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

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Volcanic fumarole sampling - the old fashioned way

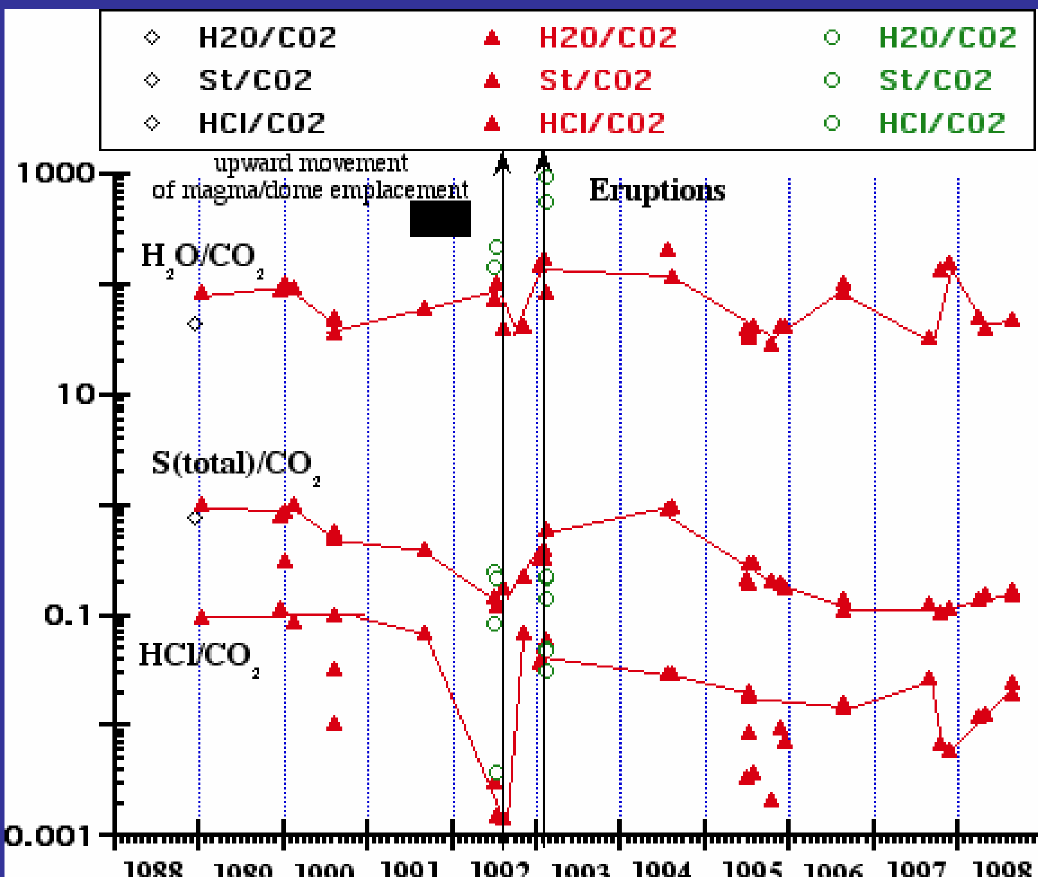
Iwodake Volcano, Satsuma Iwojima, Japan
700° C fumarole (don't fall in!)

People Die Doing this Stuff!

Galeras Volcano, Colombia
225° C fumarole (hard to run away inside crater at 4000+ m!)

