Development of a Mass Spectrometer-based Instrument for Volcanic Gas Monitoring

Gary M. McMurtry, SOEST, Univ. Hawaii
David R. Hilton, Univ. California, San Diego
Tobias Fischer, Univ. New Mexico
A. Jeffrey Sutton, HVO, USGS
Tamar Elias, HVO, USGS
Volcanic fumarole sampling
- the old fashioned way

Iwodake Volcano, Satsuma Iwojima, Japan
700° C fumarole (don’t fall in!)

People Die Doing this Stuff!

Galeras Volcano, Colombia
225° C fumarole (hard to run away inside crater at 4000+ m!)
The 1992 eruption was preceded by drastic decreases in H$_2$O/CO$_2$, S/CO$_2$ and HCl/CO$_2$, interpreted to result from gas pressure accumulation in the volcanic edifice that also resulted in decrease of SO$_2$ flux.

However, the January 1993 eruption (with many lives lost) was not preceded by the same gas ratios decreases and, conversely, some ratio changes were not eruption precursors.

This example clearly illustrates the need for continuous measurements of gas chemistry to begin understanding the natural variations that occur in such dynamic volcanic systems.
Isotopes as Magmatic Cursors

$^{3}\text{He} / ^{4}\text{He}$ Systematics with Magmatic Activity

Change in $^{3}\text{He} / ^{4}\text{He}$ following magmatic activity at Oshima Volcano, Japan. Note the gradual decrease in $^{3}\text{He} / ^{4}\text{He}$ following the main active period. Arrows indicate earthquakes (from Sano et al., 1995)

Helium isotope variations at Umbria-Marche, Italy during the seismic swarms of 1997-1998. Arrow indicates beginning of swarm (Italiano et al., 2001)
Mass Spectrometer Pros & Cons

- **Pros**
  - Multi-molecular, quasi-simultaneous analysis possible
  - High sensitivity analysis (ppb to ppt)
  - Reasonably compact & robust MS now available
  - Promise of isotopic analysis
  - Applications are diverse and growing

- **Cons**
  - Usually a large lab instrument with high power consumption
  - Most MS require high vacuum (10^{-5} Torr or better = power)
  - What to do with waste gas in a pressure housing? (underwater applications)
  - High precision requires frequent calibration
  - Expensive, unless self-made
Volcano Mass Spectrometer Schematic

**Features:**
- Designed for corrosive gas resistance (volcanic gases)
- Capable of long-term deployments, using solar panel
- Capable of real-time data via wireless or cabled telemetry
- Capable of simultaneous multi-molecular monitoring of dissolved gases & volatile organic compounds
Prototype VMS System

Internal components of the QVMS prototype on its aluminum chassis

QVMS titanium housing with gas drying cartridge under PVC sun shield (black)

(Q = quadrupole MS)
System Software Development

We use a Rabbit-based microprocessor system with user-adjustable programming in C code.
Remote Communications

Schematic of Quasi-Real Time Gas Data Monitoring

Fumarole

Mass Spect.

Ethernet

Radio Transmitter

Radio Receiver

Cable or Satellite Link

Dedicated PC

Modem

+ Software to Display/Record
Data to Hard Drive + Back-up

Ethernet out, then radio or cell-phone comm. to base
Turrialba Summit

Four-wheel drive Recommended...
Inside Turrialba

Sub-boiling fumarole area

Humm, kinda steep…

Lighter than the batteries!
VMS Set-Up & Ground-Truth

Taking standard gas sample

Above: Rocket scientist, two professors and a Ph.D. student
Camouflage!

⇒ Embarrassing lack of appreciation for thermodynamics

⇒ System became isothermal with Volcano at 70° C!

Good news: only lost op amp!
Kilauea Volcano Test - March, 2006
Suphur Banks Fumaroles - “Jagger Vault”, 98° C

Volcanologist
Twin 12V deep-cycle batteries
Portable refrigeration unit
Dedicated “Reefer” battery
Condenser Trap (water)
Sample Spectra

QVMS mass/charge spectrums, with electron multiplier (EM) detection, for a typical sample from the time-series experiment at Sulphur Banks in March, 2006.

The major species peaks are truncated in the bottom, vertically expanded view.
Kilauea

time-series

Arrows indicate standard gas bottle sampling at the fumarole during deployment, recovery and two of the battery changes.

Yellow bars indicate periods of thermal and gas anomalies detected within this short time-series test.

- All show enrichments of SO$_2$ and He, and decreases in CO$_2$/He.
- Last, much hotter event displays increases in CO$_2$, N$_2$, O$_2$, Ar, and water vapor. It corresponds with dryer weather conditions.
Comparison with bottle sampling

Table 1. Comparisons of standard bottle gas sampling (SB-2, SB-4) with *in situ* quadrupole volcano mass spectrometer (QVMS) scans, Sulphur Banks, Kilauea Volcano, March 14-17, 2006.

<table>
<thead>
<tr>
<th>Bottle ID</th>
<th>Collection Date/Time</th>
<th>Location</th>
<th>SO$_2$/CO$_2$*</th>
<th>SO$_2$/Ar</th>
<th>CO$_2$/Ar</th>
<th>CO$_2$/He</th>
<th>He/Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB-2</td>
<td>3/15/06 1230 hrs</td>
<td>After condenser</td>
<td>0.02002</td>
<td>10.239</td>
<td>511.46</td>
<td>86,014</td>
<td>0.0059</td>
</tr>
<tr>
<td>QVMS</td>
<td>3/15/06 1230 hrs</td>
<td>---</td>
<td>0.00025</td>
<td>0.0060</td>
<td>24.0</td>
<td>3,000</td>
<td>0.0080</td>
</tr>
<tr>
<td>SB-4</td>
<td>3/16/06 0630 hrs</td>
<td>After condenser</td>
<td>0.02341</td>
<td>89.417</td>
<td>3,819.8</td>
<td>134,064</td>
<td>0.0285</td>
</tr>
<tr>
<td>SB-4</td>
<td>3/16/06 0630 hrs</td>
<td>Before condenser</td>
<td>0.03041</td>
<td>24.238</td>
<td>796.95</td>
<td>73,219</td>
<td>0.0109</td>
</tr>
<tr>
<td>QVMS</td>
<td>3/16/06 0630 hrs</td>
<td>---</td>
<td>0.00014</td>
<td>0.0034</td>
<td>24.3</td>
<td>8,090</td>
<td>0.0030</td>
</tr>
</tbody>
</table>

*Molar ratios. The QVMS ratios are of uncalibrated detector response in counts.*
Conclusions

• A prototype autonomous, mass spectrometer-based gas monitor has been built and field tested. First results at Sulphur Banks, Kilauea, show interesting anomalies beyond obvious artifacts, like interruptions for sampling and power.

• Despite forward planning and design, low-power management of copious water vapor (steam) in fumaroles remains a challenge.

• Comparison with standard gas sampling indicates substantial losses of reactive gases (SO₂, CO₂) and perhaps some He. Further lab testing is underway, but our present bias (working hypothesis) is most of these gases are lost inside the instrument, in unprotected metal areas, not in the two water traps.

• The remaining major issues to overcome are: low-power water management, and elimination or at least mitigation of reactive gas loss. Remote communications/solar power should not pose a challenge.

• Such instruments continue to hold promise to obtain the much needed monitoring of multi-species gas chemistry (and isotopes) on active volcanoes.