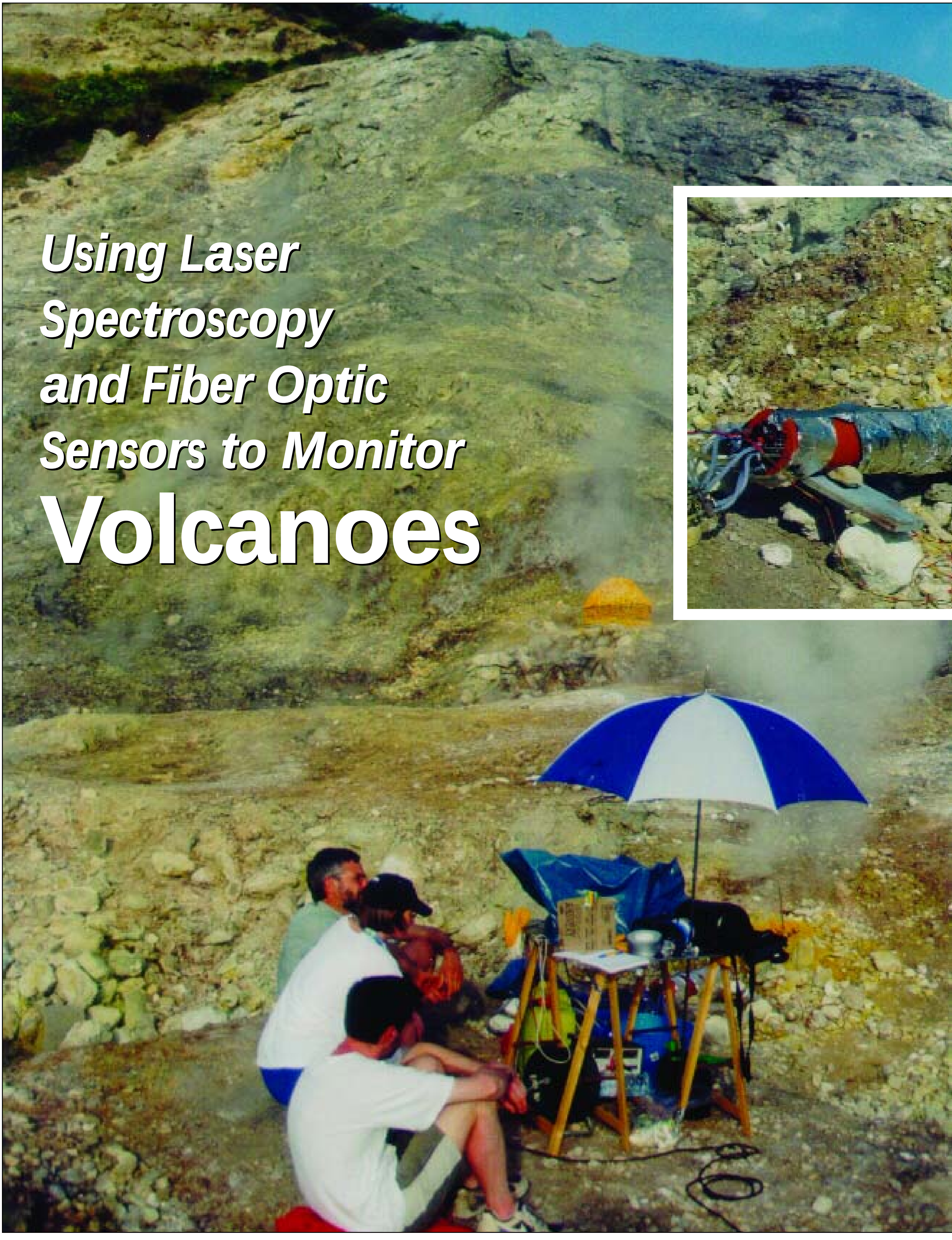
Using Laser Spectroscopy and Fiber Optic Sensors to Monitor Volcanoes



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Geochemical reactions and seismic activity lead to changes in the temperature and composition of the gases emitted by volcanoes. The authors describe the use of laser spectroscopy for online, in situ concentration monitoring of volcanic gases. They also discuss the potential of a new fiber optic laser sensor that can help scientists improve their understanding of the mechanisms underlying volcanic activity and may one day serve as the basis for a new type of eruption warning system.

Measurements at the Solfatara volcano in southern Italy. The inset shows the tube—in which the optics and electronics are integrated—in the vicinity of a volcanic fumarole.

