



Mount Etna, Italy, emitting gases from its summit craters, and ash from the Laghetto cone, formed in 2001.

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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.



Yasur volcano, Vanuatu, in eruption. This kind of eruption is termed “strombolian” and is characterized by brief but powerful explosions as bubbles of gas burst at the surface of a lava pond.

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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



Mt. Etna, Europe's largest volcano, with the Sicilian city of Catania in the foreground.

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instruments capable of field deployment. Now, a new kind of laser-based gas sensor is set to change this and revolutionize isotope geochemistry.

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.

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, CO₂ 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 CO₂ in volcanic regions that can greatly complicate the interpretation of any changes in observed emissions.

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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 ¹²CO₂ and ¹³CO₂; 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 δ is defined by:

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

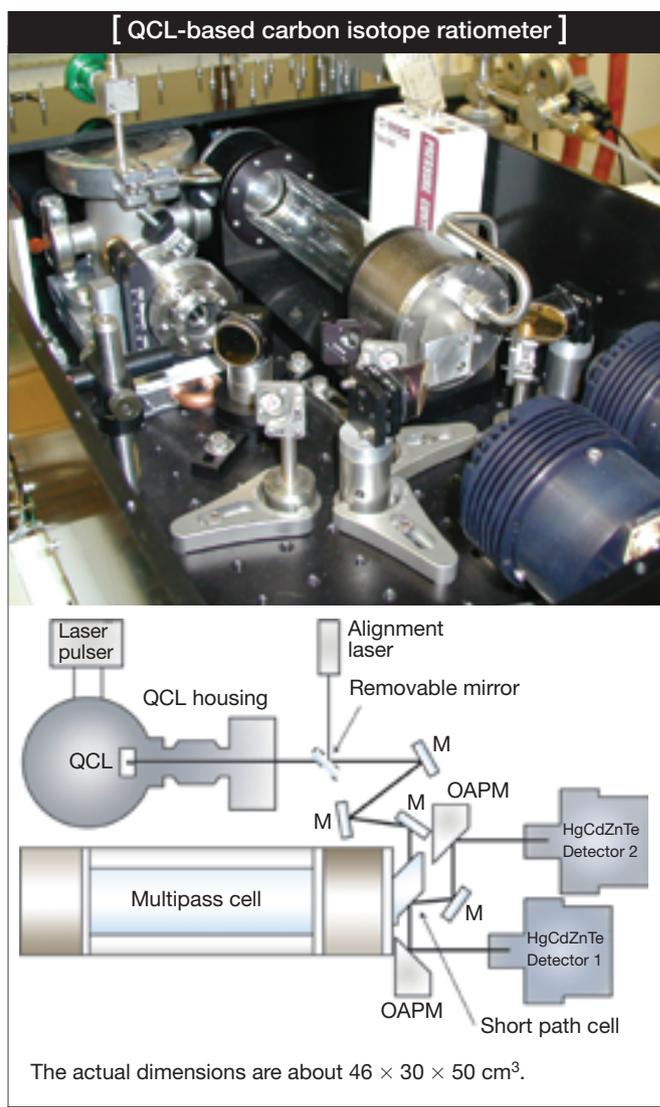
R_X denotes the ratio of the heavier isotope to the lighter one in the sample to be measured, and *R_S* refers to the isotopic ratio of a reference material. For the ¹³C/¹²C ratio, the international reference standard has been defined as the Pee Dee Belemnite (PDB), a carbonate formation whose accepted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

As an example, the average δ¹³C for atmospheric CO₂ is roughly −8 ‰, which implies that the Earth’s atmospheric carbon dioxide is globally depleted in ¹³C 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 δ¹³C 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.

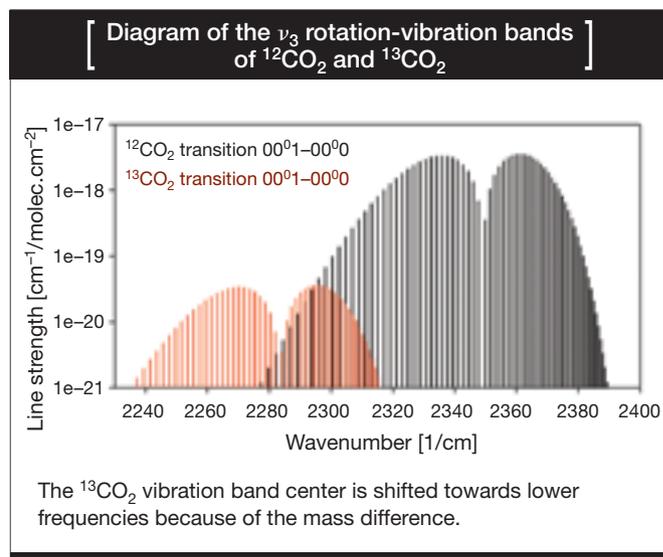
Within the mid-infrared, the most suitable choices are continuously tunable laser sources based on infrared semiconductor diode lasers, nonlinear optical mixing (e.g., difference frequency generation) and quantum cascade lasers (QCL). QCLs have several advantages: compact size and robustness, thermoelectrically 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 ν_3 rotation-vibration absorption bands (corresponding to the fundamental asymmetric stretch vibration mode) of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ is shown in the figure above.

