

Reconnaissance gas measurements on the East Rift Zone of Kīlauea volcano, Hawai‘i by Fourier transform infrared spectroscopy

By Kenneth A. McGee¹, Tamar Elias², A. Jefferson Sutton², Michael P. Doukas¹, Peter G. Zemek³ and Terrence M. Gerlach¹

Open File Report 2005-1062

2005

Use of any trade, firm or product name is for descriptive purposes only and does not constitute endorsement by the U.S. Government

**U.S. GEOLOGICAL SURVEY
U.S. DEPARTMENT OF INTERIOR**

¹*U.S. Geological Survey, Cascades Volcano Observatory, Vancouver, WA, 98685*

²*U.S. Geological Survey, Hawaiian Volcano Observatory, Hawaii National Park, HI 96718*

³*MIDAC Corporation, Costa Mesa, CA 92626*

Abstract. We report the results of a set of measurements of volcanic gases on two small ground level plumes in the vicinity of Pu‘u ‘Ō‘ō cone on the middle East Rift Zone (ERZ) of Kīlauea volcano, Hawai‘i on 15 June 2001 using open-path Fourier transform infrared (FTIR) spectroscopy. The work was carried out as a reconnaissance survey to assess the monitoring and research value of FTIR measurements at this volcano. Despite representing emissions of residual volatiles from lava that has undergone prior degassing, the plumes contained detectable amounts of CO₂, CO, SO₂, HCl, HF and SiF₄. Various processes, including subsurface cooling, condensation of water in the atmospheric plume, oxidation, dissolution in water, and reactions with wall rocks at plume vents affect the abundance of these gases. Low concentrations of volcanic CO₂ measured against a high ambient background are not well constrained by FTIR spectroscopy. Although there appear to be some differences between these gases and Pu‘u ‘Ō‘ō source gases, ratios of HCl/SO₂, HF/SO₂ and CO/SO₂ determined by FTIR measurements of these two small plumes compare reasonably well with earlier published analyses of ERZ vent samples. The measurements yielded emission rate estimates of 4, 11 and 4 t d⁻¹ for CO, HCl and HF respectively for the ERZ.

Keywords: volcanic gases · Fourier transform infrared spectroscopy · degassing · plume · East Rift Zone · Kilauea volcano · Hawaii · FTIR

Introduction

Kīlauea volcano, one of five volcanoes located on the Big Island of Hawai‘i, is one of the most active volcanoes in the world and has been in nearly continuous eruption since 3 January 1983 (Tilling and Dvorak 1993; Heliker and Mattox 2003). Kīlauea lies on the southeastern flank of Mauna Loa volcano and consists of a summit caldera and two major zones, the east rift zone (ERZ) and the southwest rift zone (Fig. 1). The middle portion of the ERZ is the site of the current activity. The ongoing Pu‘u ‘Ō‘ō – Kūpaianaha eruption has been one of the most voluminous eruptions on the ERZ in the recent past, producing more than 2 km³ of lava by the beginning of 2002 (Heliker and Mattox 2003). The current phase of the eruption, termed episode 55, began in February 1997 and continues to this day, characterized by multiple vents on and around the flanks of Pu‘u ‘Ō‘ō. Before injection into the rift system, basaltic magma supplied from the mantle first passes through a reservoir complex beneath the summit caldera where the majority of its CO₂ is degassed (Gerlach and Graeber 1985; Gerlach et al. 2002). Then, magma with its remaining stored volatiles, such as SO₂, travels down rift and exsolves under lower pressure as it approaches the ground surface at the eruption site. Pu‘u ‘Ō‘ō cone and several nearby point sources are presently the main degassing sites of the current mid-ERZ eruption at Kīlauea.

Open-path Fourier transform infrared (FTIR) spectroscopy has been employed in recent years with increasing frequency at a variety of volcanoes throughout the world using natural as well as artificial sources of infrared energy (Mori et al. 1993; Francis et al. 1995; Oppenheimer et al. 1998; Burton et al. 2000; Edmonds et al. 2002). The

technique can be useful in many topographic settings for in-situ measurement of several volcanic gas species at once in volcanic plumes. In some cases, only the ratios of volcanic gases can be determined, but when the FTIR path length is accurately known, the average concentration of each of the detectable gas species in the plume can be computed. FTIR spectroscopy can be especially useful in characterizing the gas chemistry of volcanoes where direct sampling of fumaroles is either not practicable or too dangerous.

In this paper we demonstrate the feasibility of using open-path FTIR spectroscopy to measure a suite of volcanic gases in the plumes emanating from two vents near Pu‘u ‘Ō‘ō cone on the middle ERZ of Kīlauea volcano. We then compare the results with analyses of earlier gas samples collected from eruptive vent areas by means of evacuated bottles containing alkaline solution (Giggenbach, 1975). We then combine our plume measurements with independent measurements of SO₂ emission rates made by correlation spectroscopy (COSPEC) to estimate emission rates for other gases of interest.

Procedure and Instrumentation

The reconnaissance measurements reported here were made over several hours on 15 June 2001, with meteorological conditions on that day consisting of clear skies, dry weather, and northeasterly trade winds of about 4 ms⁻¹. A total of 130 infrared spectra were collected through two small ground level plumes. The measurements were made on the upper lava flow field southeast and down rift of the Pu‘u ‘Ō‘ō cone. At the time of the measurements, a complex lava tube system existed, with multiple tubes and degassing

sites extending from Pu‘u ‘Ō‘ō to below 550-m elevation and one central tube branch reaching the ocean. Small breakouts from the tube system were active along the east and west branches roughly 2 km inland of the coast. Small sparse surface lava flows were also present at 600- and 520 to 550-m elevation.

The first measurement plume (HORNITO) emanated from a 9-m-tall spatter cone located approximately 160 m southeast of Pu‘u ‘Ō‘ō at an elevation of about 800 m (Fig. 2). The actively degassing cone formed in September 1999 on the edge of a deep skylight. The fume from this cone on the day the measurements were taken was blue and mostly translucent. The second measurement plume (PITER) was adjacent to a large collapse pit located ~60 m west of the spatter cone. The voluminous plume emanating from the west wall of this pit was white and opaque and contained a significant amount of condensed water. A slight odor of SO₃ was suspected, but any SO₃ present would react rapidly with water to form H₂SO₄. Measurements at this site had varying amounts of the plume in the FTIR measurement path due to some meander of the PITER plume edge. Some of the earlier measurements at HORNITO also had occasional fume from PITER in the measurement path. Both plumes remained at ground level during the course of the measurements. At some distance downwind, the fume from these and other nearby sources were incorporated into the larger Pu‘u ‘Ō‘ō plume. Since both plumes were derived from degassing lava of the upper lava flow field southeast of Pu‘u ‘Ō‘ō, our measurements are likely to represent emissions of residual volatiles from lava that underwent prior degassing at Pu‘u ‘Ō‘ō cone.

