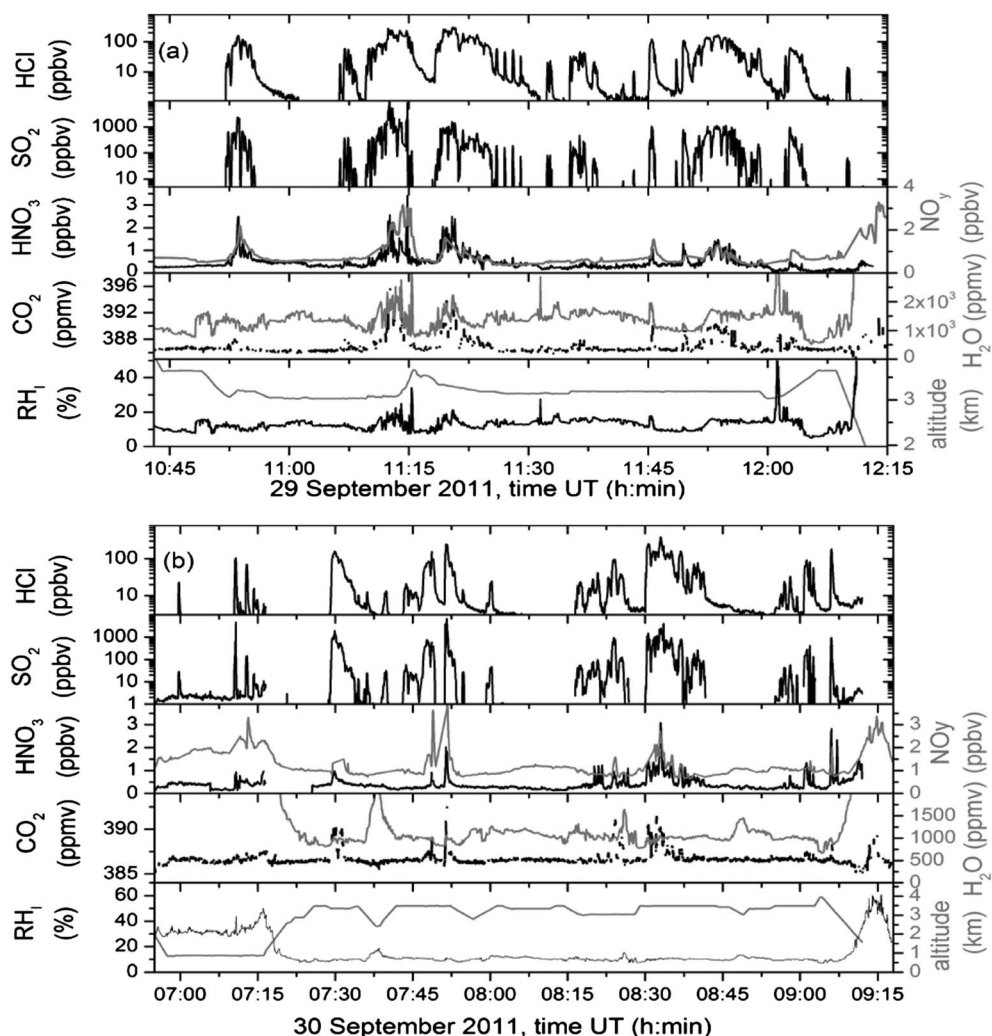
Figure 2. Aircraft observations of trace gases in the Etna plume on (a) 29 September and on (b) 30 September 2011. Time series of HCl, SO₂, HNO₃, NOᵧ, CO₂, and H₂O mixing ratios. Pressure altitude and relative humidity with respect to water (RH$_l$) are also given.

3.1. SO$_2$, HCl, HNO$_3$, CO$_2$, and H$_2$O in the Etna Plume

Figures 2a and 2b show the trace gas mixing ratios detected on 29 and 30 September 2011 above Sicily. Strongly correlated increases and high mixing ratios of SO_2, HCl, HNO_3, CO_2, and H_2O indicate volcanic plume encounters. Up to 10.4 ppmv SO_2 and 0.3 ppmv HCl were detected in the Etna plume at a distance of 20 km to the Etna summit on 29 September 2011. The maximum values decrease with increasing distance to the main craters mainly due to dilution. Mean values averaged over all plume encounters on both days are 314 ppbv SO_2 and 73 ppbv HCl.