Two rotation-vibration spectra coincide between 2280 and 2320 cm^{-1} (4.386 to $4.310\text{ }\mu\text{m}$). This overlapping spectral region is ideal for monitoring $\delta^{13}\text{C}$ in CO_2 (i.e., the relative amounts of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$). 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 CO_2 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 CO_2 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 $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ 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.

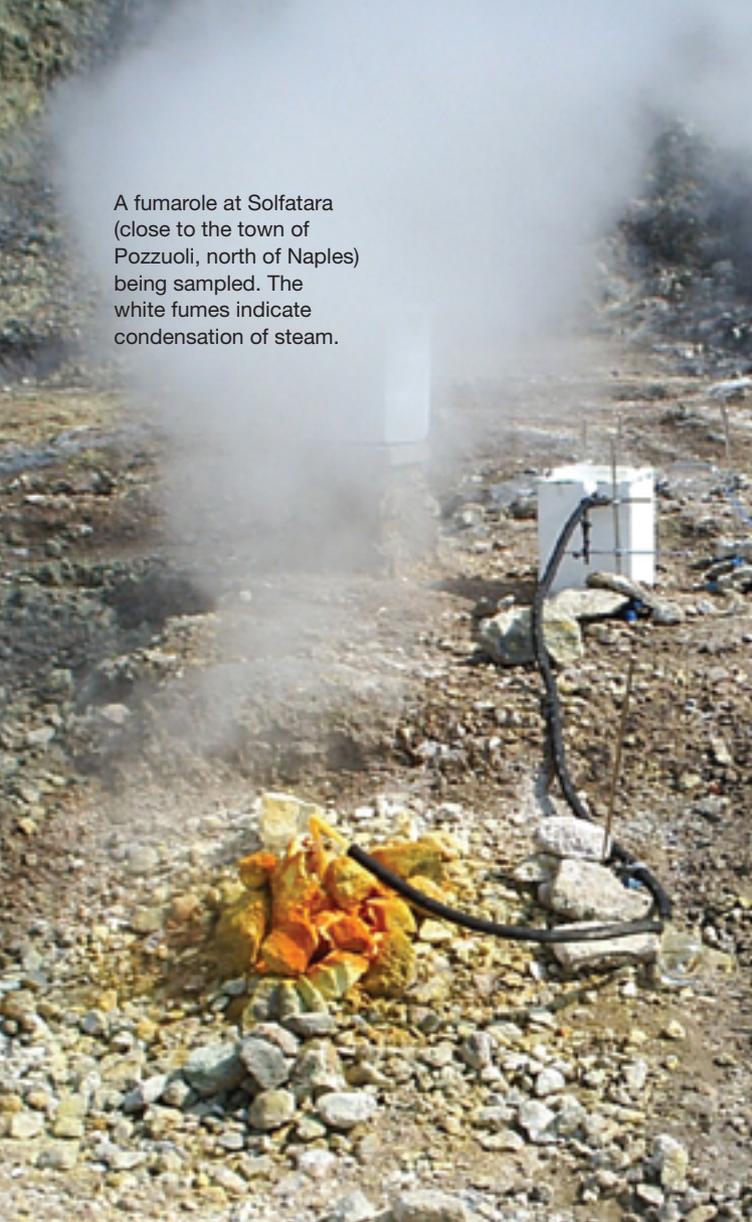
Other parameters. Additional parameters may be dictated by the spectroscopic source. For example, the two selected absorption lines must lie within the available tuning range of the laser, and the source linewidth should be less than the absorption widths of the selected isotopic line pair.

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.

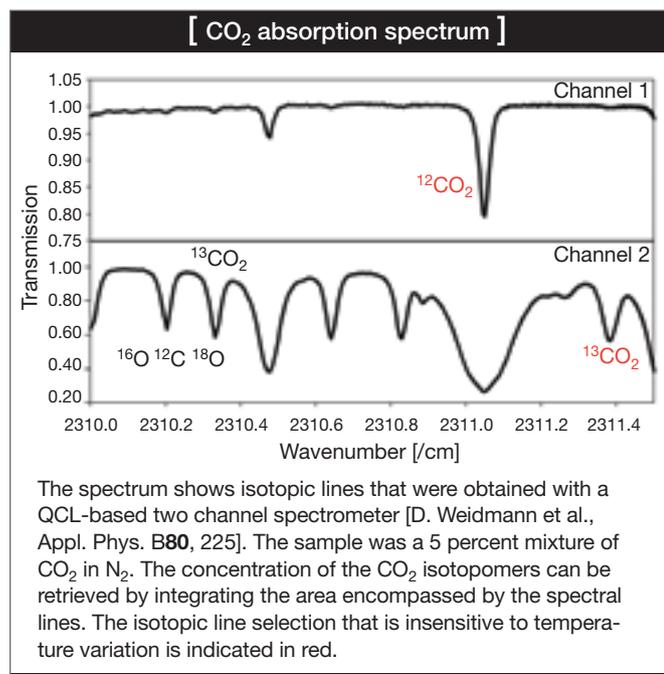
Given the importance of stable and known temperature and pressure during measurement, the sample (and, alternately,

Typically, hot volcanic gases contain steam, potentially leading to water vapor interference and condensation in the absorption cell.