For this study, we utilized a leased commercial open-path FTIR spectrometer from MIDAC Corporation. The system includes a plane mirror Michelson-type scanning interferometer with a spectral resolution of 0.5 cm^{-1} . The spectrometer, operating between $5000\text{-}600 \text{ cm}^{-1}$, is optically coupled to a 25-cm diameter Newtonian telescope with a 3 mrad field-of-view to extend the path length for open-path measurements. Liquid nitrogen provides cooling for a 1-mm^2 mercury-cadmium-telluride (MCT) detector. Each scan of the interferometer produces an interferogram that is converted to a single beam spectrum using a Fast Fourier Transform (FFT). In this study, 32 consecutive scans were co-added to improve the signal-to-noise ratio. Instrument control and data collection were performed with a notebook computer; a 12-volt DC deep-cycle battery powered the entire system.

All of the measurements reported here were made in bistatic configuration using a remote silicon carbide glower with a 50-cm aperture located either in the plume or on the opposite side of the plume under study. The path lengths in this study were determined by measuring tape and ranged from 32 to 73 m. Because the path lengths are precisely known, plume concentrations as well as gas ratios, could be determined. Sample absorbance spectra were generated by first computing the ratio between each sample single-beam spectrum and a background single-beam spectrum of clean ambient air collected well away from these and other vents.

The data were reduced using AutoquantPro software from MIDAC Corporation. The software uses MIDAC's Classical Least Squares K-Matrix calculations coupled with an interpolative piece-wise calibration algorithm and multiple reference spectra to generate individual target species concentrations. All reference spectra are scaled and

subtracted simultaneously according to a classical least squares fitting routine based on the spectral regions chosen in the method. Interferences are visually identified and included in the analysis. The software then automatically accounts for any interfering species during calculations. In order to minimize residual spectra and concentration uncertainties, the piece-wise concentration algorithm utilizes the concentrations of two reference spectra, the results of two independent classical least squares analyses, each of which uses a single reference spectrum, and a concentration-based interpolation involving an empirically determined parameter.

For CO₂, the available laboratory reference spectra proved inadequate so we instead used a set of CO₂ reference spectra made from a series of open-path FTIR atmospheric CO₂ measurements over several distances. The path lengths between the spectrometer and the remote glower light source were precisely measured by tape measure and ranged from 25 m to 300 m. Average CO₂ concentrations along each light path were then measured using a LICOR nondispersive infrared spectrometer (LI-6252). Temperatures and pressures were also recorded and used to correct all concentrations reported here. The result is a set of CO₂ reference spectra that ranges from column amounts of 9,073 ppm-m to 110,040 ppm-m that could be used in place of laboratory standards in the AutoquantPro software to reduce the ERZ FTIR measurements for CO₂. A plot of the field-based CO₂ reference data is shown in Fig. 3. For gases other than CO₂, laboratory spectra were used in the retrieval.

The CO₂ exhibited non-linearity in the calibration curve but there were enough reference spectra to cover the range of CO₂ detected in the samples. One CO₂ point did not fit the curve as well as expected but was determined to be acceptable based upon a 2nd

order fit of the model. The curve was based upon a piece wise linear fitting routine as described above and in the caption for Fig. 3. The background spectra were manually adjusted to remove CO₂ so that all calculations were performed with CO₂ absorbance bands manually removed from the background transmission spectrum (single beam).

Results

A total of 130 spectra were collected and they clearly reveal the presence of SO₂, CO₂, CO, HCl, HF and SiF₄ in the plumes under study. Sulfur dioxide and CO₂ were detected in all of the collected spectra, while HCl, HF and SiF₄ were present in 65%, 33% and 53% of the measurements, respectively. Carbon monoxide was found in 46% of the measurements but was confined only to the HORNITO plume. The results from all of the FTIR measurements are shown in Fig. 4. All concentrations and ratios are presented here and elsewhere in this paper on a molar basis. Most of the spectra from the HORNITO plume were collected using a path length of 64 m and these are designated as HORNITO1 in Fig. 4. A subset of the HORNITO measurements was collected after increasing the path length to 73 m by moving the infrared light source back toward the PITER plume; these are designated as HORNITO2 in Fig. 4. Because of the dense nature of the PITER plume, a path length of only 32 m was used to insure that adequate infrared energy from the glower source was available for the FTIR detector.

Plume concentrations of SO₂ can be clearly subdivided into different populations (Fig. 4a). The PITER plume, which had a mean concentration of 24.5 ppm at the

sampling site, contained more than double the amount of SO₂ than the HORNITO plume. In-situ SO₂ measurements by a hand-held chemical detection tube (Dräger) in both the PITER and HORNITO plumes were similar and also showed SO₂ levels in PITER to be about twice those of the HORNITO plume. The FTIR data show that the mean concentration of SO₂ in the HORNITO1 measurements was 6.9 ppm while that of the HORNITO2 measurements was slightly higher at 10.5 ppm, possibly explained by a small portion of the PITER plume having been incorporated into the extended HORNITO2 measurement path.

Carbon dioxide was detected in all 130 spectra, however plume concentrations of volcanic CO₂ computed by subtracting ambient atmospheric CO₂ (367 ppm), measured by a LICOR LI-6252 nondispersive infrared spectrometer, from total CO₂ were highly variable and 37% of the values fell into the negative range. In general, plume CO₂ is similar to SO₂ in that the HORNITO2 measurements have a higher average concentration of CO₂ than the HORNITO1 measurements (Fig. 4b). Carbon dioxide concentrations in the PITER plume were more widely scattered. We cannot rule out another CO₂ source being intermittently in the measurement path as the source of some of this variability. Likewise, some plume meander due to changes in wind speed and direction was noted during the measurements resulting in variable amounts of the plume in the measurement path. Meteorology, however, cannot account for lower than ambient CO₂ levels so it is likely that much of the difficulty in quantifying CO₂ is inherent in the current FTIR methodology for CO₂.

Carbon monoxide was detected in 59 of 60 spectra from HORNITO1, with an average concentration of 44 ppb, but not detected at all in the HORNITO2 or PITER

measurements (Fig. 4c). The halogen acid gases, HCl and HF, were detected in a number of spectra throughout both plumes, with the PITER plume containing a distinctly higher concentration of HF (Figs. 4d and 4e). With its relatively strong absorption band centered around 1032 cm^{-1} , SiF_4 was easily detected in many of the spectra from both plumes; concentrations of SiF_4 averaged 4 ppb in the HORNITO plume and 20 ppb in the PITER plume (Fig. 4f).