Throughout history, people who live in the vicinity of volcanoes have been threatened—as well as fascinated—by sudden, violent eruptions. Considered in ancient times to be the dwelling places of powerful gods, volcanoes have been central over the course of the centuries to many legends and myths. In Greek and Roman times, some believed that Etna—the highest and most active volcano in Europe—was the workshop of Vulcan, the son of Zeus, a blacksmith who forged the weapons used by the gods. Others were convinced it was the home of the giant one-eyed monster, Cyclops, or of Typhon, a monster with 100 dragon heads. Homer placed the cave of Polyphemus, who captured Odysseus and his comrades, on Etna's slopes.

Our fascination with volcanoes persists to this day: because we cannot alter or control the forces of nature, the only way to minimize the damage caused by volcanic events is to evacuate the affected areas in time and for a sufficiently long period. A better understanding of the mechanisms that lead to eruptions, as well as the identification of reliable precursors to volcanic activity, are a necessary foundation of preventive measures. Alongside the traditional tool of seismic monitoring, geochemistry has recently attracted increasing interest among volcanologists because the concentrations of specific gases—e.g., H_2O, CO_2, CO, SO_2, H_2S and CH_4—their temperature and even their isotopic ratios are indicators of magmatic movements, connections between magmatic chambers and changes in deep layers of the earth. The study of volcanic gases can alert us to volcanic activities before eruptions take place and enable a new type of warning system. Permanent monitoring of the composition of the gases, by use of chemical or spectroscopic methods, is essential to this end.

Samples of gas or of the condensate of emitted vapors are needed for chemical analysis. To prevent reactions of the compounds after sampling, the volcanic gas is conducted into a washing flask where the acid compounds are precipitated in an alkaline solution. These compounds are later determined by their cations; inert gases, collected above the solution, are measured directly. Although chemical analysis does provide accurate data, it is not suited to constant monitoring because of the need to take and handle samples. The measurements made by means of chemical sampling are, however, very valuable as a reference point for other methods with superior temporal resolution. The aggressive chemical environment in proximity to volcanoes and the high temperature of the gases to be measured demand robust, inert systems: semiconductor sensors, for example, which are often used in industry and for process control, are not suitable for the long-term measurements entailed by this type of application because their surfaces can be poisoned by the volcanic gases. In this context, optical methods such as spectroscopy, and in particular laser spectroscopy, offer great potential for nonintrusive, in situ gas analysis and long-term monitoring applications.

The pros and cons

For measurements in the vicinity of volcanic fumaroles (the holes in or near a volcano from which fumes arise), the choice of suitable materials is extremely important. Since metals corrode very quickly, ceramics or polymers—capable of withstanding high temperatures—are the materials of choice. A significant challenge in taking accurate spectroscopic measurements is the high content of water vapor in volcanic gases, which gives rise to the scattering of light beams. In addition, the position of the laser beam can change because of fluctuations of gas temperature. In practice, two methods are used: measurement of the gases is conducted in the plume of the volcanic emission at high elevation, or spectroscopic analysis is performed in absorption cells or with gas chromatography after (automatic) gas sampling.

An advantage of taking measurements in high altitudes, for example with differential optical absorption spectroscopy (DOAS)[1] or Fourier transform infrared spectroscopy (FTIR),[2] is that the system can be placed at a secure distance from the volcano and its gases so that corrosion is not a problem. A major drawback is the fact that gas concentrations are measured after contact with the surrounding atmosphere, which allows chemical reactions to take place and

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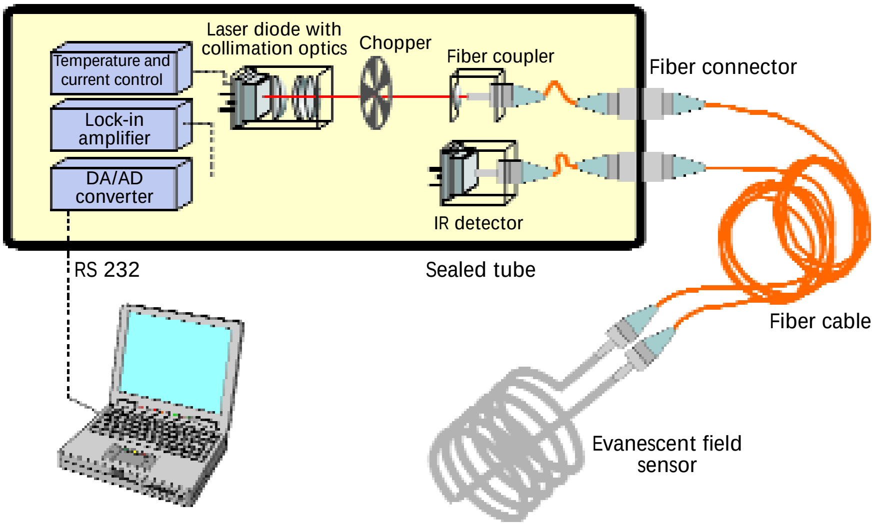

