Gas composition of Popocatépetl Volcano between 2007 and 2008: FTIR spectroscopic measurements of an explosive event and during quiescent degassing

W. Stremme [a,*], I. Ortega [a], C. Siebe [b], M. Grutter [a]

[a] Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México, Mexico City, Mexico
[b] Departamento de Vulcanología, Instituto de Geofísica, Universidad Nacional Autónoma de México, Mexico City, Mexico

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ABSTRACT

On December 1, 2007, the solar absorption infrared spectra of the Popocatépetl volcanic plume was recorded during an eruptive event and complementarily on November 17, 2008, the passive quiescent degassing was measured from the same site. A portable FTIR spectrometer with a scanning mirror for fast tracking of the sun provided the flexibility, quality, and simplicity needed for field deployment. Slant columns of the gases SO_2, HCl, HF, and SiF_4 were retrieved and strong differences could be observed when comparing gas ratios in both time periods. During the explosive eruption, the SO_2/HCl ratio was three times greater and the HF/HCl ratio was slightly smaller than during passive degassing.

While the ratios among SO_2, HCl, HF, and SiF_4 describe the chemical composition of the volcanic gas mixture, the SiF_4/HF ratio provides information about the equilibrium temperatures of the stored gases which in this study were calculated at 150° and 185 °C for the explosive and quiescent degassing episodes, respectively. We conclude that cooling of lava domes in the crater precedes Vulcanian explosions as suggested by Schaaf et al (2005). Based on SO_2 flux (Grutter et al., 2008) and measurements and data from the November 2008 event, the average fluxes for HCl, HF, SiF_4, and F through quiescent degassing are estimated to be 204, 22.7, 9.8, and 31.7 tons/day, respectively. These values are similar to those reported by Love et al. (1998) more than 10 yrs ago.

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1. Introduction

1.1. Popocatépetl

Popocatépetl (smoking mountain in Nahuatl language) is a stratovolcano (19.02°N, 98.62°W, 5465 m a.s.l.) located 60 km southeast of Mexico City and is known to be one of the world's largest SO_2 sources (Grutter et al., 2008).

During the last 15,000 yrs several high-magnitude Plinian eruptions have occurred at Popocatépetl and ejected ash and pumice has even reached the area today occupied by Mexico City (Arana-Salinas et al., 2010; Siebe et al., 1996, 1999). After almost one century of dormancy the volcano started to erupt again since 1994 (Goff et al., 1998). This activity has been characterized by short periods of dome growth accompanied by explosive activity (Macías and Siebe, 2005)

that has produced columns of ash separated by much longer and almost permanent periods of strong quiescent passive degassing.

The passive degassing has an accumulated SO_2 emission over time that compares to the amount of SO_2 produced during the Pinatubo Plinian eruption of 1991 (Delgado-Granados et al., 2001), which had an impact on global climate. The ash emitted by Popocatépetl in small, short-lived explosions with moderate frequency has been of great concern, especially for the aviation industry.

The behavior of the volcano is continuously monitored by various parameters measured by the National Center for Disaster Prevention (CENAPRED) and the Geophysics Institute of UNAM. Its SO_2 flux is estimated periodically by COSPEC measurements and more continuously by DOAS measurements as well as during special projects such as the MILAGRO international campaign, in which various methods (scanning DOAS, airborne DOAS, and imaging infrared spectrometry) were combined to estimate its flux (Grutter et al., 2008). The plume composition described as HCl, HF, and SiF_4 to SO_2 molecule ratios was reported from FTIR measurements during the initial eruptive period between 1996 and 1997 more then one decade ago (Goff et al., 2001; Love et al., 1998).

1.2. Gas composition of volcanic plumes

The analysis of the composition of volcanic gases is one possible method to learn about the internal activity of the Earth and constrain theoretical models describing volcanic degassing processes. However, in situ measurements involve a high risk and cannot be applied easily to investigate compositions of gases produced by volcanic explosions. The last direct samples from Popocatépetl were taken in 1994 by posting alkaline-traps around the crater rim (Goff et al., 1998). Since then, it has not been possible to take samples of gas from Popocatépetl as the access to the crater is highly restricted.

Remote sensing can retrieve information of the composition of volcanic plumes which defy all other in situ techniques. Electromagnetic radiation coming from the plume as thermal emission or passing through it, can be analyzed spectroscopically through a variety of techniques and geometries in order to determine its gas composition. The application of Fourier Transform Infrared (FTIR) spectroscopy in volcanology has been developed and applied during the last two decades (Burton et al., 2001; Duffell et al., 2001; Francis et al., 1996; Goff et al., 2001; Love et al., 1998; Mori et al., 1993; Notsu et al., 1993) mostly in the passive mode using natural light sources as the sun, moon, hot background or thermal emission of the volcanic plume itself. These methods have typically reported gases like SiF_4, SO_2, HCl, and HF, but also H_2S, CO, CO_2, and H_2O have been retrieved and quantified.

The FTIR technique has so far not been applied extensively at volcanoes because of the high cost of the instrument and the difficulty of its field deployment and data analysis. Especially the choice of detectors and use of optical filters often limits the spectral region, so that measurements of the complete set of gases are rare and tedious because they are usually done manually and the analysis needs individual treatment of the spectra. Different measurement techniques (FTIR, direct sampling and filter packs) have been compared and possible systematic errors have been discussed (Aiuppa et al., 2004a). However, even combining all measurements, the available datasets are still quite limited.

The relative gas compositions differ for each volcano so that model studies usually have to focus on particular cases. For example, Popocatépetl has generally a higher SO_2/HCl ratio than Etna, but a lower ratio than Kilauea (Edmonds et al., 2009; Francis et al., 1998; Love et al., 1998). Recent models qualitatively explain the observations (Edmonds, 2008; McGonigle, 2005) and the most frequently measured compounds (SO_2, HCl, and HF) are used to constrain parameters in models developed to describe the degassing mechanisms (Aiuppa, 2009; Aiuppa et al., 2004b).