Discussion

Figure 5 illustrates the concentrations of CO_2 , CO, HCl, and HF plotted against SO_2 for all published analyses of high-temperature gas samples collected during the Pu'u Ō'ō eruption. The samples—collected from 1983 to 1985 when high-temperature sampling was feasible by evacuated bottles containing alkaline solution (Giggenbach, 1975)—represent gas emissions from vents and small openings in spatter cones or spatter deposits bridging vigorously fuming fissures in vent areas. We utilize these samples from Pu'u Ō'ō source lava for comparisons with our open path FTIR results for emissions from what are likely to be relatively degassed Pu'u Ō'ō lava. Graphs for CO_2 vs. SO_2 (Fig. 5a) and CO vs. SO_2 (Fig. 5b) are based on 63 samples (Greenland 1986, 1988; Gerlach 1993a, 1993b); a subset of 39 samples with HCl and HF analytical data (Greenland 1988; Gerlach, 1993a 1993b) provide graphs of HCl vs. SO_2 (Fig. 5c) and HF vs. SO_2 (Fig. 5d). The mean CO_2/SO_2 of these gas samples (0.19) agrees well with the ratio of 0.20 obtained by airborne measurements on the Pu'u Ō'ō plume in 1995 by CO_2 analyzer and closed path FTIR (Gerlach et al. 1998; McGee and Gerlach 1998). It also

agrees with the mean ratio of 0.19 obtained for 204 samples that included, in addition to the 63 high-temperature samples above, low-temperature samples collected in evacuated bottles containing alkaline solution and all samples collected in pumped flow-through bottles and evacuated bottles without alkaline solution (Gerlach et al. 1998). Numerical mean values of X_i/SO_2 for other gases (X_i) are also shown in Fig. 5 (CO/ SO_2 , 0.0064; HCl/ SO_2 , 0.015; HF/ SO_2 , 0.018). The maximum and minimum X_i/SO_2 values vary by a factor of 4-6 except for CO/ SO_2 , which varies by a factor of 19, suggesting that CO in several samples is depleted owing to oxidation. Seven samples shown in Figs. 5c and 5d have notably lower HCl and HF concentrations, but typical SO_2 concentrations. On a graph of HF vs. HCl (Fig. 6a), these samples form a trend between near-zero values and a cluster of higher values. The SO_2 concentrations of these samples are typical of the other samples, suggesting to us that they have been depleted in HCl and HF by condensate formation in the lead-in tube during collection, a known source of error in the sampling technique (Giggenbach and Matsuo, 1991), rather than simply being the residual emissions of relatively more degassed lava.

The results of the ERZ FTIR measurements are shown in Fig. 7. Maximum, minimum and mean lines for X_i/SO_2 from the published analyses shown earlier in Fig. 5 are plotted again in Fig. 7 for comparison. Note that the plume gas concentrations, as measured by FTIR, are about 10^4 times more dilute than the vent samples. As with the raw FTIR data shown in Fig. 4, the X_i/SO_2 ratios fall clearly into different populations; those containing less than 12 ppm SO_2 are from the HORNITO plume and those with more than 20 ppm SO_2 are from the PITER plume. This may simply be due to less mixing of the PITER plume with air by the time it is measured, a likely result of a higher

mass flux rate from the PITER source. Alternatively, the different SO₂ concentrations in the two plumes could reflect the extent of prior source magma degassing (i.e. high SO₂ in the PITER plume represents the least degassed source, low SO₂ in the HORNITO plume represents the most degassed source), although this does not explain the presence of CO only in the HORNITO plume (see below). More than likely, the differences between the two plumes are due mostly to differences in mixing with air. In addition, the removal of water vapor by condensation of liquid water droplets in the PITER plume may also play a minor role in causing the differences in the plume gas concentrations.

It is evident that the CO₂ results from the FTIR measurements (Fig. 7a) are not well constrained. The CO₂/SO₂ ratios scatter considerably and nearly all are significantly above the mean line for the high temperature gas samples. We suspect much of the discrepancy for CO₂ is inherent in the FTIR methodology rather than due to meteorology (discussed earlier) or variations in fractional degassing or some other natural process unique to these vents. It may be that CO₂ levels are simply too low and variable on the ERZ of Kīlauea to resolve by existing FTIR technology. As noted earlier, it is known from earlier published analyses and airborne measurements that CO₂/SO₂ for ERZ gases is about 0.2 (Gerlach et al. 1998). Using this ideal ratio and plume averages for SO₂ from the FTIR measurements, we can calculate expected average plume CO₂ concentrations; for the HORNITO plume, CO₂ should be 1.4 ppm and for the PITER plume, CO₂ should be 4.9 ppm. If ambient air is about 370 ppm, these plume CO₂ concentrations represent only 0.4% and 1.3% respectively of the total CO₂. Considering the scatter of the CO₂ measurements here, accurately resolving differences that close to ambient CO₂ is probably asking too much of the method.

FTIR spectroscopy was used in 1998 and 1999 to measure the CO₂ emission rate from Masaya volcano, Nicaragua (Burton et al. 2000). There, CO₂/SO₂ averaged about 2.4, 12 times greater than that for the ERZ of Kīlauea, and implies a plume CO₂ concentration that is a significantly higher percentage of total CO₂ than on the ERZ of Kilauea. Using data in Burton et al. (2000, Fig. 2a), we estimate plume CO₂ concentrations at Masaya to have averaged 30-50 ppm above the elevated ambient background they report for the 9 March 1999 measurements. The scatter in X_i/SO₂ at Masaya was greater for CO₂ than for other species and was attributed to the natural variability in ambient air (Burton et al. 2000). The summit plume of Kīlauea, degassing hundreds of ppm CO₂ with a CO₂/SO₂ that ranges from 53 to 183 (Gerlach et al. 2002), may provide a better opportunity to resolve CO₂ by FTIR than the ERZ.

The CO/SO₂ ratios from the hotter HORNITO plume form a tight cluster close to the arithmetic mean of the published vent samples (Fig 7b). The lack of detectable CO in the PITER plume suggests that PITER source gases may have cooled subsurface to a greater extent before emission to the air than the HORNITO source gases, and that enough CO was reacted with water or SO₂ to CO₂ at depth to prevent later detection by FTIR spectroscopy. The average CO/CO₂ (0.0056) from the HORNITO FTIR measurements is only one-sixth that of the earlier vent samples from Pu'u Ō'ō (0.0323). All of this difference is likely due to the reaction of CO to CO₂ in the vent feeder although, because of the small amount of CO, it is unlikely to be a major factor because the mean CO/SO₂ from the FTIR measurements is essentially the same as that of the published analyses.