Maximum volcanic HNO_3 plume mixing ratios up to 3.1 ppbv with means of 0.5 ppbv are consistent with observations of the NO_y instrument. Hence, HNO_3 is the major NO_y species in the volcanic plume and the contribution from other NO_y components is small. Maximum volcanic CO_2 concentrations are 8.9 ppmv averaged over 5 s at 20 km distance to the summit, CO_2 increases above the atmospheric background on average by 1.47 ppmv in the plume. Water vapor is elevated in the tropospheric volcanic plume on average by 175 ppmv relative to background concentrations outside the plume, which are highly variable.

3.2. Age and Dilution of the Etna Plumes

The age of the Etna plume is calculated with the HYSPLIT trajectory model [*Draxler and Hess*, 1998] using Global Forecast System/Global Data Assimilation System reanalysis data (23 pressure levels, 1° × 1° resolution) as meteorological input. It is initialized with the mean bulk SO_2 flux of 2200 (2800) Mg/d observed on
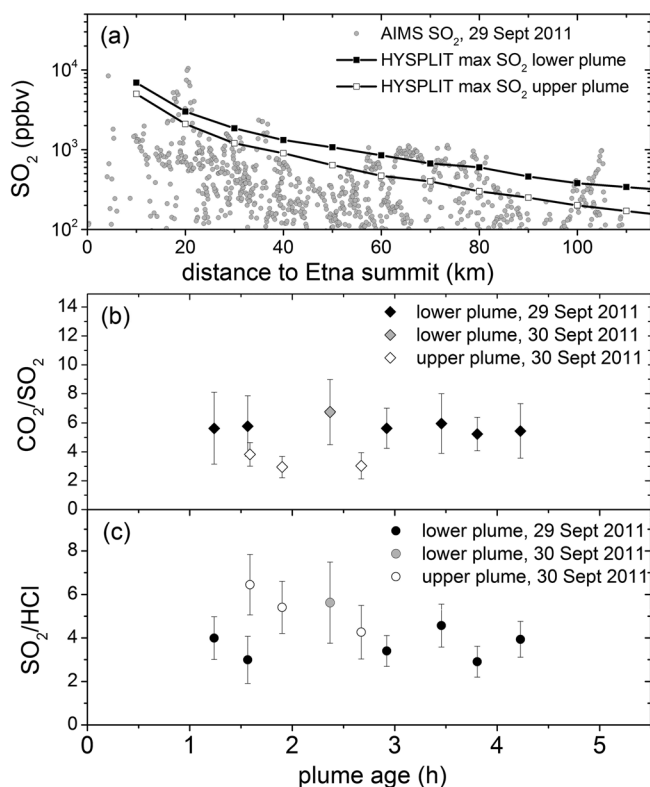
Figure 3. Temporal evolution of trace gases in the Etna plume. (a) SO_2 mixing ratios (gray solid circles) detected from aircraft with respect to distance to the Etna summit (110 km correspond to 5.4 h plume age) and HYSPLIT model results of maximum SO_2 concentrations in the upper plume from North East crater (hollow squares) and the lower plume from Bocca Nuova crater (filled squares) at 12 UT initialized with the mean SO_2 flux observed with the DOAS FLAME network. (b and c) Temporal evolution of SO_2/HCl and CO_2/SO_2 molar ratios of the two plumes.