General Goal of Eruption Prediction Using Gas Chemistry

1992-1993 Eruptions of Galeras Volcano, Colombia



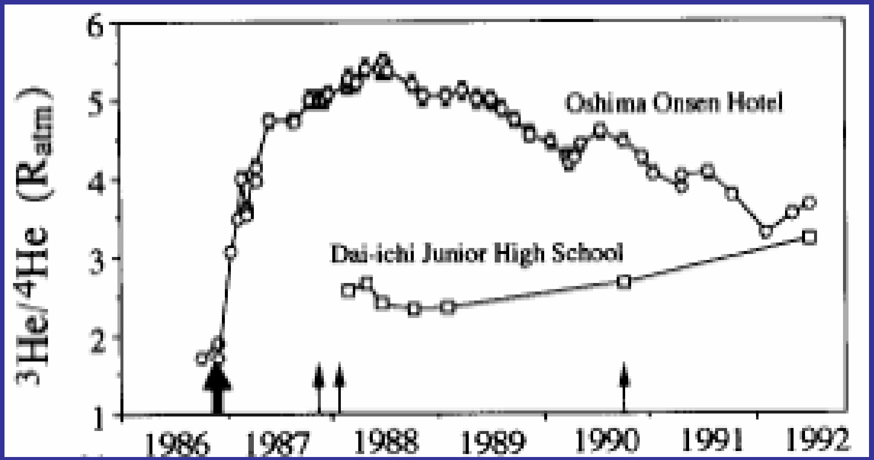
The 1992 eruption was preceded by drastic decreases in H_2O/CO_2, S/CO_2 and HCl/CO_2, interpreted to result from gas pressure accumulation in the volcanic edifice that also resulted in decrease of SO_2 flux.

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 pre-cursors.

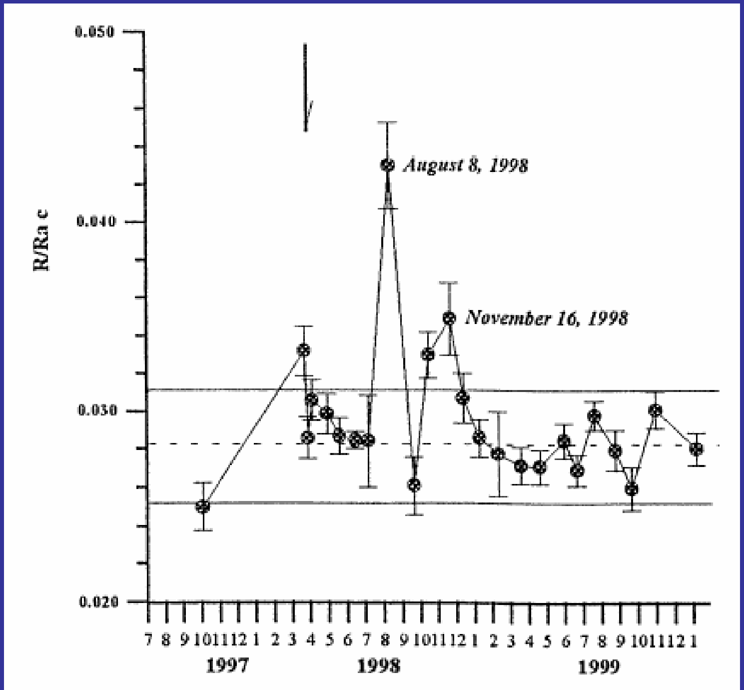
This example clearly illustrates the need for continuous measurements of gas chemistry to begin understanding the natural variations that occur in such dynamic volcanic systems.

Isotopes as Magmatic Cursors

$^3He/^4He$ Systematics with Magmatic Activity



Change in $^3He/^4He$ following magmatic activity at Oshima Volcano, Japan. Note the gradual decrease in $^3He/^4He$ 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