The HCl/SO₂ ratios scatter throughout (and outside) the range for the published analyses, although a significant number of the PITER points are below the average for the vent samples (Fig. 7c), suggesting that some HCl may have been lost to dissolution in the abundant water droplets in the PITER plume or the product of prior degassing. Though the HF/SO₂ ratios from the PITER plume are distinctly higher than those from the HORNITO plume, essentially all of the points from the FTIR measurements are below the average for the vent samples (Fig. 7d). Figure 6b shows a graph of HF versus HCl from the FTIR measurements. Note that a majority of points fall below the solid line representing a 1:1 ratio. The mean value of HF/HCl from the FTIR measurements is 0.6 as compared to 1.3 for the published analyses. A recent study of gases from the four summit craters of Mount Etna as well as from a nearby lava flow showed a fairly constant HCl/HF throughout but distinctly higher HCl/SO₂ and HF/SO₂ in the gases from what was interpreted to be fractionally degassed magma and from the residual gases of the lava flow (Burton et al. 2003).

Owing to different solubilities, HCl may be dissolving to a slightly greater degree in the water droplets in the PITER plume than HF. However, some HF is probably also lost in the formation of SiF₄ (Fig. 8). Symonds et al. (1992) showed that volcanic gases typically contain trace amounts of SiF₄ and that the gas may be present in greater abundance at lower temperatures due to reactions of HF with various silicates. As HF is present in Kīlauea gases, our FTIR results suggest that SiF₄ may be forming by reaction of HF with the wall rocks at the ERZ plume vents. This is consistent with the results of Francis et al. (1996) who found SiF₄ in the plumes from both Mt. Etna and Vulcano using FTIR. For the HORNITO plume, the SO₂/SiF₄ ratio is 1.8×10^3 while that for the PITER

plume is lower at 1.2×10^3 . Both of these ratios lie between those for Mt. Etna and Vulcano reported by Francis et al. (1996). Although SiF₄ was not reported, a more recent study of fumaroles on Vulcano Island utilizing three different methods, FTIR measurements, filter pack measurements and direct fumarole sampling, revealed generally consistent agreement in HCl/HF between the methods (Aiuppa et al. 2004). However, the same study showed a significant increase in the amount of total sulfur in the direct fumarole samples over the amount of SO₂ detected by FTIR and filter pack samples, a difference the authors attribute to the presence of H₂S which would not be picked up by the two plume measurement methods (Aiuppa et al. 2004).

If the plume concentrations determined by FTIR measurement can be considered representative of ERZ gases, an indirect method for estimating the emission rates of some of these gases is to compare the average X_i/SO_2 ratio determined by FTIR to the ERZ emission rate of SO₂ determined independently by standard COSPEC measurements. For example, the mass emission rate of a gas (E_{xi}) can be determined from

$$E_{xi} = k(X_i/SO_2)E_{SO_2} \quad (1)$$

where X_i/SO_2 is the average molar concentration ratio from the FTIR measurements, k is the ratio of the molecular weight of X_i to SO₂, and E_{SO_2} is the mass emission rate of SO₂ from the ERZ (for CO, HCl, and HF, X_i/SO_2 is 0.0065, 0.0138 and 0.0082; and k is 0.44, 0.57 and 0.31, respectively). Although there was no SO₂ emission rate measurement on the same day as the FTIR campaign, we can use a monthly average of COSPEC data to estimate an emission rate for the day. Combining the four ERZ COSPEC measurements

for June 2001 gives an average E_{SO_2} of $1440 \pm 380 \text{ t d}^{-1}$; the daily average for all of the ERZ COSPEC measurements in 2001 is similar at 1438 t d^{-1} (Elias and Sutton 2002). Thus using Eq. (1), we can estimate the emission rates for CO, HCl and HF to be 4, 11 and 4 t d^{-1} , respectively. Because of the poor quality of the FTIR CO_2 measurements, we are not able to compute a mass emission rate for CO_2 , but from earlier studies the ERZ emission rate of CO_2 was determined to be $240\text{-}300 \text{ t d}^{-1}$ (Gerlach et al. 1998). The caveat is that Eq. (1) may not accurately predict emission rates for the other gas species if the X_i/SO_2 of the relatively small plumes of HORNITO and PITER do not reflect that of the total ERZ gas output that is largely dominated by the plume from Pu'u Ō'ō.

It is clear from this reconnaissance study that the two degassing sources studied here are very different from one another and that, in fact, any small degassing source has the potential to differ from its neighbor due to a variety of processes. This has significant implications for the routine use of FTIR on the ERZ of Kīlauea. Future FTIR measurements aimed at determining gas emission rates should be made such that as much of the main ERZ plume as possible is measured so that the overall signature is as close as possible to the total plume. Conversely, this study also shows that FTIR spectroscopy has the potential to look at variations between small degassing sources in a quantitative manner, enabling researchers to better understand very localized changes in the gas phase on the ERZ.

Conclusions

Plumes emanating from two point sources on Kīlauea's ERZ a short distance down rift from Pu'u Ō'ō are derived from magma that has previously lost most of its CO₂ at the summit and much of its SO₂ at Pu'u Ō'ō. Open-path FTIR measurements of these plumes conclusively reveal the presence of CO₂, CO, SO₂, HCl, HF and SiF₄. Distinct differences in the physical character of the two plumes are reflected in plume chemistry. The water-rich PITER plume contains more than double the concentration of SO₂ than the HORNITO plume due largely to higher vent gas output. HCl dissolves to a greater extent than HF in the wet PITER plume, although significant HF from both plumes may be lost in the formation of SiF₄. CO, while present in the HORNITO plume, is not detectable by FTIR in the PITER plume, a likely result of some oxidation to CO₂ during subsurface cooling. Although there appear to be some differences between these gases and Pu'u Ō'ō source gases, ratios of HCl/SO₂, HF/SO₂ and CO/SO₂ determined by FTIR measurements of these two small plumes compare reasonably well with earlier published analyses of ERZ vent samples and suggest that further studies of ERZ gases by FTIR are warranted.

The procedures for measuring CO₂ in volcanic plumes against a high and variable ambient air background are not yet well constrained by open-path FTIR, but can be improved possibly with the production of more applicable laboratory standards or optimization of CO₂ field standards that better define the concentration-pathlength conditions likely be encountered in volcanic plumes. However, the prospect of successfully measuring very low concentrations of plume CO₂ that may represent only a

small fraction of total CO₂, as on the ERZ of Kīlauea, remains uncertain. Further FTIR measurements directed at determining total gas emission rates should be made with a configuration such that the entire plume is imaged.

Acknowledgments

This work was supported by the U.S. Geological Survey through the Volcano Hazards Program. We are grateful to Marie Edmonds, Larry Mastin and Clive Oppenheimer for insightful reviews and comments.