Figure 1(a). Set-up of the evanescent field sensor. The optics and electronics are in a sealed box.

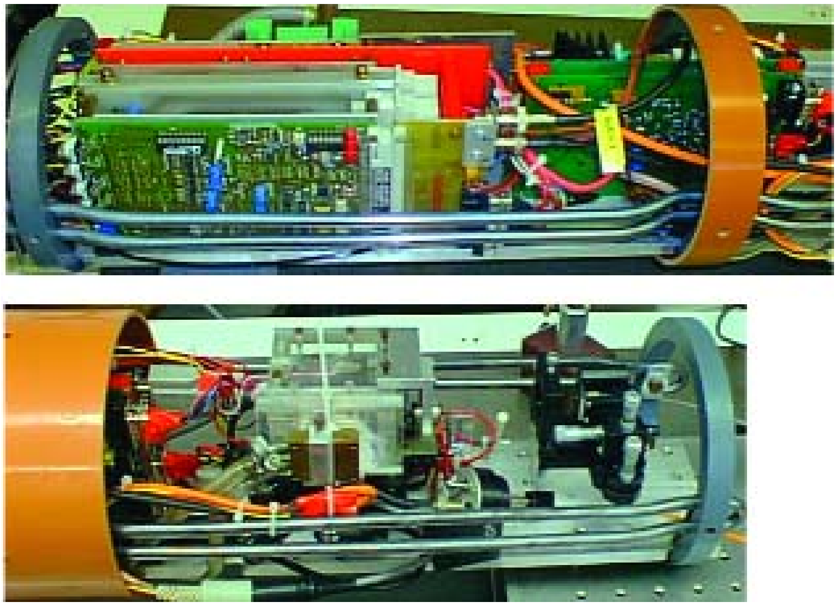

Figure 1(b). Photograph of the tube in which the optics and electronics are located.

makes it difficult to make correlations between the measured data and the mechanisms that lead to volcanic events. In addition, meteorological forces, such as changes in air pressure or wind velocity, can exert a significant influence on measured data. Since some spectroscopic methods use the sun as the light source,[1] they can only be applied during daytime.

Yet although correlation with magmatic mechanisms is complicated, the measurement of the chemical composition of the plume is important in evaluating the impact of the volcano on the environment and the atmosphere. Since huge amounts of gases emitted by volcanoes rise to high altitudes, their influence on the atmosphere is of global importance. Sometimes the gases are also an immediate hazard to people and animals in the vicinity; this is particularly true in the case of carbon dioxide.

To gain as much insight as possible into the processes that lead to a change in gas composition, it is desirable to take measurements as close as possible to—or better yet, directly in—the gas streams emitted by volcanoes. For this reason, conventional spectroscopic methods and gas chromatography are applied to samples taken from the fumaroles. The disadvantages of conventional spectroscopy and gas chromatography are that gas concentrations are measured in some cases after: contact with the surrounding air; cooling; and/or drying of the gas. All these factors can result in chemical reactions and in a change of the composition to be measured, either of which make it difficult to correlate measured gas concentration with volcanic activity.

The time resolution of measurements is also restricted to the speed at which samples can be taken. As reported by Zimmer and co-workers, the automated collection of gas samples from a fumarolic gas flow recently enabled analysis by means of gas chromatography of measurements taken with a time resolution of 35 minutes.[3] Continuous gas measurements with this level of temporal resolution performed at different volcanic systems have shown that the concentrations and temperatures of volcanic gases change rapidly and, for some systems, periodically.[3, 4] This underlines the need for methods of measurement that can supply concentration data with high temporal resolution to allow for better understanding of the processes that lead to changes in gas composition and temperature. Since meteorological changes also influence gas flow, to allow for correlation with either meteorological or volcanic parameters, it is essential to measure them simultaneously.

