Laser Absorption Spectroscopy for Volcano Monitoring

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Recent advances in infrared laser spectroscopy may enable scientists to make accurate, in situ, real-time measurements of the isotopic composition of gas species emitted from volcanoes—an important indicator of volcanic activity.
On a typical day, at least 20 of Earth’s volcanoes will be erupting as you read this article. Some of these eruptions will have been sustained for years, decades or even centuries. For example, Stromboli Island—also known as the “lighthouse of the Mediterranean”—appears to have been illuminating the night sky with its pyrotechnics at least as far back as the Greco-Roman era.

Others may include previously dormant volcanoes that have recently reawakened, threatening local populations with falling ash, acid gas clouds and incandescent lava flows. In fact, in the last 10,000 years, some 1,500 volcanoes are known or suspected to have erupted, and could be potentially active. Monitoring all these volcanoes presents considerable logistical and technical challenges, largely because of the violent nature of volcanic activity.

Constant surveillance is essential to forecasting eruptions. A long dormant volcano can reignite in a matter of weeks, culminating in widespread destruction of land, property and livelihoods. At least 500 million people live within potential exposure range of a historically active volcano. Indeed, many volcanic regions are densely populated, and several are close to major cities (Naples, Mexico City, Seattle and Tokyo among them). Moreover, large eruptions can change global climate due to the influence of very fine particles released into the atmosphere.

Improved forecasting of the behavior of volcanoes mitigates the risks of eruptions. Optical methods have supported volcanology for decades, notably through the application of ground-based ultraviolet spectroscopy for measuring sulfur dioxide emissions, and more recently through the use of infrared spectroscopy to record a broader suite of volcanic gas species. These volatiles are emitted both during and between eruptions, and their composition can reveal much about the abundance, movements and explosivity of subterranean magma—vital information for the purposes of hazard assessment.

In addition to the molecular chemistry of these gases, their isotopic make-up also carries crucial clues to their origin, potentially distinguishing between an impending eruption and a harmless incursion of groundwater into hot rock. Until recently, optical methods have not yielded the sensitivity required to resolve the small differences in isotopic content that characterize volcanic gas emissions—at least not in the form of practical
Much research has been directed toward the development and application of methods to measure the chemistry and flux of volcanic gas emissions. The principal species released are water and carbon dioxide, which are combined with trace quantities of a wide range of sulfur and halogen species. While volcano surveillance efforts still largely focus on seismological and geodetic approaches, gas geochemistry is widely recognized as an important and highly desirable component of multidisciplinary monitoring, and increasingly sophisticated remote sensing techniques are becoming available to measure volcanic volatile emissions.

One of the key gas species to measure is carbon dioxide. Since it is one of the least soluble volatiles in magma, it tends to bubble out of magma early on in new episodes of volcanic unrest and percolate up to the surface where it can be measured. However, CO$_2$ is also abundant in the atmosphere and soils, and can be released by the heating of limestone in the Earth's crust. Hence, there are several potential origins of CO$_2$ in volcanic regions that can greatly complicate the interpretation of any changes in observed emissions.

Volcanic degassing

Many volcanoes discharge gases from vents called fumaroles, or by more diffuse emission through the soil. Fumarole emissions are very often composed of both magmatic and hydrothermal gases, the latter evolving through complex chemical and physical interactions between magmatic fluids, meteoric water, seawater and rock. The degassing of magma—the partition of magmatic volatiles from the melt into the gas phase and their subsequent separation—that is responsible for these effluents is one of the key processes that influences the timing and nature of volcanic eruptions.

Degassing exerts fundamental controls on magma overpressure, viscosity and density, and thereby on the chemical evolution, storage and transport (notably, the ascent rate) of magmas, and the style, magnitude and duration of eruptions. Without gas, there would be no explosive volcanic eruptions.
Measurements of CO₂ isotope ratios can discriminate among these different sources. Monitoring the isotopic composition of volcanic CO₂ emissions by tunable infrared laser spectroscopy could, in combination with other surveillance data, provide valuable early warning of eruptions.

**Stable isotope geochemistry**

Isotopomers are molecules that contain isotopes (forms of an element with the same atomic number but different mass). Isotopomers have different chemico-physical properties arising from their mass differences, and natural fractionations occur in the environment due to changes of state, biological activity and chemical reactions. For carbon dioxide, the two most abundant stable isotopomers are $\text{^{12}CO}_2$ and $\text{^{13}CO}_2$; the global average natural abundance for the former is 98.4204 percent and for the latter is 1.10574 percent.