References

- Aiuppa A, Burton M, Murè F, Inguaggiato S (2004) Intercomparison of volcanic gas monitoring methodologies performed on Vulcano Island, Italy. *Geophys Res Lett* 31: L02610, DOI:10.1029/2003GL018651
- Burton M, Allard P, Murè F, Oppenheimer C (2003) FTIR remote sensing of fractional magma degassing at Mount Etna, Sicily. In: Oppenheimer C, Pyle DM, Barclay J (eds) *Volcanic Degassing*. Geological Society, London, Special Publications 213:281-293
- Burton MR, Oppenheimer C, Horrocks LA, Francis PW (2000) Remote sensing of CO₂ and H₂O emission rates from Masaya volcano, Nicaragua. *Geology* 28:915-918
- Edmonds M, Pyle D, Oppenheimer C (2002) HCl emissions at Soufrière Hills volcano, Montserrat, West Indies, during a second phase of dome building: November 1999 to October 2000. *Bull Volcanol* 64:21-30, DOI 10.1007/s00445-001-0175-0
- Elias T, Sutton AJ (2002) Sulfur dioxide emission rates from Kilauea volcano, Hawai'i, an update: 1998-2001. *US Geol Surv Open-file Rep* 02-460:1-29
- Francis P, Maciejewski A, Oppenheimer C, Chaffin C, Caltabiano T (1995) SO₂:HCl ratios in the plumes from Mt. Etna and Vulcano determined by Fourier transform spectroscopy. *Geophys Res Lett* 22:1717-1720
- Francis P, Chaffin C, Maciejewski A, Oppenheimer C (1996) Remote determination of SiF₄ in volcanic plumes: A new tool for volcano monitoring. *Geophys Res Lett* 23:249-252
- Gerlach TM (1993a) Oxygen buffering of Kilauea volcanic gases and the oxygen fugacity of Kilauea basalt. *Geochim et Cosmochim Acta* 57:795-814
- Gerlach TM (1993b) Thermodynamic evaluation and restoration of volcanic gas analyses: An example based on modern collection and analytical methods. *Geochem Jour*, 27:305-322
- Gerlach TM, Graeber EJ (1985) Volatile budget of Kilauea Volcano. *Nature* 313:273-277
- Gerlach TM, McGee KA, Sutton AJ, Elias T (1998) Rates of volcanic CO₂ degassing from airborne determinations of SO₂ emission rates and plume CO₂/SO₂: Test study at Pu'u 'O'o cone, Kilauea Volcano, Hawaii. *Geophys Res Lett* 25:2675-2678
- Gerlach TM, McGee KA, Elias T, Sutton AJ, Doukas MP (2002) Carbon dioxide emission rate of Kilauea volcano: Implications for primary magma and the summit reservoir. *J Geophys Res* 107(B9): 2189, DOI:10.1029/2001JB000407

- Giggenbach WF (1975) A simple method for the collection and analysis of volcanic gas samples. *Bull Volcanol* 39:132-145
- Giggenbach WF, Matsuo S (1991) Evaluation of results from second and third IAVCEI field workshops on volcanic gases, Mt. Usu, Japan, and White Island, New Zealand. *Appl Geochem* 6:125-141
- Greenland LP (1986) Gas analyses from the Pu'u O'o eruption in 1985, Kilauea volcano, Hawaii. *Bull Volcanol* 48:341-348
- Greenland LP (1988) Gases from the 1983-84 east-rift eruption. *US Geol Surv Prof Pap* 1463:145-153
- Heliker CC, Mattox TN (2003) The first two decades of the Pu'u 'Ō'ō – Kūpaianaha eruption: Chronology and selected bibliography. *US Geol Surv Prof Pap* 1676:1-27
- McGee KA, Gerlach TM (1998) Airborne volcanic plume measurements using a FTIR spectrometer, Kilauea volcano, Hawaii. *Geophys Res Lett* 25:615-618
- Mori T, Notsu K, Tohjima Y, Wakita H (1993) Remote detection of HCl and SO₂ in volcanic gas from Unzen volcano, Japan. *Geophys Res Lett* 20:1355-1358
- Oppenheimer C, Francis P, Burton M, Maciejewski AJH, Boardman L (1998) Remote measurement of volcanic gases by Fourier transform infrared spectroscopy. *Appl Phys B* 67:505-515
- Symonds RB, Reed MH, Rose WI (1992) Origin, speciation, and fluxes of trace-element gases at Augustine volcano, Alaska: Insights into magma degassing and fumarolic processes. *Geochim et Cosmochim Acta* 56:633-657
- Tilling RI, Dvorak JJ (1993) The anatomy of an active basaltic volcano. *Nature* 363:125-133

Figures

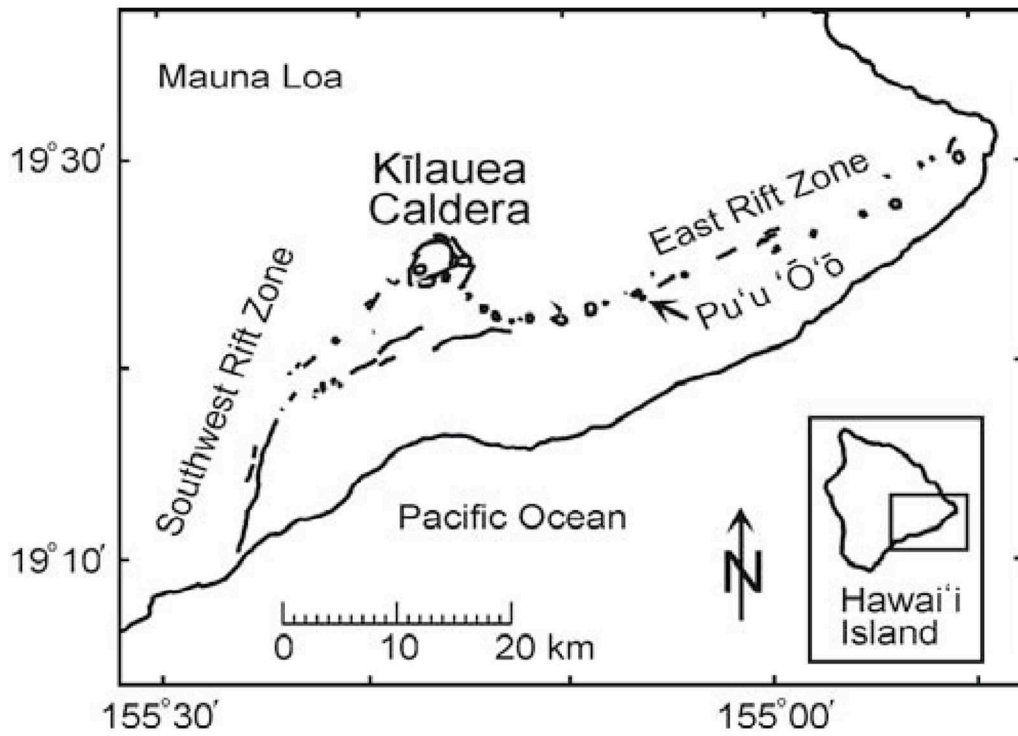


Figure 1. Location map for Kīlauea volcano, Hawai'i, showing the East Rift Zone and Pu'u 'Ō'ō cone.