The SO_2/HCl and HF/HCl ratios contain information about the location where the gases are dissolved or if they are of shallow or deeper origin (Burton et al., 2007a). This could explain systematic differences between explosive and quiescent degassing periods as observed on volcanoes like Etna (Allard et al., 2005), Yasur (Oppenheimer et al., 2006), and Stromboli (Burton et al., 2007b). There is evidence that an eruption is usually accompanied by strong enhancements of the SO_2/HCl ratio and slight decreases of the HF/HCl ratio. The opposite behavior was observed at Asama volcano, but Notsu and Mori (2010) state that more measurements are needed to confirm this observation.

Fluorine is not always emitted as HF, but also as SiF_4 which was detected for the first time by Francis et al. (1996) at Vulcano, Italy. An enhancement of the SiF_4/SO_2 ratio seems to occur characteristically before an eruption and could be interpreted as a warning signal (Love et al., 1998; McGonigle, 2005). SiF_4 exists in volcanic gases mainly because of the reaction in Eq. (1), which was predicted for HF-rich, low temperature plumes (below 300 °C) by Rosenberg (1973). The cooling mechanism has been suggested to take place by adiabatic expansion during the fast ascent of gas bubbles in the magma (Rosenberg, 1973; Sahagian and Proussevitch, 2010; Symonds and Reed, 1993) or after extrusion of a viscous lava dome that cools mostly by emitting thermal radiation so that temperature decreases rapidly (Schaaf et al., 2005).

$$SiO_2 + 4 \cdot HF \rightarrow SiF_4 + 2 \times H_2O \qquad (1)$$

The SiF_4/HF ratio can provide information of the thermodynamical conditions (pressure, temperature) in which the gas existed before it was released in an eruption or by passive degassing (Love et al., 2000; Mori et al., 2002; Rosenberg, 1973; Symonds and Reed, 1993). The increased SiF_4/SO_2 ratio measured before and during an eruption (Love et al., 1998) might have resulted from an increase in the SiF_4/HF ratio. It is therefore important to measure SiF_4 and HF simultaneously. Mori et al. (2002) measured SiF_4 and HF using open-path FTIR spectroscopy at Satsuma-Iwojima volcano and found a mixture of low and high temperature gases. They concluded that the SiF_4 emission contributed up to 70% of the total fluorine emission.

1.3. This work

Several trips to Popocatépetl volcano in 2007 and 2008 allowed for taking several measurements of the thermal emission of the plume. On two occasions it was also possible to measure the gas composition by direct solar absorption as shown in Fig. 1. One of these days (Dec. 1, 2007) coincided with a moderate Vulcanian-type eruption and this contribution focuses on the results obtained during this event. The results are compared with those obtained on Nov. 17, 2008 in which a solar absorption measurement of a quiescent degassing plume was taken. Data collected from the thermal emission measurements will be presented elsewhere.

Solar absorption spectroscopy using direct sunlight has more commonly been applied for continuously monitoring atmospheric gases and during the last 15 yrs, a wide variety of tools and techniques has been developed for this application, especially by the scientific community of the Network for the Detection of Atmospheric Composition Change (NDACC). In the present study the information of slant columns from each spectrum, in the presence of the volcanic plume, is calculated using the retrieval code SFIT2 (Hase et al., 2004). Love et al. (1998) used the sunlight scattered from stratospheric clouds, which allows the calculation of absorbance because the light-path in the troposphere remains constant. Direct solar occultation (as applied by Francis et al. (1998) and also in this study) requires,
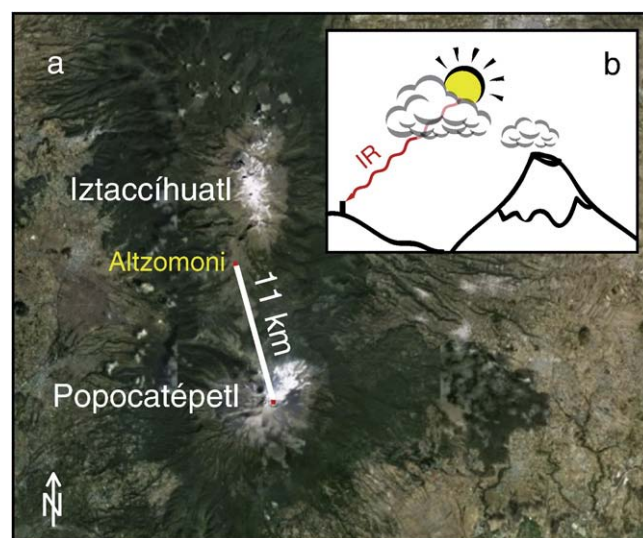

Fig. 1. (a) Image of the Popocatépetl and Iztaccíhuatl national park and location of the measurement site Altzomoni. (b) Measurement configuration used to determine gas compositions of the volcanic plume with solar absorption FTIR spectroscopy.

for the complete spectrum to be simulated, to take into account all atmospheric gases involved in the specific spectral window.

2. Site and instrumentation

The measurement site at Altzomoni (19.12 N, 98.65 W, 4010 m. a. s.l) is a high-altitude location on the S flank of Iztaccíhuatl and at a 11 km distance from the active Popocatépetl crater (Fig. 1a). Located within a national park and surrounded by forests at lower altitudes, this site was used previously to investigate for example the volcanic SO_2 plume with a scanning infrared system for its visualization (Grutter et al., 2008) and to observe pollution transport and boundary layer dynamics in the region (Baumgardner et al., 2009). The Altzomoni site is most of the time well above the contaminated mixing layer except for a few hours in the afternoon and has a quasi-horizontal line-of-sight of the active volcano, providing excellent conditions for remote sensing observations. The measurement geometry used for investigating the gas composition of the plume with solar absorption FTIR spectroscopy is shown in Fig. 1b.

