

Volcanic Gas Emissions: New Insights from New Instruments

A team of scientists at the University of Cambridge and Alphasense Ltd in Braintree, England has developed highly portable, low-power, low-cost instruments for volcanic gas detection and measurement. These new electrochemical sensor based instruments, with demonstrated capacity to characterise in situ volcanic gas plumes, present a technological advance in volcanic gas emissions monitoring.

volcano observatory team¹, now in a state of high-alert, embarked on round-the-clock monitoring of the hazard situation using a combination of seismic, thermal and gas sensors.

Our planned field-testing of instruments for volcanic gas detection was thus particularly timely. Volcanoes release a cocktail of toxic gases and aerosol, at concentrations that can exceed several 100s of ppmv (parts per million) close to the vent. This mixture of gases, at very high concentrations, and accompanied by highly acidic volcanic aerosol, presents a challenge for field measurement scientists: how to build an instrument that can accurately measure the complex mixture of acid gases in a volcano plume, that can withstand harsh, acidic environments, and can be deployed in remote and often very difficult to access regions?

To meet this goal, an interdisciplinary, industry-academia collaboration was established between scientists, a gas sensor company Alphasense², and the Chemistry and Geography Departments of the University of Cambridge. The team built an instrument that houses a suite of 6 Alphasense sensors connected to a palmtop computer data logger, recording the sensor output each second. Air is drawn over the sensors by a miniature pump with a filter on the inlet preventing volcanic aerosol and ash from entering the instrument. A sturdy outer-casing protects the electronic components from acid damage, whilst the electrochemical sensors inside measure the concentrations of plume gases SO₂, H₂S, HCl, CO, H₂ and NO₂, all of which are detected simultaneously. The instrument is powered by a 12V battery pack and, being shoe-box sized, is highly portable, easily fitting into a backpack for a day-hike up a volcano.

Our first field-campaign in the plume of Mt. Etna in 2006 put the instrument's durability and measurement capabilities to the test. Equipped with gas masks, sturdy boots and hard hats, and with a couple of prototype instruments on our backs, we ascended the mountain; admittedly the first 2900m by cable-car but the remaining 400m on foot over Etna's rocky terrain.

After some minutes, we could see the actively-erupting vent, and not long afterwards we could smell it too; occasional whiffs of sulphurous gases with a hint of rotten-egg. This signalled it was time to strap on our gasmasks and power up the instruments. After a couple of false starts, in-field reading of the

instrument PDA-screen indicated it was functioning correctly, recording fluctuating concentration readings when in the plume, then returning to low, background values on encountering clean air. It was a promising start. We continued further into the nearby grounding plume where the high concentrations of ash and aerosol particles reduced visibility at times to a few tens of meters. Ahead, a group of volcanologists had gathered on Etna's flank, close to the active lava-flow.

The lava turned out to be surprisingly viscous, owing to its high silica content, thus oozed downhill rather slowly, building lava-levées either side as it cooled at the edges. Standing on the levée and clad in a heat-reflective suit, one of the volcanologists attempted to extract chunks of fresh, hot (near 1000°C) lava from the flow, for subsequent chemical analysis. By comparing the chemical composition of the lava matrix, the trapped volatiles (sulphur, chlorine, fluorine, and so on) within it, and the observed plume gas composition, we strive to form a better understanding of the subsurface processes and establish links between gas emissions and volcanic activity. It is the gases, after all, that drive eruptions and trigger high-pressure explosions.

Back at our hotel, after a long day in the field, followed by a long shower to remove the acidic layer of grime deposited on my skin, I found time to analyse the field data from our new gas sensing instrument. Both in-plume SO₂ and H₂S were detected at ppmv concentrations, and the 1 Hz data-logging of the rapidly fluctuating sensor output accurately recorded the plume heterogeneity. Thus a successful first in-plume testing of the instrument, and of me as a volcanologist.