Figure 2. Photograph taken 15 June 2001 of the HORNITO and PITER plumes in the foreground with Pu'u 'Ō'ō cone and plume in the background. View is to the northwest. HORNITO is located about 160 m southeast of Pu'u 'Ō'ō and PITER is about 60 m west of HORNITO. The FTIR measurements were taken across the mid-point of each plume perpendicular to the axis of plume travel in this field of view.

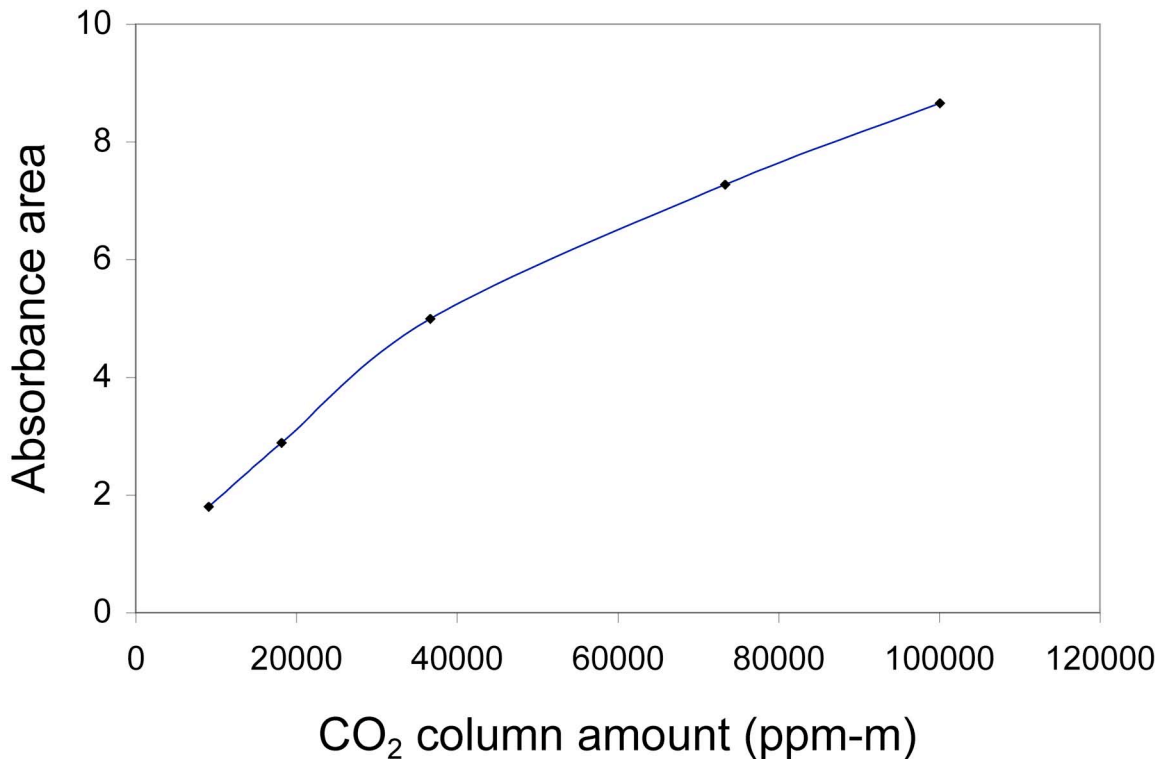


Figure 3. Plot showing CO₂ calibration points. The absorbance area is a unitless relative function of the background over the wavelength range 2223-2284 cm⁻¹. The areas are calculated using an integral function and plotted against column amounts to determine any points that are outliers to the data set. The curve demonstrates a non-linear compound over a large differential optical density range; not uncommon for MCT detectors. The processing software uses each calibration point in its unknown sample calculation by fitting a piece-wise calibration curve to these data and adding in an interpolative function analogous to a spline curve. The actual samples and reference spectra were calculated using the AutoquantPro interpolative Classical Least Squares function.