The propagating direction of the volcanic plume is predominantly towards the east and only on few occasions to the north. The latter is needed in order to measure the composition of the plume in the solar absorption mode from this site. For this reason, measuring with this configuration was possible only on 2 days of a total of 15 days of the campaigns carried out during the 2007–2008 period. One of these days coincided with the Vulcanian-type eruption discussed in this work, which occurred on December 1, 2007. The other opportunity that surfaced to measure in this configuration was on November 17, 2008, in which the more common passive degassing-type of emission was observed. Photographs taken on these 2 days are shown in Fig. 2.

The instrument used to measure infrared spectra of solar radiation combines a scanning mirror to actively track the sun, a 4:1-telescope (7.5 mrad), and a compact FTIR spectrometer (Bruker, Opag 22), both controlled by a computer for signal processing and data acquisition (Harig et al., 2002). The spectrometer measures with a maximum unapodized resolution of 0.5 cm^{-1}, using a KBr beam-splitter and a closed cycle cryo-cooled Mercury-Cadmium-Tellure (MCT) detector, covering the range between 600 and 6000 cm^{-1}. For attenuating the intense solar radiation entering the spectrometer, a variable number of wire meshes are used. The system is easy to operate, can record solar spectra without much assistance for a few hours and weights all togetherless than 30 kg, making it ideal for field deployment.

3. Solar absorption FTIR-spectroscopy

In order to apply direct solar absorption spectroscopy on volcanic plumes, two main conditions need to be met: a) the sky must be clear and b) the sun, parts of the volcanic plume, and the instrument need to be on one line. Continuously degassing plumes can be followed with some effort depending on the wind direction and the availability of roads around the volcano. However, the possibility to catch the plume created by a short explosion is rare and a rapid response may not always be possible. Another problem arises when the amount of ash in the plume is too dense after such an event so that little or no sunlight passes through the plume. On December 1, 2007 a moderate Vulcanian explosion occurred at Popocatépetl and the ash reached an altitude of 7.4 km (Volcanic Ash Advisory Center, 2007) as shown in Fig. 2a. Our group happened to be at the Altzomoni site during the eruptive event and the conditions were given to take solar absorption spectra of the plume. As can be seen in Fig. 2a the emitted ash-gas-cloud consisted of two parts, an upper and a lower one. The wind with a higher velocity of ca. 2–3 m/s at the altitude of the Vulcanian plume efficiently isolated this plume from the subsequent plume formed by quiescent degassing, and the two parts of the plume became separated (Fig. 6a). The plume was then transported north over the observation site and was sufficiently dispersed so that the ash did not hinder the measurement. The vertical wind profile is measured daily by radiosondes ascending at the Mexico City airport at 6 am LT, but can also be estimated by observing the propagation of the volcanic plume itself. Fig. 2b shows the passive degassing plume on November 17, 2008, also dispersed by favorable wind conditions for solar absorption measurements from the Altzomoni site.

3.1. Spectral evidence

A compact spectrometer with a resolution of 0.5 cm^{-1} has many advantages, although the absorption lines due to atmospheric gases cannot be resolved completely and the interferences need therefore to be considered with caution. The aim of the computational codes used in these applications is to simulate the spectra using known absorption features of different gases and a number of parameters in order to fit the measured spectra. During this process the atmospheric column of the gas of interest is retrieved. Since the measured spectrum is dominated by the composition of the background atmosphere, it is convenient to
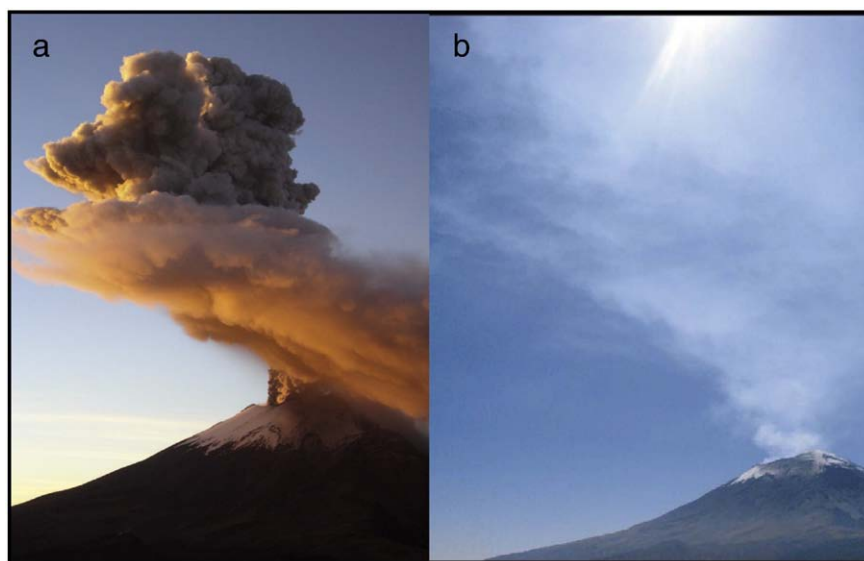

Fig. 2. Photographs of the Popocatépetl plume taken from Altzomoni. (a) The explosive event on the early morning (6:20 h, LT) of December 1, 2007, where the ash plume reached an altitude of 7.4 km a.s.l. (Volcanic Ash Advisory Center, 2007). (b) Continuously passive-degassing plume as observed on November 17, 2008 (morning hours).

show spectroscopically the information of the specific molecules in the spectra as proof.