29 (30) September with the FLAME network. Variations of 1600 to 4000 Mg/d are in the range of previous observations [*Allard et al.*, 1991; *Salerno et al.*, 2009]. The total SO_2 flux is split 3:1 to a lower and an upper plume branch, see Figure 1. Two Gaussian-shaped concentration profiles forming the lower (upper) plume at 3.1 (3.7) km injection height above sea level with a σ of 120 (40) m are used for model initialization, and the plume dilution is calculated with 2 min time resolution. The dilution of the maximum SO_2 concentration of both plumes on 29 September 2011 is shown in Figure 3a and compared to aircraft SO_2 observations at distances of 1 to 110 km from the summit (up to 5.4 h plume age). There is a general agreement of the observations and the model SO_2 suggesting that model initialization and plume dilution are reasonably covered. Slightly lower or higher simulated values compared to the observations could be caused by uncertainties in model initialization and by temporal variations in the initial SO_2 flux.

4. CO_2/SO_2 Molar Ratio in the Etna Plumes

We integrate the data over all plume encounters shown in Figure 2 and derive a mean bulk molar CO_2/SO_2 ratio of 5.2. Then we separate observations in the upper plume centered near 3.5 km altitude and the lower plume at 3.2 km altitude. Mean CO_2/SO_2 ratios of 3.3/6.1 are observed in the upper/lower plume, respectively, suggesting different crater origins of the two plumes. Indeed, ground-based Multi-Gas observations on 30 September 2011 suggest higher CO_2/SO_2 ratios from the Bocca Nuova crater (12.4 $\pm$ 0.8) compared to North East crater emissions (0.9 $\pm$ 0.3). Differences in ground-based and aircraft observations may result from fumarolic contributions to the Multi-Gas plume study. In addition, we hypothesize that a partial mixing of the plumes may explain the distant plume composition, as also suggested from photo observations (Figure 1).

Up-to-date aircraft observations of the Etna plume are rare. In fact, to our knowledge, there has not been any aircraft Etna plume study since pioneering work in the 1980s [*Allard et al.*, 1991]. In contrast, the Etna

plumes are routinely probed using ground-based instrumentation. *Shinohara et al.* [2008] find CO_2/SO_2 plume ratios of 0.6–30 (0.5–15) in the nascent plumes from the four Etna craters in 2005 and 2006. Average CO_2/SO_2 of 6.5 ($\pm$1.3) from Bocca Nuova, 5.5 ($\pm$1.1) from Voragine, and 2.2 ($\pm$0.4) from North East crater were detected with a Multi-Gas instrument in July 2005 [*Aiuppa et al.*, 2008]. For the combined central craters, they derive a bulk mean value of 5.7 ($\pm$1.1), similar to our study. In extension to those studies, we detected a partial mixing of the individual crater plumes shortly after injection in the atmosphere, which may depend on emission rates and meteorological conditions.

4.1. Temporal Evolution of CO_2/SO_2 and SO_2/HCl

The temporal evolution of the CO_2/SO_2 ratio is shown in Figure 3b. CO_2/SO_2 in each plume is constant with increasing plume age. Hence, both species can be treated as inert tracers over time scales of hours. *Martin et al.* [2008] report on SO_2/SO_4^{2-} molar abundances of ≈100 in the nascent Etna plume, suggesting that the major fraction of volcanic sulfur components is present in the form of SO_2. During plume evolution, SO_2 conversion to H_2SO_2 and subsequent condensation to sulfate aerosol takes place, mainly dependent on ambient solar flux and OH concentrations. While *Jurkat et al.* [2010] and *Schmale et al.* [2010] find SO_2 lifetimes up to 2 months in stratospheric volcanic plumes, the lifetime of SO_2 at tropospheric conditions is in the range of 1 to 2 weeks [*Logan et al.*, 1981].

In addition, we derive a mean molar SO_2/HCl ratio of 4.4 averaged over all plume observations. Generally, the volcanic SO_2/HCl ratio depends on magma composition and therefore on the location of the volcano. A compilation of volcanic gas compositional analysis globally from 27 volcanoes [*Aiuppa*, 2009] summarizes SO_2/HCl ratios of 34 for Kilauea, Hawaii, with tholeiitic-basalt type magma to 0.08 for Klyuchevskoi, Kamchatka, with calcalkaline-basaltic magma. For the Etna volcano with hawaiite type magma, we further investigate the dependence of this ratio on the individual crater origin. Within the experimental uncertainties (see Figure 3c), there is a trend to higher values in the upper plume with an average of 5.4 and of lower values in the lower plume with an average of 3.5. This is consistent with data from the Dechsler bottle on 30 September 2011 showing an SO_2/HCl of 3.1 ($\pm$0.1) for emissions from the Bocca Nuova crater. SO_2/HCl ratios of 2 to 5 have been reported previously for the emissions of these craters [*Allard*, 1986; *Burton et al.*, 2003; *La Spina et al.*, 2010].