The instrument has been deployed in subsequent field-campaigns worldwide, enabling studies of volcanic emissions from Kilauea (Hawaii), Erebus (Antarctica), Masaya (Nicaragua), Poas (Costa Rica), Aso (Japan) and Villarrica (Chile). These investigations repeated electrochemical measurements of volcanic SO₂ and H₂S but added several other volcanic gas species to the repertoire, including HCl, H₂ and CO. Pre- and post-fieldwork calibrations demonstrate good stability of the sensors, despite the harsh conditions, and a linear response to the target gases. Due to the nature of the plume as a 'cocktail of gases', sophisticated analysis methods needed to be developed to achieve gas specificity which accounted for interferences that cannot always be removed through gas-filters on the sensors themselves. This was achieved through use of multiple simultaneous sensor outputs to extract the interferences, combined with individual sensor laboratory testing of cross-sensitivities.



An additional complication is the wide range of humidity and temperatures encountered in the field. Water vapour is a major volcanic gas, and vent temperatures can reach more than 1000°C, but due to rapid near-vent plume dispersion, temperatures and humidities at the deployment sites: typically at the crater-rim, several m to 100's m from the vent - were dominated by local environmental conditions. Nevertheless, measurements at Mt. Erebus volcano, Antarctica, in particular, required calibrated corrections for the unusually low temperatures encountered (< -30°C), and the instrument was field-tested to an extreme.



The data analysis shows that each volcanic plume exhibits its own chemical signature. The chemical composition of emitted gases depends on the source magma and the subsurface processes of crystallisation and re-melting, influenced by the plate-tectonic setting and the local geology. In-plume chemistry also plays a role; high-temperature near-vent chemistry is believed to generate radicals that can initiate rapid formation of sulphate aerosol.

Low-temperature gas and aerosol chemistry in the downwind plume sustains rapid autocatalytic chemical cycles as the plume disperses into the background atmosphere. Indeed, recent research³ has demonstrated that volcanic plume chemistry destroys ozone, creating mini ozone holes as it disperses downwind. Thus, measurements that characterise volcanic gas composition not only contribute towards volcano monitoring as a hazard prediction tool, but can also be used to assess local and global impacts of volcanoes, such as downwind acid deposition and impacts on the atmosphere.

Instruments used for volcanic gas observations include remote sensing methods such as Differential Optical Absorption Spectroscopy, using scattered UV-sunlight as a source (DOAS) and Fourier Transform Infra-red (FTIR) spectroscopy, sometimes using lava as an IR source¹, as well as in situ gas and aerosol sampling via traditional bottle and filter-trap methods, followed by laboratory analysis. The application of electrochemical sensors to volcanology, capable of measuring gas concentrations in situ and in real time, is a relatively new development but it offers real advantages in terms of cost and sustained operation.



In developing our low-cost, low-power, high-durability instrument based on electrochemical sensors, we highlight the strong potential for electrochemical sensors to contribute to long-term volcano monitoring. The field-deployments demonstrated the capability of electrochemical sensors to endure the harsh, acidic environment of a volcano and to detect a range of gases in the plume-mixture, through newly developed

analysis methods. The next step is to build a network of such instruments designed for autonomous use, for deployment on an active volcano, to transmit data streams to a remote observatory (for instance via satellite communications). This would enable volcanologists to monitor in situ plume gas concentrations at different locations, in real-time. The wealth of data generated would expand our knowledge of how volcanoes work and what impacts they have on the atmosphere and environment. This approach will surely become the standard for volcano geochemical surveillance and is sure to inform hazard assessment and risk management in the future.

References

- 1 From the Istituto Nazionale di Geosifca e Vulcanologia: www.ct.ingv.it
- 2 <http://www.alphasense.com>
- 3 Modelling Reactive Halogen Formation and Ozone Depletion in Volcanic Plumes. T.J. Roberts et al., *Chemical Geology*, 2009

Tjarda Roberts obtained her PhD at the University of Cambridge in 2009 in the measurement and modelling volcanic plume chemistry. Working at the interface between Atmospheric Sciences, Geography and Geology, she has developed new instruments and numerical model methods to characterise volcanic emissions and explore the impacts of volcanic plumes on atmospheric chemistry. She is now a Research Associate at the Norwegian Polar Institute where she combines her volcano-interests with research into pollution in the Arctic.

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CoGDDEM
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