The absorption features of SO_2 and HCl can clearly be seen in the measurement (Fig. 3). The black trace is a measured absorption spectrum using two single spectra recorded with a solar zenith angle (SZA) which changed by only 4% (43.5° and 41.0°). In the spectral region around 4000 cm^{-1}, however, H_2O (among other interferences) dominates blurring the HF-absorption feature. It is nevertheless possible to show from one measurement that the HF-signal in the volcanic plume (blue trace), calculated by the difference between two forward simulations, one without (green trace) and the other with HF (red trace), is larger than the noise and a quantitative analysis is feasible (Fig. 4).
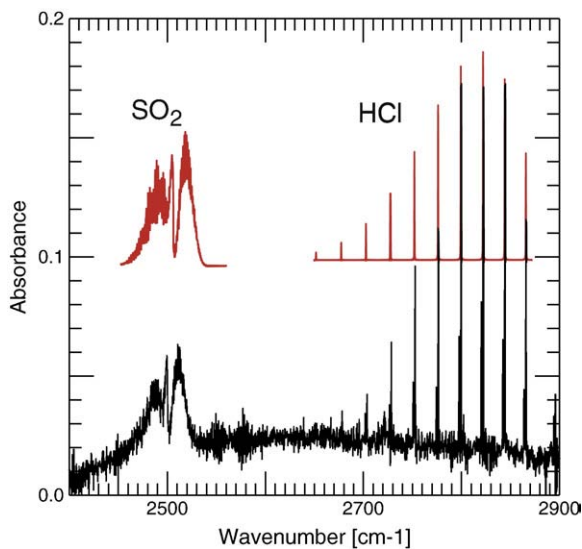
Although it is possible to retrieve SiF_4 from solar spectra passing through the volcanic plume, it is more complicated to show its absorption features in the spectra since strong absorptions due to O_3 between 990 and 1060 cm^{-1} interfere significantly. To our knowledge this is the first time that SiF_4 is retrieved from solar absorption spectra, and in order to demonstrate its presence, two sets of spectra were averaged. Spectra with high-SO_2 slant columns were averaged in one set (Spec$_{plume}$), and those with low-SO_2 slant columns were averaged separately (Spec$_{sky}$). Prior to this, a conversion of each spectrum to normalized transmission using SFIT2 was calculated. As the SiF_4-absorption is small, the difference instead of the true absorbance

$$A_{plume} = ln\left(Spec_{sky}/Spec_{plume}\right) \approx K \cdot Spec_{sky} - Spec_{plume} \qquad (2)$$
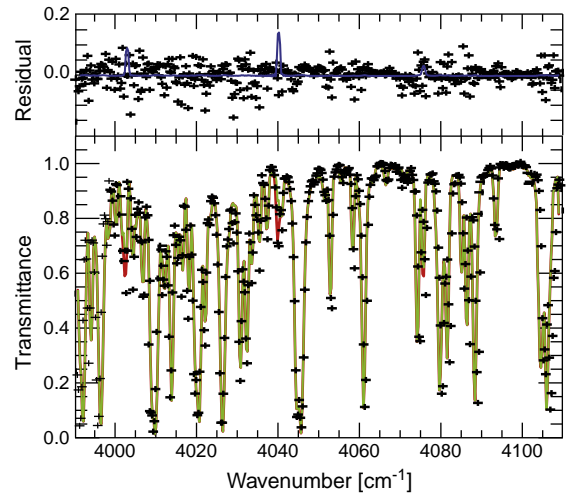
was calculated. The slight difference in SZA is taken into account by adjusting a factor K which minimizes the visible ozone absorption feature between 1040 and 1070 cm^{-1}. The resulting absorbance spectrum (black trace) in Fig. 5 shows, after smoothing with a running average of 20 spectral points (red trace), a clear similarity with the characteristic absorption feature of the SiF_4-reference (bluetrace) and smoothed in same manner (green trace).

3.2. Column retrievals

Since the location of the measurements was the same (Fig. 2), it was important to keep the retrieval settings, spectral window, a


Fig. 4. Lower plot: measured solar spectrum (crosses) around the HF absorption feature. In the same plot is the simulated spectrum including all fitted parameters (red trace). The green trace is the same as the red trace but excluding HF in the simulation. Upper plot: the residual of the first fit (measured−red) is shown as crosses, and the residual of the second fit (measured - green) is shown in blue. The peaks in the blue trace belong to HF. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

priori-information and interference gases equal so that possible systematic errors would cancel when looking at molecular ratios and comparing them in both events. The instrumental line shape (ILS) was described by a maximum optical path difference (OPD) of 1.8 cm and an effective field of view (FOV) of 41 mrad (Stremme et al., 2009) and no additional apodization was applied. Only measurements taken between 8:00 and 11:30 h LST were considered (SZA below 75°) in

Fig. 3. Absorption spectrum (black) measured on November 17, 2008 obtained from two solar spectra recorded at 10:00 and 10:24 (LT). The SO_2 (left) and the HCL (right) features are clearly visible when compared to a reference spectrum (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
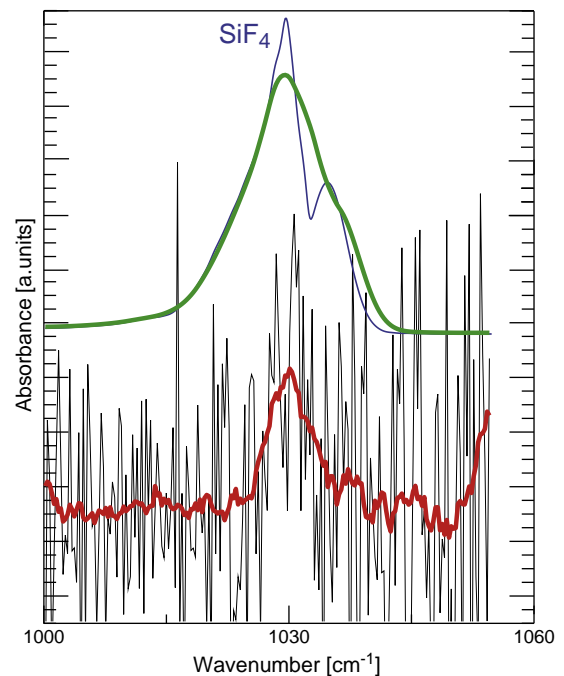
Fig. 5. Solar absorption spectra around the SiF_4 region recorded on November 17, 2008 (black). The absorbance is calculated with two averages of measured spectra, one containing large SO^2 columns and the other with comparatively lower SO^2 columns. The same measured spectrum smoothed by a running average of 20 data points is shown in red. A laboratory SiF_4-reference spectra is shown in blue. The reference spectrum smoothed in the same manner as the measured spectrum (green) looks quite similar to the smoothed absorbance measured (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the comparison so that a possible influence from the contaminated mixing layer could be avoided.