Within the experimental uncertainties, we do not find a temporal variation in the SO_2/HCl ratio for dry tropospheric conditions. Hence, while the total CO_2, SO_2, and HCl emissions may vary significantly, both CO_2/SO_2 and SO_2/HCl are rather stable in the degassing Etna plume for plume ages up to 5 h. Although the observations have not been performed in a Lagrangian approach and a direct separation of initial plume variations is difficult, we suggest that volcanic CO_2, SO_2, and HCl can be regarded as inert tracers over time scales of hours in dry tropospheric conditions.

5. Discussion and Outlook

On 29/30 September 2011, the Etna plume was extensively probed in a quiescent degassing state with the research aircraft Falcon. The plume had two branches with different CO_2/SO_2 and SO_2/HCl molar ratios, suggesting different crater origins. Uniquely, we could follow the chemical evolution of the Etna plume over 5 h plume age. We detect stable molar CO_2/SO_2 and SO_2/HCl ratios in the plume with time and distance. Neither SO_2 conversion to sulfate nor HCl uptake in sulfate aerosol play a major role in the aging plume under dry tropospheric conditions.

Martin et al. [2012] calculated the equilibrium partitioning for HCl into acidic sulfate droplets using an aerosol inorganics model. Their results suggest that HCl partitioning exceeds 1% of the total HCl at low temperatures (<298 K) above 80% relative humidity (RH_l) and is almost complete above 95% RH_l. Still, the actual acidic composition of the plume particles is unknown and might affect the uptake. Our measurements at 10 to 20% RH_l confirm the model results. However, at higher RH or lower temperatures, for example, at night time, HCl uptake in volcanic aerosol may erroneously enhance measured gas phase SO_2/HCl ratios and should be taken into account in the composition analysis of volcanic plumes and in future research flight planning.

Volatiles are important factors for magma dynamics, ascent, type, and timing of volcanic activity. Higher CO_2/SO_2 and SO_2/HCl ratios of the Etna plume were monitored in eruptive volcanic events [*Allard et al.*, 2005; *Aiuppa*, 2009] and lower ratios during quiescent degassing caused by the pressure (depth) and

solubility dependent exsolvation of CO_2, S, and Cl from the magma. During magma ascent, CO_2 exsolves earlier from the magma than S and S earlier than Cl. Hence, the coexisting gas phase changes from high CO_2/SO_2 and SO_2/HCl ratios at high pressures to lower ratios at atmospheric pressures latter implying a shallow gas source. Thus, the interpretation of composition changes of the volcanic plumes can give insights into magmatic processes and can help to predict changes in volcanic activity.

Scaling the SO_2 flux with the HNO_3/SO_2 molar ratio of 0.02, we derive a HNO_3 flux of 77 Mg/d for the Etna volcano, which is slightly smaller than the yearly mean estimate from *Mather et al.* [2004]. Still, the formation of HNO_3 in the volcanic plume remains a mystery. Photochemical models suggest atmospheric NO_x to HNO_3 conversion times of days in summer midlatitudes. In addition, nitrogen fixation to NO at temperatures above 1200 K on the hot magma exposed to the atmosphere, and the yield of this reaction channel to the HNO_3 budget may be too small to explain recent observations [*Mather et al.*, 2004]. Lightning strokes might contribute to the volcanic NO_x levels. However, we did not observe a significant NO_x contribution to the volcanic NO_y reservoir. Hence, the origin of volcanic HNO_3 demands further discussion. Given the above mentioned uncertainties, Lagrangian measurements in combination with simulations are required to better constrain gas release from magma and its atmospheric processing.