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



A. Castrillo et al. *Opt. Express* **12**, 6515-23.



reference) must be drawn into a closed absorption cell within the instrument. The volcanic gas must be drawn into such a cell using a pump. Contamination with ambient air should be limited since such mixing would modify the CO₂ isotopic ratio measurements. This can be achieved by inserting the sampling tube deep into the volcanic vent or by placing a funnel over the vent in order to generate a small overpressure of the emitted gas.

Nevertheless, atmospheric contamination is almost inevitable because mixing can occur below the ground. It is therefore important to characterize the $\delta^{13}\text{C}$ of ambient air so that mixing lines can be inferred between air and the volcanic gas.

Typically, hot volcanic gases contain steam, potentially leading to water vapor interference and condensation in the absorption cell. For this purpose, a gas dryer and cooler can be added to the sampling line. Allowing a continuous flow of gas through the instrument purges the system and permits frequent measurements of the isotopic composition of the volcanic sample.

The laser frequency is scanned over the isotopic transition of interest while the transmitted laser power is detected. The observed spectrum can be modeled according to known absorption line parameters, from which the concentration of each isotopic species can be retrieved, and hence their ratio determined.

Alternatively, the sample $\delta^{13}\text{C}$ can be measured against a calibrated isotopic mixture used as a reference in an additional optical channel. Frequency scans require several milliseconds. Around ten measurements can be achieved per second (including the time required for processing the spectra and retrieving the isotopic abundances).

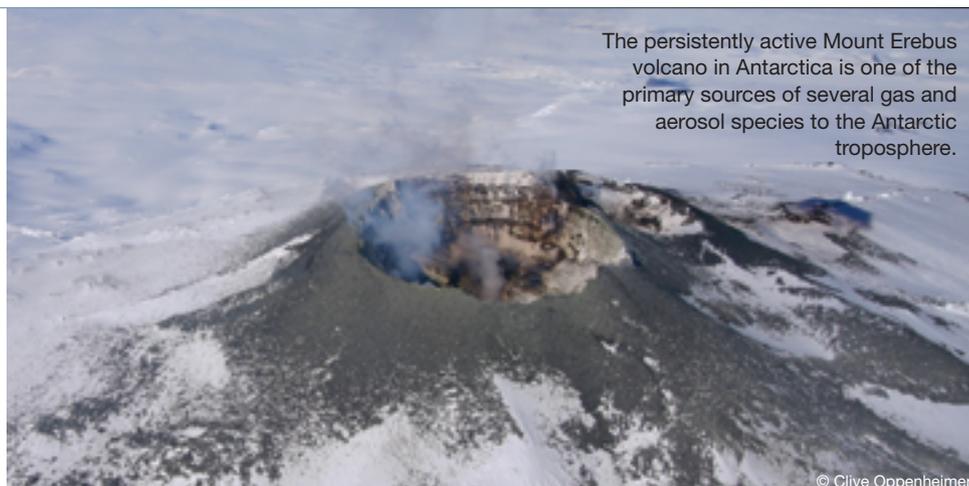
Isotopic ratio measurements of volcanic CO₂ emission do not require the same level of accuracy as needed for the identification of atmospheric carbon sources and sinks. Measurements using IRMS typically yield a 0.05‰ precision of the delta value. Optical techniques require a relative precision of isotopomer abundances in the 10⁻⁵ range to achieve levels of precision similar to IRMS.

To date, delta value precisions between 0.2 and 0.3‰ have been reported in the laboratory or in the field using cryogenic tunable, mid-infrared laser sources. However, the operation of such ratiometers has yet to be verified in the harsh environmental conditions encountered on a volcano. So far, the only field measurement of the $\delta^{13}\text{C}$ in volcanic CO₂ has been performed using a 2 μm diode laser system in the Solfatara crater near Naples, Italy, with precision and accuracy levels of about 0.5‰.

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

Isotopic ratio measurements of volcanic CO₂ emission are less demanding in terms of accuracy than the identification of atmospheric carbon sources and sinks.



The persistently active Mount Erebus volcano in Antarctica is one of the primary sources of several gas and aerosol species to the Antarctic troposphere.

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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 CO₂ 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 H₂S, SO₂, HCl, CH₄, CO, CO₂, 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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