3.2.1. SO2 and HCl

The SO_2 and HCl columns were retrieved with SFIT2 v.39.3 using the HITRAN 2004 spectral database (Rothman et al., 2005). SO_2 was retrieved in the 2470–2535 cm^{-1} spectral window, similar as described by Francis et al. (1998), fitting CH_4, N_2O, and H_2O simultaneously as interferences and switching on the solar-model by Hase et al. (2006), which gave better results. The a priori profile was adapted according to an estimated upper limit of the volcanic gas layer of 7.4 km, reported as the upper limit of the emitted ash on 1 December 2007 by the Volcanic Ash Advisory Center (2007). Because of the large spectral window taken, the slope and curvature of the spectra are automatically fitted. The retrieval of the HCl columns was done using eight micro windows around the HCl absorption lines. A broad spectral region as chosen by Francis et al. (1998) was not used because the strong water-vapor lines caused problems in the simulation when using the HITRAN 2004 database. However, the improved 2008 version of HITRAN was tested with SFIT2 v.39.4 on a subset with the broad spectral window and no significant changes in the HCl results were found when compared to the first method.

3.2.2. HF

The HF columns were retrieved with SFIT2 v.39.4 and HITRAN 2008. Although the HF lines in both versions of HITRAN are the same, the improvements in the H_2O lines (Rothman et al., 2009) included in HITRAN 2008 were crucial to analyze HF. The chosen spectral window (3990–4110 cm^{-1}), which contains several HF absorption lines, is a compromise between getting enough information to fit all interference gases and obtaining a good residual. This window is similar to the one used by Francis et al. (1998) and Love et al. (1998) although slightly narrower. The noise in the measurements and thus the random error in the HF retrieval, is larger than for SO_2 and HCl, as can be inferred from the low signal and the residual (Fig. 4).

3.2.3. SiF4

Since the SiF_4 cross sections are not contained in the HITRAN database, this molecule could not be analyzed directly with SFIT2 and hence, a different approach was adopted. Ozone was retrieved from the solar spectra using SFIT2 and the residuals where then used to quantify the absorbance due to SiF_4. The thermal emission of the instrument and the wire-mesh used to attenuate the radiation interferes strongly in the region around 1000 cm^{-1}. The correction applied for carbon monoxide in the 2000–2200 cm^{-1} spectral window (Stremme et al., 2009) was not sufficiently good for O_3 near 1000 cm^{-1}. A second correction scheme was applied: first, a polynomial together with an estimated transmission (with reduced resolution) of the slant-O_3 column was fitted and the polynomial was subtracted. To test the first step of the correction, the SO_2 column was retrieved using the ν_1-band and compared with the SO_2-columns retrieved from the 2500 cm^{-1} region, the systematic overestimation of 8% is consistent with a study that compared results using both bands (Mori et al., 2002).

In the second step, the O_3 column was retrieved from the spectra and an average vertical-O_3 column was obtained for each event. The O_3-column from each measurement was then constrained to the above value and the zero-level was fitted to improve the correction due to thermal emission of the instrument. The interference gases H_2O and SO_2 were fitted as well. Between 8:00 and 11:30 h LT, Altzomoni is not affected by ozone from the mixing layer and the change of the stratospheric ozone within 3 h is sufficiently small so that the vertical O_3-column can be expected to remain fairly constant. Moreover, the region between 1020 and 1050 cm^{-1}, in which SiF_4 is active, was deweighted in the ozone fits and the average of all residuals was first subtracted from each residual to reduce the interference arising from

other unknown spectral features. Finally, a SiF_4-absorption reference spectrum (55 ppm m at 300 K and 1000 hPa) together with a polynomial was fitted to the residuum/$simulation_{SFIT2}$ spectrum. The resulting SiF_4 columns are shown in Fig. 6a and b. The errors are estimated in a top-down manner from the confidence interval in Fig. 9 and presented in Table 1.

4. Results and discussion

4.1. Gas composition of Vulcanian explosion products and quiescent degassing

The relative composition of gases can be described by the molecular ratios of a specific volcanic gas and SO_2. The ratios are obtained by the slope of a linear fit of the data collected during the events and their uncertainties are calculated from the 95% confidence interval in Fig. 9. The results in Table 1 show quite clearly that the relative SO_2 content is significantly larger in the Vulcanian explosion than during quiescent degassing. The SO_2/HCl ratio was three times greater during the explosive eruption while the HF/HCl ratio was slightly smaller (Table 1), similar to values reported for Stromboli (Burton et al., 2007b), Etna (Allard et al., 2005), and Yasur (Oppenheimer et al., 2006) volcanoes.

For Stromboli volcano it is suggested that the SO_2 becomes exsolved at depth, while HCl and fluorine exsolve at lower pressures or smaller depths (Burton et al., 2007b). The enhancement of SO_2 found here might therefore indicate that a large amount of gas of deeper origin was involved in this explosion.

That the sulfur/chlorine ratio can vary by a factor of 3 is consistent with the range reported by Goff et al. (2001)) for 1998. A recent model study by Roberge et al. (2009) suggests that degassing of S is driven by initial decompression during intrusion from middle to upper crustal depths followed by additional gas exsolution due to crystallization. Magma involved in intrusion, which ascends through the upper crust, suffers strong under-cooling through degassing of mainly H_2O, and leads to rapid crystallization. Only a small part of it reaches the surface, while the main magma volume suffers the "viscosity death." The typical amount of involved magma on the timescale of 2 yrs are estimated for 1995–1997 to be larger than 0.8 km^3 (Roberge et al., 2009). The model curve by Roberge et al. (2009) shows that the S/Cl ratios between passive degassing and explosive events can differ by a factor of 3 if the eruption is correlated with gas exsolved at 400 MPa while passive degassing takes place at shallow depths.