References

Aiuppa, A., G. Giudice, S. Gurrieri, M. Liuzzo, M. Burton, T. Caltabiano, A. J. S. McGonigle, G. Salerno, H. Shinohara, and M. Valenza (2008), Total volatile flux from Mount Etna, *Geophys. Res. Lett.*, *35*, L24302, doi:10.1029/2008GL035871.

Aiuppa, A. (2009), Degassing of halogens from basaltic volcanism: Insights from volcanic gas observations, *Chem. Geol.*, *263*, 99–109, doi:10.1016/j.chemgeo.2008.08.022.

Allard, P. (1986), Geochimie Isotopique et Origine de latmeau, du Carbone et du Soufre dans les Gaz Volcaniques: Zones de Rift, Marges Continentales et Arcs Insulaires, PhD thesis, Univ. Paris 7, Paris.

Allard, P., et al. (1991), Eruptive and diffuse emissions of CO_2 from Mount Etna, *Nature*, *351*, 387–391, doi:10.1038/351387a0.

Allard, P., M. Burton, and F. Mure (2005), Spectroscopic evidence for a lava fountain driven by previously accumulated magmatic gas, *Nature*, *433*, 407–409.

Burton, M., P. Allard, F. Mure, and C. Oppenheimer (2003), FTIR remote sensing of fractional magma degassing at Mount Etna Sicily, in *Volcanic Degassing*, edited by C. Oppenheimer, D. Pyle, and J. Barclay, pp. 281–294, Geological Society, Special Publication 213, London.

Burton, M., P. Allard, F. Mure, and A. La Spina (2007), Magmatic gas composition reveals the source depth of slug-driven Strombolian explosive activity, *Science*, *317*, 227–230, doi:10.1126/science.1141900.

Draxler, R. R., and G. D. Hess (1998), An overview of the HYSPLIT4 modeling system of trajectories, dispersion, and deposition, *Aust. Meteor. Mag.*, *47*, 295–308.

Huey, L. G. (2007), Measurement of trace atmospheric species by chemical ionization mass spectrometry: Speciation of reactive nitrogen and future directions, *Mass Spec. Rev.*, *26*, 166–184, doi:10.1002/mas.20118.

Jurkat, T., C. Voigt, F. Arnold, H. Schlager, H. Aufmhoff, J. Schmale, J. Schneider, M. Lichtenstern, and A. Dörnbrack (2010), Airborne stratospheric ITCIMS-measurements of SO_2, HCl, and HNO_3 in the aged plume of volcano Kasatochi, *J. Geophys. Res.*, *115*, D00L17, doi:10.1029/2010JD013890.

Jurkat, T., C. Voigt, F. Arnold, H. Schlager, J. Kleffmann, H. Aufmhoff, D. Schäuble, M. Schaefer, and U. Schumann (2011), Measurements of HONO, NO, NO_y and SO_2 in aircraft exhaust plumes at cruise, *Geophys. Res. Lett.*, *38*, L10807, doi:10.1029/2011GL046884.

Kaufmann, S., C. Voigt, P. Jeßberger, T. Jurkat, H. Schlager, A. Schwarzenboeck, M. Klingebiel, and T. Thornberry (2014), In situ measurements of ice saturation in young contrails, *Geophys. Res. Lett.*, *41*, 702–709, doi:10.1002/2013GL058276.

La Spina, A., M. R. Burton, and G. G. Salerno (2010), Unravelling the processes controlling gas emissions from the central and northeast craters of Mt. Etna, *J. Volcanol. Geotherm. Res.*, *198*, 368–376.

Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy (1981), Tropospheric chemistry: A global perspective, *J. Geophys. Res.*, *86*, 7210–7254.

Martin, R. S., T. A. Mather, D. M. Pyle, M. Power, A. G. Allen, A. Aiuppa, C. J. Horwell, and E. P. W. Ward (2008), Composition-resolved size distributions of volcanic aerosols in the Mt. Etna plumes, *J. Geophys. Res.*, *113*, D17211, doi:10.1029/2007JD009648.