Use of direct laser absorption spectroscopy[5] inside volcanic fumaroles is difficult because of the high amount of water vapor in the fumes, which leads to scattering of the laser light, and because the gas in a fumarole is accessible from one side only. A spectroscopic sensor placed directly inside the fumarole is preferable, although accessibility, high temperatures and the presence of chemically aggressive substances are all problems in this case. Together, these factors make it essential to exercise great care in the choice of materials for long-term measurements. Corrosion of the metallic parts occurs in particular at the point at which the vapor condenses.

To facilitate interaction between the light in the fiber and the surrounding medium, in the active sensor region the jacket and cladding are removed so that the bare fiber core is exposed to the gases to be analyzed.

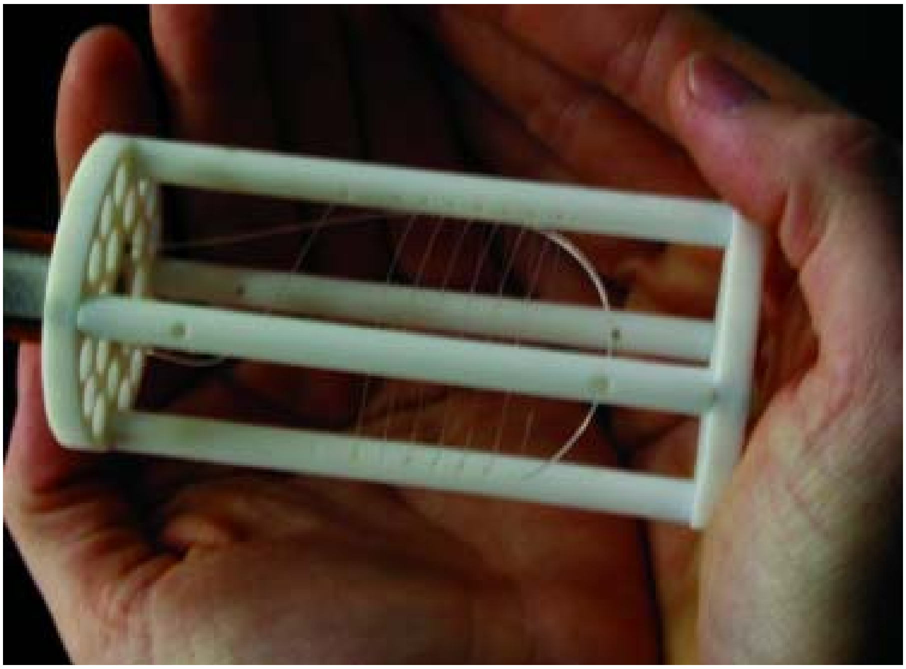

Figure 2. Photograph of the evanescent field sensor. The coiled geometry ensures that the two fibers end at one side of the sensor.

To get around these problems, we used evanescent field spectroscopy and a new sensor that can be used directly inside the gas flow of a fumarole. The method is based on the attenuation and frustration of total internal reflection, which means that the light is guided in the material because of total internal reflection but that there is also interaction with the surrounding medium at the places at which total internal reflection occurs.[6] Since multiple reflections are preferable, standard optical fibers are ideal. Using optical fiber, we built a sensor in a coiled geometry, with diameter d = 5 cm, which can be inserted into a volcanic fumarole because the input and output fibers are at the same side of the sensor. The light of a single-mode distributed feedback (DFB) laser diode ($\lambda \approx 1.57\ \mu\text{m}$) is coupled into the glass fiber.

In the fiber, light is guided to the active sensor region, which is made from the same fiber. To facilitate interaction between the light in the fiber and the surrounding medium, in the active sensor region the jacket and cladding are removed so that the bare fiber core is exposed to the gases to be analyzed. At the points within the fiber at which total internal reflection occurs, the electromagnetic field penetrates the surrounding space, building a so-called evanescent field; in time average and without any interaction, all the energy returns to the propagating wave within the fiber. The evanescent field results from the superposition at the boundary of the incoming wave and the reflected wave. If the laser wavelength is tuned to coincide with a molecular transition of the molecules surrounding the fiber, a fraction of the energy is absorbed and a decrease in intensity is measured at the end of the fiber. When the sensor is made with a long, small-diameter fiber, the number of reflections, and as a consequence the interaction length, are increased. Additionally, to maximize interaction with the surrounding medium, the field distribution within the fiber should not be concentrated in the center. This means that single-mode fibers are not suitable for this application. A trade-off between decreasing diameter and field distribution must therefore be made. We use multimode glass fibers with a diameter d = 200 μm. A photodiode is applied as a detector and a lock-in technique is used for noise reduction and amplification. All the electronics and optics are placed inside a sealed tube (see Fig. 1) to avoid contact with aggressive gases. Current and temperature control of the diode laser, both necessary for accurate wavelength setting, are carried out by means of a programmable chip, data analysis and storage with a laptop computer that communicates with the peripheral interface controller (PIC) via RS232 data interface. The entire system is supplied with a voltage U = 12V.