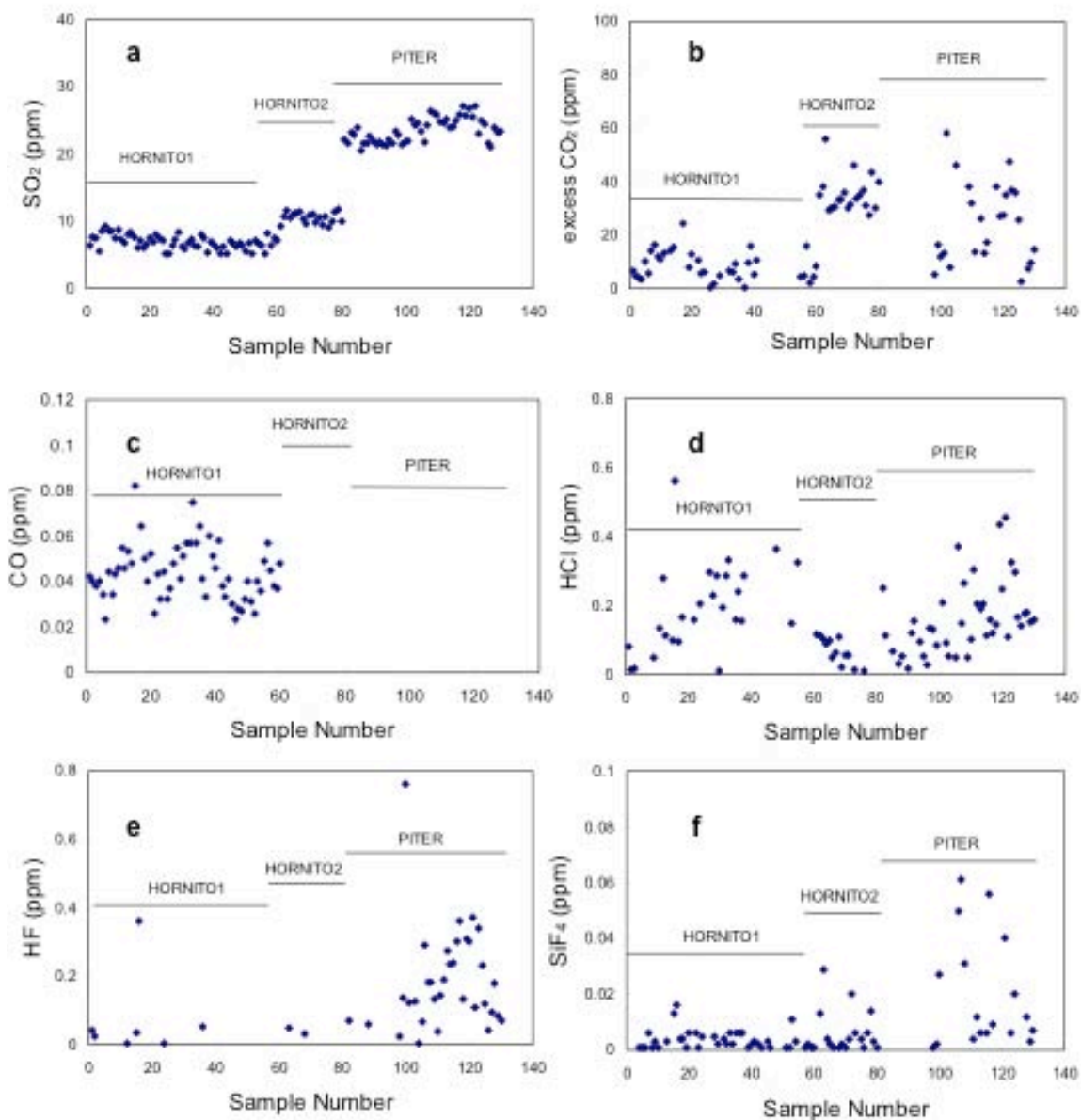


Figure 4. Volcanic gas concentrations in ppm (molar) from FTIR measurements of two plumes on the East Rift Zone of Kīlauea volcano, Hawai‘i on June 15, 2001 for (a) SO₂, (b) CO₂, (c) CO, (d) HCl, (e) HF, and (f) SiF₄. Absorbance spectra for SO₂, CO₂, CO, HCl, HF and SiF₄ were collected in the following spectral windows: 1071-1234, 2223-2284, 2033-2269, 2655-3095, 3963-4293 and 979-1092 cm⁻¹. A total of 130 spectra were collected, but not every gas was detected in every spectrum. Errors ($\pm 1\sigma$) for SO₂, CO₂, CO, HCl, HF and SiF₄ from these measurements were 0.28, 11.73, 0.04, 0.13, 0.24, 0.002 ppm respectively. Solid horizontal lines represent the temporal extent of measurements for each plume, HORNITO or PITER. The HORNITO measurements are further subdivided into HORNITO1 and HORNITO2 with HORNITO1 representing those measurements taken with a path length of 64 m and HORNITO2 a path length of 73 m. The path length used for the PITER plume was 32 m.

Figure 4 (cont.) CO was only detected in the shorter path length HORNITO1 measurements and was not found at all in the cooler PITER plume. As can be seen in (c), the HORNITO1 CO concentrations were very low. By increasing the path length for the HORNITO2 measurements to incorporate either fresh air devoid of CO or a small slice of the adjacent PITER plume also devoid of CO, the signal-to-noise ratio of the measurements was reduced to a level where the low CO signal became obscured by the increased noise.

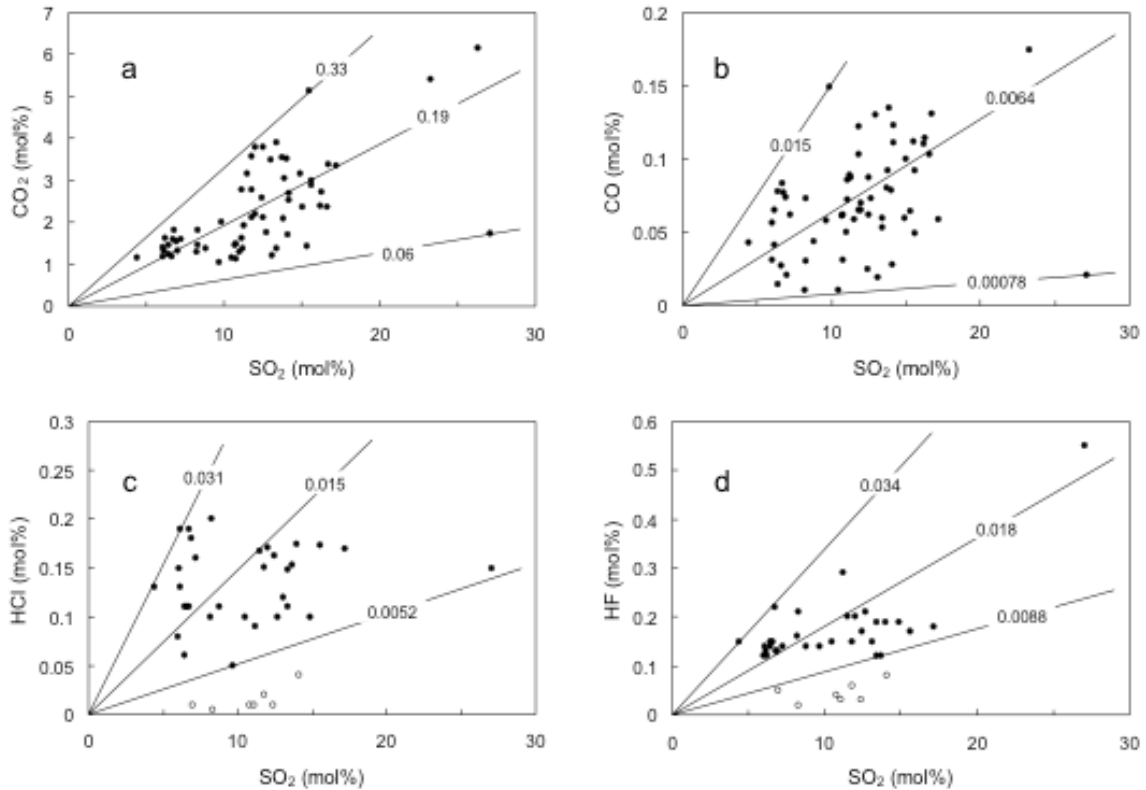


Figure 5. Concentrations of CO_2 , CO, HCl, and HF versus SO_2 in high-temperature gas samples of the Pu'u Ō'ō eruption, 1983 to 1985. Graphs (a) and (b) are based on 63 samples (Greenland 1986, 1988; Gerlach 1993a, 1993b); (c) and (d) are based on 39 samples (Greenland 1988; Gerlach 1993a, 1993b). Lines show ranges and means of CO_2/SO_2 , CO/SO_2 , HCl/SO_2 , and HF/SO_2 . Open circles represent samples depleted in HCl and HF likely due to condensate formation in the lead-in tube during sample collection.