The isotopic composition is expressed in terms of the so-called “delta value,” where $\delta$ is defined by:

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\delta = \left[ \frac{R_X}{R_S} - 1 \right] \times 1000.
$$

$R_X$ denotes the ratio of the heavier isotope to the lighter one in the sample to be measured, and $R_S$ refers to the isotopic ratio of a reference material. For the $^{13}C/^{12}C$ ratio, the international reference standard has been defined as the Pee Dee Belemnite (PDB), a carbonate formation whose accepted absolute ratio of $^{13}C/^{12}C$, $R_S$, is 0.0112372. Delta values are expressed in parts per thousand (often written “per mil” or ‰).

As an example, the average $\delta^{13}C$ for atmospheric CO₂ is roughly –8 ‰, which implies that the Earth’s atmospheric carbon dioxide is globally depleted in $^{13}C$ compared to the PDB standard. In general, natural fractionations between different geochemical reservoirs are only a few parts, or tens of parts, per million, placing severe requirements on the resolution and accuracy of isotope ratiometers.

Real-time monitoring of $\delta^{13}C$ in volcanic emissions of CO₂ could detect new episodes of magmatic unrest that may presage eruptions. Other fields in which carbon isotope monitoring offers important insights include atmospheric chemistry, ecology and biomedical diagnostics.

**Laser absorption spectroscopy for volcanic monitoring**

Traditionally, field sampling and post-sample analysis using laboratory-based mass spectrometry has been the method of choice in gas geochemistry for both chemical and isotopic investigations. Isotope ratio mass spectrometry (IRMS) can reach impressive levels of precision and accuracy, provided that sample collection and treatment are performed carefully to avoid possible fractionation effects.

However, the geographical and temporal sampling resolution is inherently low. This is because scientists are limited in how much glassware they can take into the field (long hikes up volcanoes carrying glass vessels do not always end well), and they face competition for time on suitable laboratory instruments. IRMS instrumentation cannot be used in remote and harsh field environments.

Optical methods, especially remote sensing techniques, overcome such limitations: Both ultraviolet and infrared spectroscopy have been widely used in volcanology. Nevertheless, conventional, field-portable instruments cannot deliver the spectral selectivity and sensitivity required for isotopic measurements.

Laser absorption spectroscopy offers several excellent spectroscopic advantages. The use of a continuously tunable infrared laser source allows the development of compact, rugged and autonomous analyzers that can provide real-time data. Optimum instrument versatility with good sensitivity can be achieved in the mid-infrared between about 3 and 25 μm, where most
Poás volcano, Costa Rica, famous for its hyperacid crater lake and strong gas emission.
molecules exhibit intense, fundamental rotational-vibrational transition bands. But also attractive is the near-infrared region, where weaker overtone and combination bands can be reached with inexpensive diode lasers.

Within the mid-infrared, the most suitable choices are continuously tunable laser sources based on infrared semiconductor diode lasers, nonlinear optical mixing (e.g., difference frequency generation) and quantum cascade lasers (QCL). QCLs have several advantages: compact size and robustness, thermoelectrically cooled operation, good optical power (several mW to tens of mW) and excellent spectral purity. QCLs provide wavelength coverage spanning two key atmospheric windows (at 3-5 and 8-12 μm), where spectral interference effects from water vapor and other atmospheric trace gases are limited.

These merits, along with the ability to tune the wavelength over a range of around 10 cm⁻¹ by varying both the injection current and the laser temperature, make QCL-based spectrometers promising for volcanic gas monitoring. The Rice University Laser Science group developed a field-deployable QCL-based instrument for carbon isotope analysis, which is pictured in the photo and schematic on page 27.

Because of isotopic mass differences, each isotopomer exhibits unique spectral features, allowing discrimination among them with a single-frequency laser source. Thus, isotope ratios in a sample can be quantified by analyzing their absorption spectrum. As an example, the ν₃ rotation-vibration absorption bands (corresponding to the fundamental asymmetric stretch vibration mode) of ¹²CO₂ and ¹³CO₂ is shown in the figure above.