Figure 2 shows a photograph of an evanescent field sensor, its coiled geometry visible. The mount is made of polytetrafluoroethylene (PTFE), a material inert against most chemicals, stable at temperatures of up to 260 degrees C and suitable for measurements inside a fumarolic gas flow (if the emitted gas is cooler). For higher temperature fumaroles, ceramic mounts must be applied. Figure 3 shows the sensor inserted into a fumarole at the Solfatara volcano in Pozzuoli, Italy. The Solfatara belongs to the Phlegraean Fields, a conglomeration of volcanoes at the western border of Naples. This region, which has a diameter of 15-20 kilometers, is considered an active seismic zone. The Solfatara's crater, which contains several fumaroles, is elliptical in shape, with a semimajor axis of 770 meters and a semiminor axis of 580 meters. We took measurements at the Soffionissimo, a fumarole where the gas stream is emitted with a velocity of approximately 15 meters/second and a temperature of about 150 degrees C. The velocity, coupled with the high temperature of the fumes, prevents the adsorption of substances on the sensor surface,

Figure 3. Photograph of the evanescent field fiber sensor inserted into a volcanic fumarole. The titanium tube for simultaneous collection of gas samples and a temperature sensor can also be seen.

ensuring its sensitivity even during long-term measurements. The portion of the fiber in the region where condensation of vapor occurs because of the cooling of gases is protected with furcation tubing and is part of the guiding fiber, not of the sensor region. The water vapor content of this specific fumarole is approximately 90 percent. The major components of the dry gases are approximately: 98 percent CO_2 ; 1 percent H_2S; and 150 ppm CH_4 (Ref. 7). During a field campaign in May 2003, we operated the evanescent field laser sensor system inside the fumarole for several hours to demonstrate that the method can be used for time-resolved determination of concentrations over a long period of time.

Figure 4 shows spectra that were measured with the sensor inserted in the fumarole. The wavelength of the laser is tuned across an absorption line of CO_2 by applying a current ramp to the laser diode. A decrease in measured intensity is visible as the internal reflection is frustrated and attenuated. The wavelength region in which these effects occur (marked with arrows) is analyzed in search of information on changes in gas composition over time. As can be seen in Fig. 5, there are rapid fluctuation in the concentration of CO_2 as well as in the temperature—which was measured simultaneously—of the volcanic gases. The correlation emerges clearly in the part of Fig. 6 that shows measurements in the time interval 5,000-8,300 seconds: there is a positive correlation between CO_2 concentration and gas temperature. Because of the high CO_2 content of the surrounding air, it is difficult to acquire reference data to use as background for an absolute calibration of the measurements. For this reason, the absolute concentration values can only be estimated by comparison with data from measurements performed in the laboratory.

The chemical analysis of condensates sampled simultaneously to our spectroscopic measurements during the field campaign yielded a CO_2 concentration in the overall composition of $c_{CO_2} = 15.66$ percent (Ref. 8).

Our results show that an evanescent field laser sensor is valuable for tracing the concentration of specific volcanic gases in situ and in real time. Depending on the wavelength of the laser used, it is possible to probe different gases simultaneously. This is desirable because the ratio of concentrations, e.g. the ratio of CO_2 to CO, is linked to changes in temperature in deep layers of the earth[7] and can therefore yield information regarding magmatic movements. The use of networking fiber optics allows gas concentrations from more than one fumarole to be recorded by use of a single light source: this enables us to trace the connections between magmatic chambers through analysis of the different gas compositions and how they change over time.

Although the DFB laser diode is a suitable light source because of high spectral selectivity and ease of operation, it would be desirable to operate further in the mid-infrared, where, in the so-called “fingerprint region,” nearly all molecular species exhibit fundamental absorption lines with stronger line strength; operating in this region, one could increase the signal/noise ratio—and hence the detection limit—significantly. In this spectral region, sapphire would be an appropriate sensor material. A mid-infrared-region laser spectrometer based on difference frequency generation was set up in our group using two off-the-shelf laser diodes as pump and signal sources and an $AgGaS_2$ crystal, or periodically poled lithium niobate (PPLN), for nonlinear interaction. The system has proven its robustness during measurements at industrial glass furnaces. Depending on the diode lasers used, it operates in the 3-5 μm wavelength range.[9] In the future, we plan to apply this light source in field campaigns at volcano sites as well.