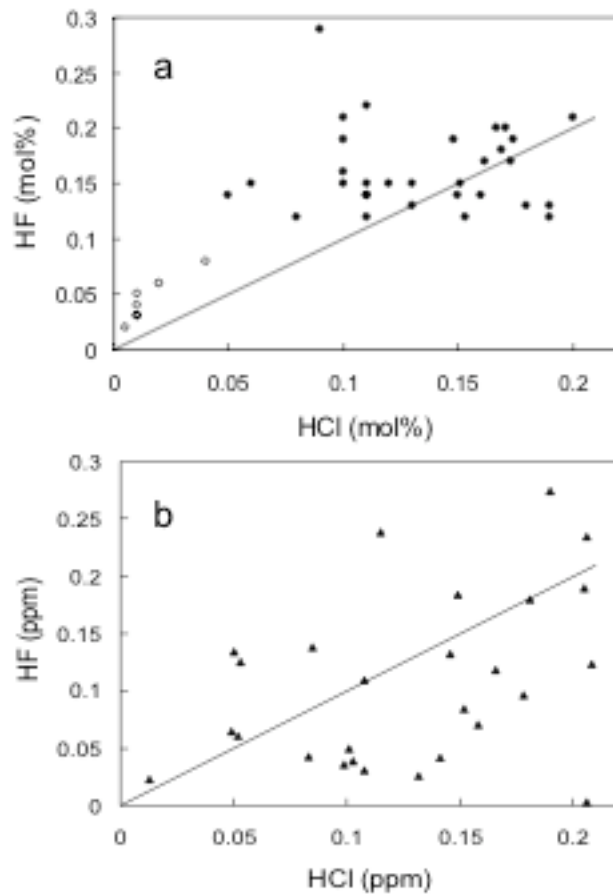


Figure 6. Concentrations of HCl and HF (a) in high-temperature gas samples of the Pu'u Ō'ō eruption, 1983 to 1985 and (b) in East Rift Zone gases from both degassing sources measured by FTIR spectroscopy on June 15, 2001. Solid lines represent an HF/HCl ratio of 1:1. Samples in (a) are the same as in Figs. 5c and 5d except for omission of an outlier at 0.55 mol % HF in Fig. 5d. As in Figs. 5c and 5d, open circles represent samples depleted in HCl and HF where condensate formation in the lead-in tube during sample collection is suspected.

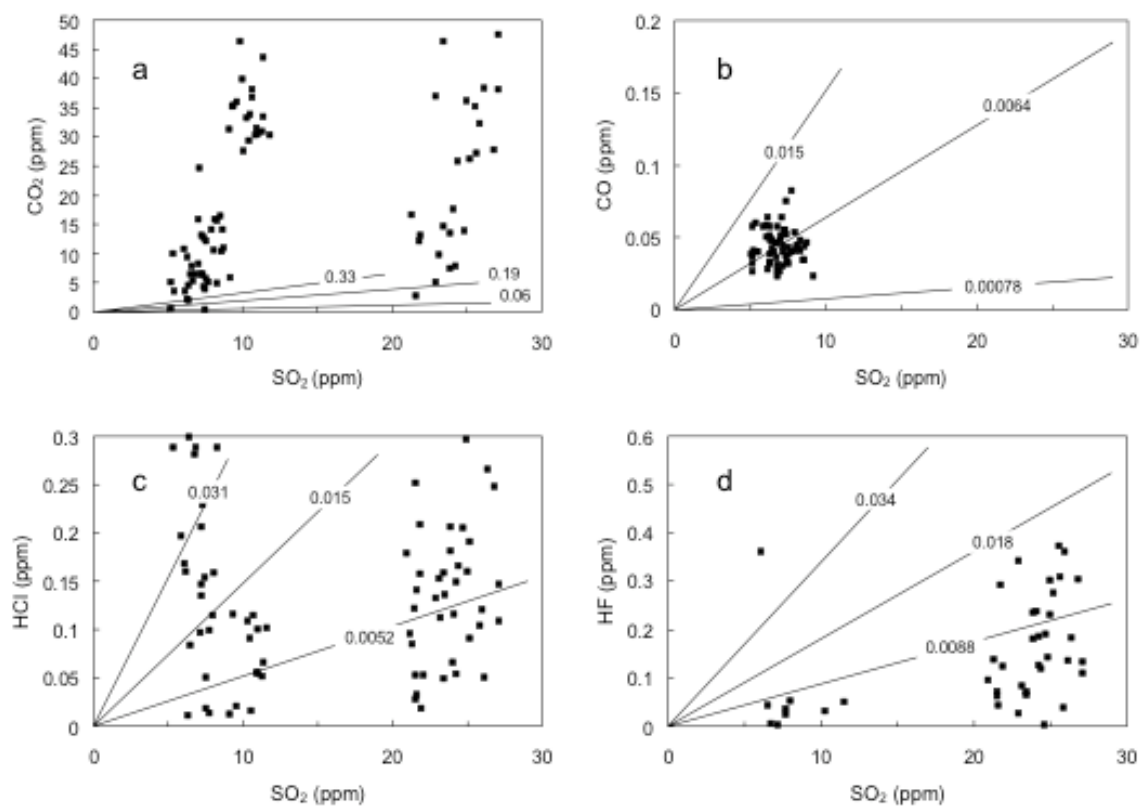


Figure 7. Concentrations of CO₂, CO, HCl, and HF versus SO₂ derived from FTIR measurements. Maximum, minimum and mean lines for X_i/SO_2 for the published analyses shown earlier in Fig. 5 are plotted again for comparison. Samples with SO₂ concentrations >20 ppm are from the PITER plume; those with lower concentrations are from the HORNITO plume. Negative CO₂ values produced after subtracting ambient CO₂ from total CO₂ are not shown in 7a.

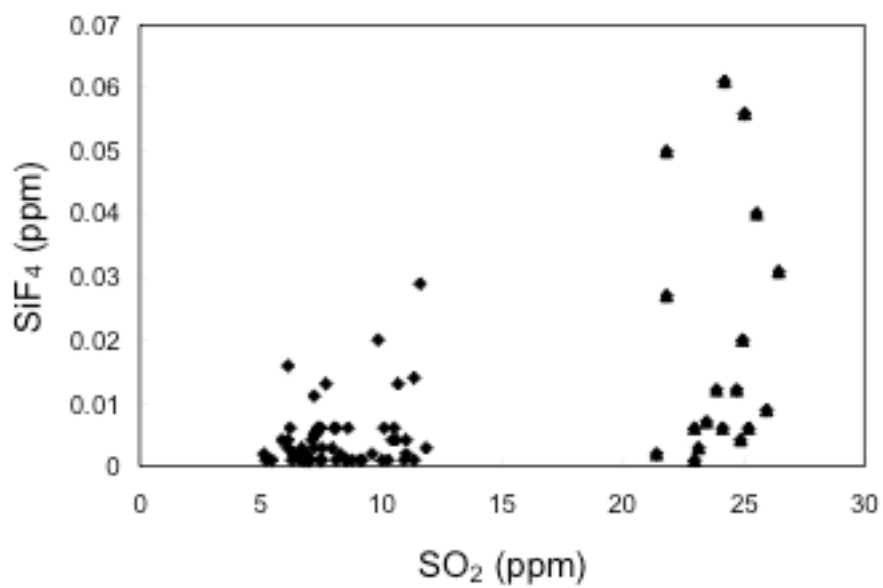


Figure 8. Graph of SiF₄ versus SO₂ concentrations derived from open-path FTIR measurements. As in Fig. 7, samples with SO₂ concentrations >20 ppm are from the PITER plume; those with lower concentrations are from the HORNITO plume.