Martin, R. S., J. C. Wheeler, E. Ilyinskaya, C. F. Braban, and C. Oppenheimer (2012), The uptake of halogen (HF, HCl, HBr and HI) and nitric (HNO_3) acids into acidic sulphate particles in quiescent volcanic plumes, *Chem. Geol.*, *296-297*, 19–25, doi:10.1016/j.chemgeo.2011.12.013.

Mather, T. A., A. G. Allen, B. M. Davison, D. M. Pyle, C. Oppenheimer, and A. J. S. McGonigle (2004), Nitric acid from volcanoes, *Earth Planet. Sci. Lett.*, *218*, 17–30, doi:10.1016/S0012-821X(03)00640-X.

Oppenheimer, C., D. M. Pyle, and J. Barcaly (eds.) (2003), *Volcanic Degassing*, Geological Society, Special Publication 213, London.

Platt, U., and J. Stutz (2008), *Differential Optical Absorption Spectroscopy: Principles and Applications*, Springer, Heidelberg.

Salerno, G. G., M. R. Burton, C. Oppenheimer, T. Caltabiano, D. Randazzo, N. Bruno, and V. Longo (2009), Three-years of SO_2 flux measurements of Mt. Etna using an automated UV scanner array: Comparison with conventional traverses and uncertainties in flux retrieval, *J. Volcanol. Geotherm. Res.*, *183*, 76–83, doi:10.1016/j.jvolgeores.2009.02.013.

Schlager, H., P. Schulte, F. Flatoy, F. Slemr, P. V. Velthoven, H. Ziereis, and U. Schumann (1999), Regional nitric oxide enhancements in the North Atlantic flight corridor observed and modeled during POLINAT2, a case study, *Geophys. Res. Lett.*, *26*, 3061–3064, doi:10.1029/1999GL900349.

Schmale, J., et al. (2010), Aerosol layers from the 2008 eruptions of Mount Okmok and Mount Kasatochi: In situ upper troposphere and lower stratosphere measurements of sulfate and organics over Europe, *J. Geophys. Res.*, *115*, D00L07, doi:10.1029/2009JD013628.

Shinohara, H., A. Aiuppa, G. Giudice, S. Gurrieri, and M. Liuzzo (2008), Variation of H_2O/CO_2 and CO_2/SO_2 ratios of volcanic gases discharged by continuous degassing of Mount Etna Volcano, Italy, *J. Geophys. Res.*, *113*, B09203, doi:10.1029/2007JB005185.

Voigt, C., B. Kärcher, H. Schlager, C. Schiller, M. Krämer, M. de Reus, H. Vössing, S. Borrmann, and V. Mitev (2007), In-situ observations and modeling of small nitric acid-containing ice crystals, *Atmos. Chem. Phys.*, *7*, 3373–3383, doi:10.5194/acp-7-3373-2007.

Voigt, C., H. Schlager, A. Roiger, A. Stenke, M. de Reus, S. Borrmann, E. Jensen, C. Schiller, P. Konopka, and N. Sitnikov (2008), Detection of NO_y containing particles in the tropopause region - Evidence for a tropical nitric acid trihydrate (NAT) belt, *Atmos. Chem. Phys.*, *8*, 7421–7430, doi:10.5194/acp-8-7421-2008.

Voigt, C., et al. (2010), In-situ observations of young contrails - Overview and selected case studies from the CONCERT campaign, *Atmos. Chem. Phys.*, *10*, 9039–9056, doi:10.5194/acp-10-9039-2010.

Voigt, C., U. Schumann, P. Jessberger, T. Jurkat, A. Petzold, J.-F. Gayet, M. Krämer, T. Thornberry, and D. W. Fahey (2011), Extinction and optical depth of contrails, *Geophys. Res. Lett.*, *38*, L11806, doi:10.1029/2011GL047189.

von Glasow, R., N. Bobrowski, and C. Kern (2009), The effects of volcanic eruptions on atmospheric chemistry, *Chem. Geol.*, *263*, 131–142, doi:10.1016/j.chemgeo.2008.08.020.