The work described here shows that evanescent field laser spectroscopy is useful for analyzing fumarolic gases directly within the gas stream and ensuring the measurement of the concentration of species of interest prior to chemical reactions with the surrounding atmosphere and cooling.

Long-term measurements are possible and the concentrations can be determined with a high temporal resolution of at least several minutes. This allows us to obtain data sets that can be used to gain a better understanding of the temporal behavior of volcanic mechanisms. One day it may provide us with a new method for forecasting volcanic eruptions.

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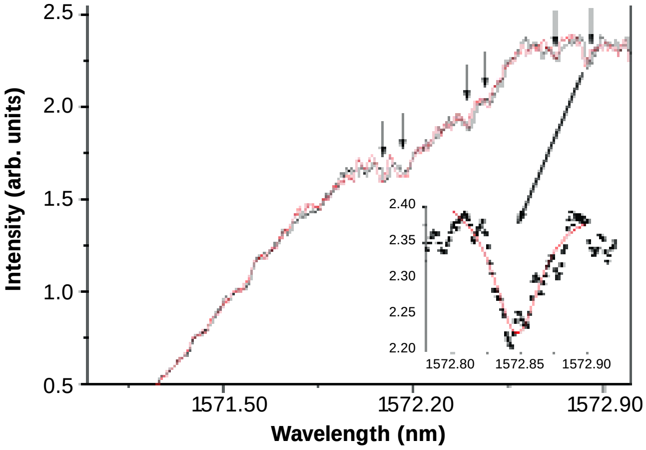

Figure 4. Intensity spectra measured with the evanescent field fiber sensor in the Soffionissimo fumarole. The positions of the single absorption lines of CO_2 are marked with arrows. The enlarged region is used for further analysis.

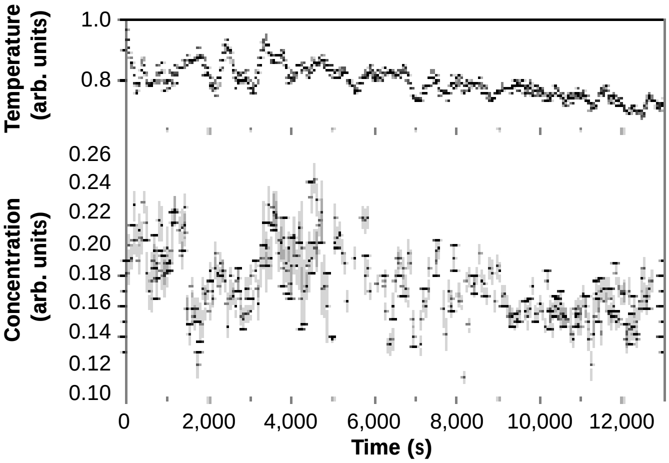

Figure 5. Evaluation of CO_2 concentration and gas temperature over time. The data were extracted from single spectra by integration of selected wavelength regions near molecular transitions of CO_2.

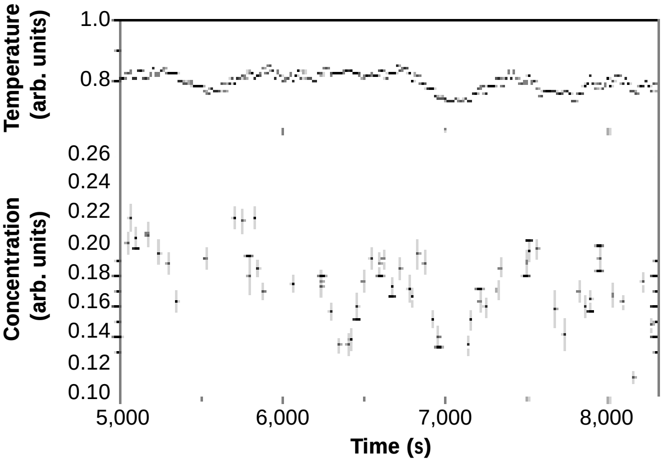

Figure 6. Enlargement of a section of Fig. 5. A positive correlation between temperature and concentration can be seen.