Two rotation-vibration spectra coincide between 2280 and 2320 cm⁻¹ (4.386 to 4.310 μm). This overlapping spectral region is ideal for monitoring δ¹³C in CO₂ (i.e., the relative amounts of ¹²CO₂ and ¹³CO₂). Individual absorption lines to be used for the quantification of these two isotopes must be carefully chosen, because the lines selected for comparison have an important bearing on the accuracy of isotopic ratio measurements. Key factors to be considered include:

**Optimum line absorption intensities of the two CO₂ isotopes.** Similar intensities are ideal so that the same gas absorption cell can be used (i.e., with the same effective optical path length) for limiting potential nonlinearities in the detection system. A single detector for the sensor system would be optimum. The line intensities need to be sufficiently large for optimal signal-to-noise ratios and to allow the use of a compact CO₂ absorption cell.

**Temperature stability of the sample being probed.** If spectral lines are not selected properly, a temperature variation would lead to inaccuracies due to the Boltzmann distribution of the ¹²CO₂ and ¹³CO₂ transitions. Hence, in terms of spectroscopic parameters, the lower energy levels must be almost identical in order to achieve temperature insensitivity.

**Potential spectral and collisional interferences by other species.** It is particularly important to consider the effect of water vapor, which is typically the most abundant gas released by volcanoes, and which is in any case prevalent in the ambient atmosphere.

**Isolated lines.** These are preferred to facilitate retrieval of the abundances of the isotopic species.

**Other parameters.** Additional parameters may be dictated by the spectroscopic source. For example, the two selected absorption lines must lie within the available tuning range of the laser, and the source linewidth should be less than the absorption widths of the selected isotopic line pair.

Once the lines are selected, the optimum performance conditions for the mid-infrared spectroscopic source are determined in order to ensure that its emission wavelength will match the optimum absorption line selection.

Given the importance of stable and known temperature and pressure during measurement, the sample (and, alternately, typically, hot volcanic gases contain steam, potentially leading to water vapor interference and condensation in the absorption cell.
The spectrum shows isotopic lines that were obtained with a QCL-based two channel spectrometer [D. Weidmann et al., Appl. Phys. B80, 225]. The sample was a 5 percent mixture of CO\textsubscript{2} in N\textsubscript{2}. The concentration of the CO\textsubscript{2} isotopomers can be retrieved by integrating the area encompassed by the spectral lines. The isotopic line selection that is insensitive to temperature variation is indicated in red.

Challenges and future prospects

Once 0.1‰ precision measurements of the $^{13}\text{CO}_2$ delta value can be routinely obtained in adverse field conditions, the effective sampling efficiency should be assessed to ensure that no bias is introduced when sampling volcanic emissions. Contamination by ambient air must be limited and modeled. During the sampling process, fractionation can occur as the temperature drops and water condenses, especially where a cold trap is used to remove water. In addition, chemical reactions

A fumarole at Solfatara (close to the town of Pozzuoli, north of Naples) being sampled. The white fumes indicate condensation of steam.

Reference

Isotopic ratio measurements of volcanic \( \text{CO}_2 \) emission are less demanding in terms of accuracy than the identification of atmospheric carbon sources and sinks.

with the sampling materials or adsorption may influence the isotope ratio measurements.

One of the most daunting challenges for the future is how to develop robust, compact, autonomous and affordable mid-infrared \( \text{CO}_2 \) sensors that can withstand the highly corrosive environment of an active volcano. Materials such as titanium, ceramics, glass or polymers can be used for the exposed parts of the spectrometer. Ideally, an operational system should require limited maintenance, and be able to transmit data to a remote observatory by telemetry. This introduces additional constraints in terms of the electrical power source.

Carbon isotopes are not the only interesting target for volcanic gas geochemistry. Other stable isotopes of H, O, N, S and Cl are of interest and can provide complementary information about a volcano’s plumbing system. Molecular proportions of \( \text{H}_2\text{S}, \text{SO}_2, \text{HCl}, \text{CH}_4, \text{CO}, \text{CO}_2, \text{OCS} \) and HF, among others, are also very useful indicators of volcanic and magmatic behavior. Wavelength multiplexing, using a set of well-defined spectral windows, or widely tunable spectroscopic sources, would allow continuous multi-species monitoring. Further optical and electronic integration will dramatically decrease the isotope ratiometer size and power consumption, and reduce the maintenance requirements.

Current research and development of laser absorption spectroscopy to isotope ratio measurements promises to open up a new era of gas geochemistry, with many significant applications, notably in the field of volcanic hazard assessment. These techniques will provide real-time and accurate isotopic data, obtained in situ without sample preparation. This is an enormous leap forward compared with conventional laboratory mass spectrometry. Further advances in optical technologies should ultimately lead to precision and accuracy levels comparable to those obtained by isotopic ratio mass spectrometry.

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### References and Resources

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