Aiuppa (2009) developed an empirical model to explain the relative fractions of sulfur, chlorine, and fluorine observed as SO_2, HCl, and HF. The empirical model is fitted to the observations of individual volcanoes by adjusting the parameters D_S/D_{Cl} and D_S/D_F, where D_x are the vapor/melt (molar) partition coefficients for the volatiles. The
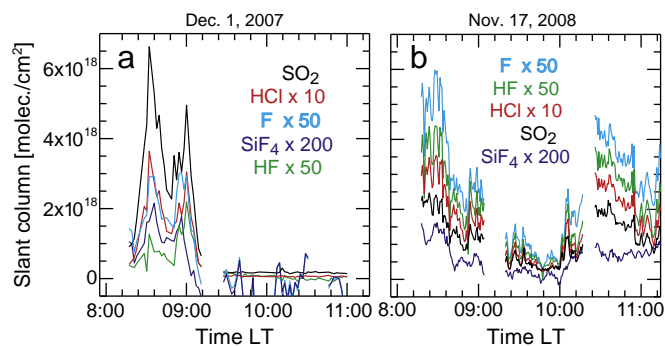

Fig. 6. Time series of SO_2 (black), HCl (red), HF (green), SiF4 (blue, dark), and F (blue light). The slant columns are scaled by 10 (HCl), 200 (SiF_4) and 50 (HF,F). (a) On December 1, 2007 and (b) on November 17, 2008. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Molecule ratios (HCl) obtained from solar absorption spectroscopy.

HCl based molec.	Eruptive event (December 1, 2007)	Passive degassing (November 17, 2008)
SO_2	18.09 ± 0.424	6.751 ± 0.081
HCl	$1.000 \pm -$	$1.000 \pm -$
HF	0.085 ± 0.013	0.244 ± 0.006
HF[a]	0.044 ± 0.019	0.244 ± 0.006
HF[b]	0.159 ± 0.007	0.244 ± 0.006
$4*SiF_4$	0.135 ± 0.028	0.069 ± 0.006
SiF_4	0.034 ± 0.007	0.017 ± 0.001
SiF_4^{org}	0.034 ± 0.007	0.020 ± 0.003
F	0.219 ± 0.029	0.314 ± 0.009

[org] without linear SZA-bias-correction (see text).
[a] First part of the explosive plume on December 1, 2007.
[b] Second part of the explosive plume on December 1, 2007.

model calculates the evolving SO_2/HCl and SO_2/HF ratios in the magmatic gas phase based on the fitted degassing coefficients for the ratio of the elements (S, Cl, F) in the melt. As the ratios in the melt might change because of degassing, the model describes how ratios might change as a function of aging of the silicate melt or through the presence of fresh melt. Fig. 7 shows the model-curve (green line) and the measurements by Goff et al. (2001), on which it is based (green diamonds). Our measurements of the SO_2/HCl and SO_2/HF ratios are shown as blue crosses. The red points represent the same measurements, but replacing the SO_2/HF ratio by the SO_2/F ratio. We assume that fluorine is only present in the form of HF and SiF_4, which is not necessarily valid for all conditions.

The fluorine/chlorine atomic ratios were found to be similar both during the eruption and quiescent degassing (0.2 and 0.3, respectively) as shown in Table 1. Similarly, the D_F/D_{Cl} ratio $= 9/36 = 0.25$ from their vapor/melt partition coefficients is a typical value (Aiuppa, 2009). However, the SiF_4 molecule contains an important part of the total fluorine as shown from the difference in the blue crosses and red diamonds in Fig. 7.

As the model describes a change in the molecular ratios in long-term degassing of a magma chamber, the rather long time of 1 yr between our measurements is unfortunate. Therefore the observation that the SO_2/HCl ratio changes from about 18 to about 6 between eruption and passive degassing during the course of 1 yr does not necessarily stem from the explosive vs. passive character of the emission, but might reflect a long term trend. The SO_2/HCl ratio of the degassing magma simply decreases with time as the magma degases more SO_2 than HCl and the remaining gas becomes more HCl-rich (Aiuppa, 2009). In order to really distinguish between SO_2/HCl ratio
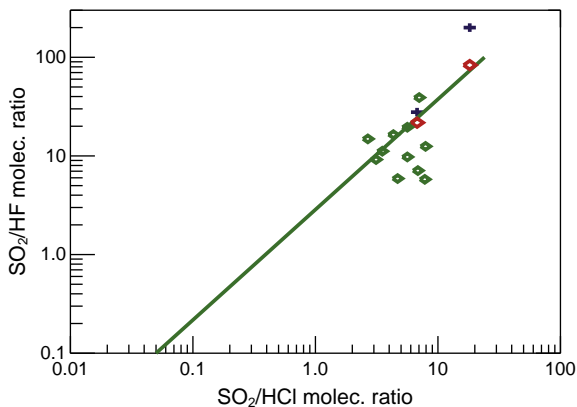
changes related to eruption and to progressive degassing, more closely spaced measurements are desirable. The previous data collected using alkaline traps by Goff et al. (1998) and FTIR by Goff et al. (2001) show that the SO_2/HCl ratio decreased from about 12 in 1994 when the volcano just started to become active to about 5 in 1998. This is consistent with a degassing trend. The high ratio of 18 in 2007 would indicate a new injection of SO_2-rich magma between 1998 and 2007, and subsequent degassing, since the ratio drops down to 6. Between 1996 and July 2003 more than 25 new domes have grown in the crater (Macías and Siebe, 2005), indicating that new magma reaches the surface periodically.

The typical D_S/D_{Cl} ratio of the degassing coefficients resulting from the model of Aiuppa (2009) is about 2.8 and greater than one, but according to the model assumption does not depend on pressure. This assumption is contrary to Burton et al. (2007b), who suggest that the D_S/D_{Cl} ratio changes as a function of pressure, but also predicts that gas, if released at depth, is richer in SO_2, because it is released from magma that is less degassed and therefore rich in SO_2. Degassing at shallow depth normally implies degassing from more aged magma and the melt should be comparably poorer in SO_2. Hence, the high SO_2/HCl ratio in gas from an explosion could be explained by its origin at greater depth.

4.2. SiF₄/HF-equilibrium temperatures

The relative fluorine content expressed as SiF_4/HF is characteristic for the equilibrium temperature, which can be estimated from model curves such as the one shown in Fig. 8. This curve follows the model of Symonds and Reed (1993) and was adapted for Popocatépetl from data taken in 1998 (Love et al., 2000). The ratios from this study result in an equilibrium temperature of 185 °C in the case of November 17, 2008, similar to the value found by Love et al. (2000), which corresponds to passive degassing. In the case of the explosion, it has been already noted and shown (Fig. 9b) from distinct SO_2/HF ratios obtained during the same event that the plume consists of two parts. According to this model the first part of the eruption plume on December 1, 2007 has a temperature of 150 °C, while the second part
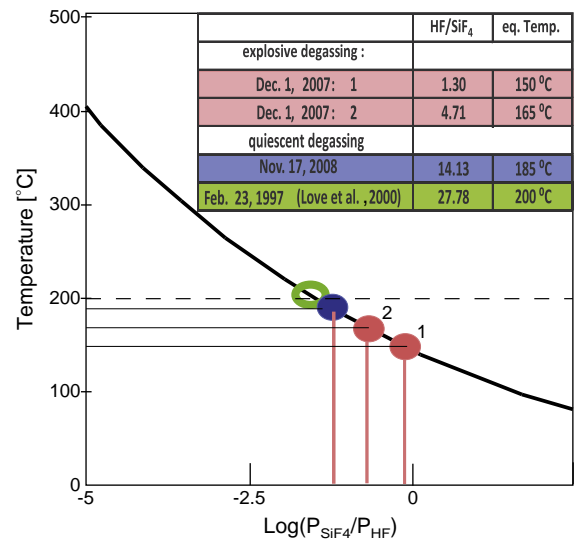
Fig. 7. Gas-measurements at Popocatépetl volcano. Green—diamonds: measurements taken 1994–1998 (Goff et al., 2001), green-line model taken from Aiuppa (2009), blue crosses: measurements taken during this study, red diamonds: SO_2/HCl versus SO_2/F (this study). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 8. Equilibrium temperature versus ratio of SiF_4 and HF partial pressure, for Log $(P_{HF}) = -2.8$ (solid black line), taken from Love et al. (2000) and calculated by following Symonds and Reed (1993). The green point is the estimate of Love et al. (2000). Estimate of equilibrium temperature from passive (blue point) and eruptive (red points) degassing in this study. The eruption took place in two consecutive explosions, red point (1) is the estimate of the equilibrium-temperature of 150 °C in the first part of the plume, while the value calculated with the HF/SiF_4 ratio measured in the second part results in a 165 °C equilibrium-temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
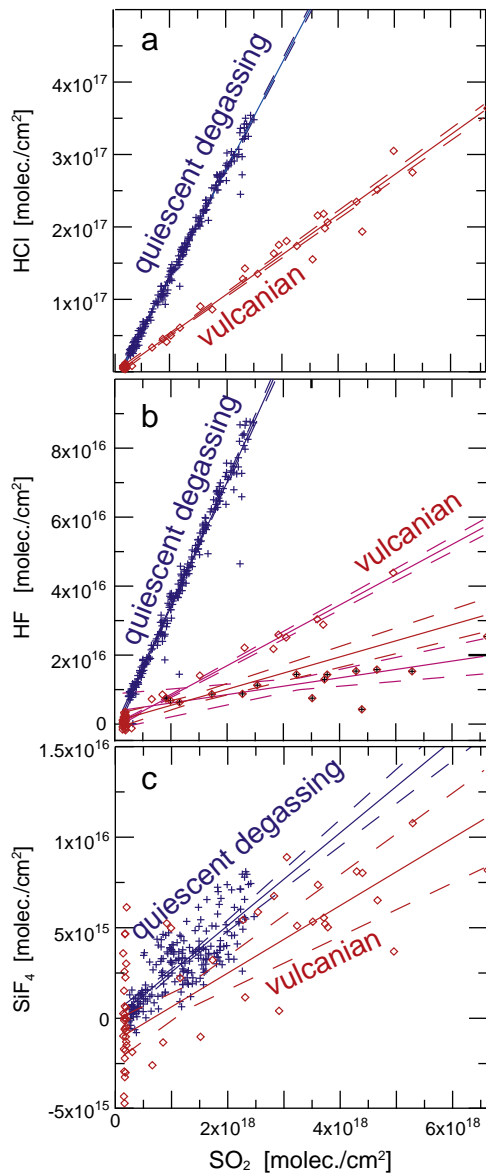
Fig. 9. Slant column ratios: Red diamonds: Vulcanian explosion on December 1, 2007; blue crosses: quiescent degassing on November 17, 2008. Straight lines in the respective color are fitted to each event. Dashed lines indicate the 95% confidence interval for the linear fits. (a) Correlation of HCl with SO_2: High correlation and small uncertainties in the slopes result in quite small errors in the calculated molecule ratios. (b) Correlation of HF with SO_2: The plume that originated by a Vulcanian explosion on December 1, 2007 (Fig. 6a) consists of two parts with different HF/SO_2 molecule ratios. The first part of the plume is marked with black crosses. Straight lines are fitted to both parts of the plume individually (linear fits and 95% confidence intervals are shown in pink by solid and dashed lines). (c) Correlation of SiF_4 with SO_2, same graph as (a) but for SiF_4. Large scattering in the SiF_4 measurement during the Vulcanian explosion is observed and the difference in the molecule ratio is only slightly larger than the 95% confidence interval. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

was slightly warmer at 165 °C. The temperature values should be taken with care and only as a relative indicator because in the model-curve some components could be missing from the assumed gas mixture. However, the values show that the gases emitted through Vulcanian explosions are cooler than those emitted passively thereafter. This low temperature can be explained only if an efficient cooling mechanism is acting prior to the explosion.

A cooling mechanism was recently put forward in the theoretical work of Sahagian and Proussevitch (2010), who describe the effect of adiabatic expansion enhanced through the presence of water or other volatile species. This idea is consistent with the suggestion that the intrusion of hot mafic magma from depth is responsible for the strong SO_2 gas-production observed at Popocatépetl and the emitted SO_2 is mainly exsolved at depth and ascends in the gaseous phase.

However, the above cooling mechanism acting during magma ascent cannot explain the cooling down from the initial magma temperature of around 1000 °C to the observed equilibrium gas temperatures below 200 °C. More probably, the emplacement of hot lava domes in the interior of the crater is followed by rapid cooling due to radiation (strong incandescence and glow can be observed at night-time). This increases the viscosity of the magma leading to pressure build-up until a sudden shallow explosion occurs, typically after a several-day period of seismic quiescence that follows immediately after dome extrusion. Hence, Vulcanian explosions at Popocatépetel can be envisaged as a cooling phenomenon as suggested by Schaaf et al. (2005).

The observed temperatures are below the critical temperature of water (374 °C), which could provide an explanation for the explosion mechanism as the super-heated water present in the hot magma is cooled under high pressure which is above the critical pressure of 22 MPa and might therefore enter the liquid phase. Finally, a small fracture in the dome carapace might trigger the explosion, as the reduction of the pressure would lead to a sudden transition of the water from the liquid to the gas phase.

Thus, two different processes might be involved in the change of the SiF_4/SO_2 ratio in Vulcanian explosions:

$$SiF_4/SO_2 = SiF_4/HF \times HF/SO_2 \qquad (3)$$

(A) The relative SiF_4 content increases because of the increase of the SiF_4/HF ratio through radiative dome cooling at the surface and (B) the HF/SO_2 ratio decreases because of mixing with SO_2-rich gas from deeper origin. The increase of the SiF_4/SO_2 ratio observed by Love et al. (1998)) might be dominated by process A (radiative dome cooling). In our case, a decrease in the SiF_4/SO_2 ratio is observed because process B (gas from depth) predominates. However, simultaneously process A is also taking place as indicated by the observed increase in the SiF_4/HF ratio.

5. Conclusions

A comparison of the composition of an isolated plume created by a Vulcanian explosion on December 1, 2007 and continuously quiescent degassing on November 17, 2008 at Popocatépetl shows strong differences, particularly in the relative sulphur content. The fluorine/chlorine ratios (0.2, 0.3) stay rather stable during both episodes and are near the value of 0.25 generally observed at most volcanoes (Aiuppa, 2009). Only the SO_2/F, but not the SO_2/HF molecular ratios plotted against SO_2/HCl are well explained by the empirical model curve of that study. Our results coincide with those of Aiuppa (2009) when the fluorine content of both, SiF_4 and HF, are considered.

An increase of the SiF_4/SO_2 ratio was not observed during the Vulcanian eruption, but an increase in the SiF_4/HF ratio was evident (from 1/14 during passive degassing to 1/1.3 in the explosive event). This means that fluorine, which is normally emitted in the form of SiF_4 as a minor contributor (below 20%), increases to 75% of the total fluorine during the explosive event. These values are similar to the SiF_4/HF ratio of 0.57 found by Mori et al. (2002) on Satsuma-Iwojima volcano (Japan), where 70% of the fluorine was found to be emitted in the form of SiF_4.

In this contribution, a measurement configuration based on solar absorption with a simple and portable instrument is presented which allowed for various molecular ratios to be determined simultaneously from the same infrared spectra. These ratios allowed us to learn about differences between emissions during explosive events and passive degassing. It was possible to estimate changes in the equilibrium

Table 2
The flux of trace gases of Popocatépetl calculated with the molecular ratios of this study and the SO$_2$-flux reported by Grutter et al. (2008) are compared to an earlier study by Love et al. (1998). Additionally, the fluxes from all arc volcanoes and the total global volcanic emissions estimated by Fischer (2008) are shown.

tons/day	Flux from continuously passive degassing		Global volcanism	
	Popocatépetl		Arc	Total
	This study	Love et al. (1998)	Fischer (2008) compilation	
	Nov. 17, 2008	Feb. 23, 1997		
SO$_2$	2450	2700	46000	55000
HCl	204	297	13000	15000
HF	27.7	41	550	660
SiF$_4$	9.8	7.3	–	–
F	32	42	–	–

temperature from SiF$_4$/HF ratios even during the same eruptive event. The design could however be improved by using bandpass filters to measure for example the spectral regions of SiF$_4$ and HF separately. This would reduce the noise and if additionally SiF$_4$ would be fitted in the original retrieval code, the analysis could be simplified and a deeper insight of errors would be obtained.

From the results presented here, it is suggested that during the Vulcanian eruption of December 1, 2007, the HCl/SO$_2$ ratio was diluted through SO$_2$-rich gas from deeper origin which is present in the gas phase. The mixture of this gas with shallower gas rich in halogens (HCl, HF) equilibrates at a rather low temperature and increases the SiF$_4$/HF ratio. Both of these ratios are therefore independent quantities which can be used to evaluate different models. The HCl/SO$_2$ ratio describes the quantity of gas from depth, while the SiF$_4$/HF ratio contains information on the thermodynamical conditions near surface prior to the explosion. Our indirectly measured temperatures confirm the conclusion of Schaaf et al. (2005) that dome explosions are the result of cooling accompanied by internal pressure build-up in the viscous and solidifying dome.

The emission of halogen (Cl, F) species from Popocatépetl could be estimated in this study by using the mean value of 2400 t/day of SO$_2$ determined by Grutter et al. (2008) and the ratios reported here (Table 1). HCl, HF, and SiF$_4$ were found to be emitted by passive degassing at a rate of 204, 27.7, and 9.8 tons/day. The resulting flux of total fluorine is estimated at 32 tons/day. Using the volcanic fluxes recently compiled by Fischer (2008), the contributions from Popocatépetl are calculated to be 1.6% for HCL and 5.1% for HF of the total output of all arcs and 4.4% and 1.3% of the global volcanic emissions that include other tectonic environments as well (Table 2).

Acknowledgements

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