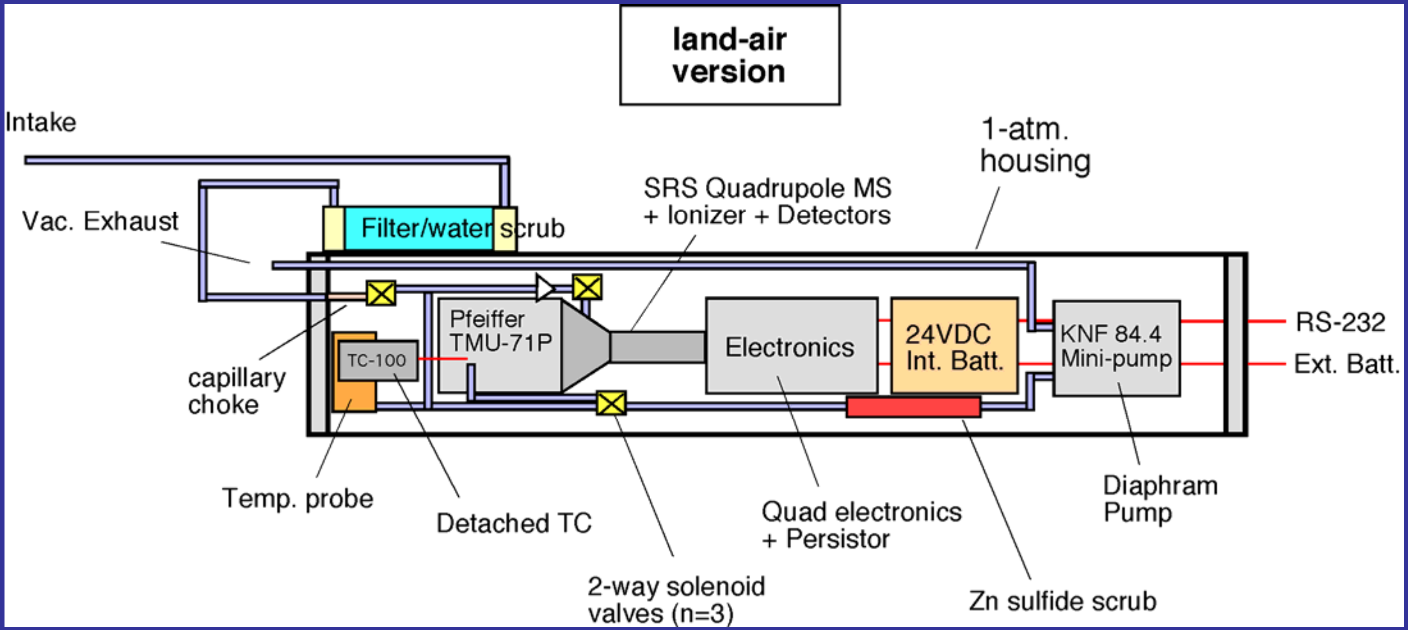
- Pros

=> 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

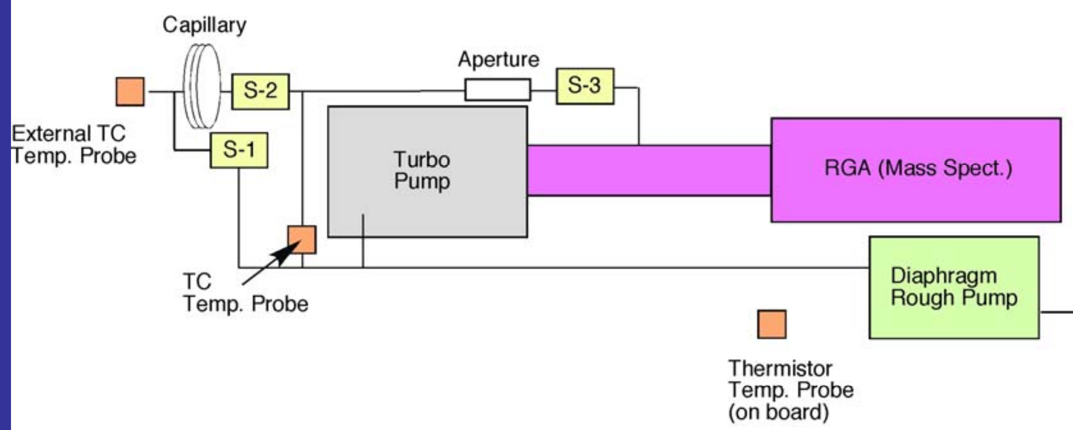
QVMS titanium housing with gas drying cartridge under PVC sun shield (black)

(Q = quadrupole MS)

System Software Development

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

Volcano Mass Spectrometer (VMS) Wiring Diagram



Board Relays:

Y-1 S-3 = Sample Solenoid Valve
Y-2 S-1 = Line Flush Solenoid Valve
Y-3 S-2 = Capillary (formerly By-Pass) Solenoid Valve
Y-5 RP = Diaphragm Rough Pump
Y-6 TP = Turbo Pump (large relay)
Y-7 RGA = RGA power (+24V)

Board Connectors:

JP-14 RGA Comm. = RS-232 comm.
JP-22 TC = Thermocouple Temp. probe

RJ-45 Ether = board comm.

Board Direct:

TT = Thermistor Temp. probe

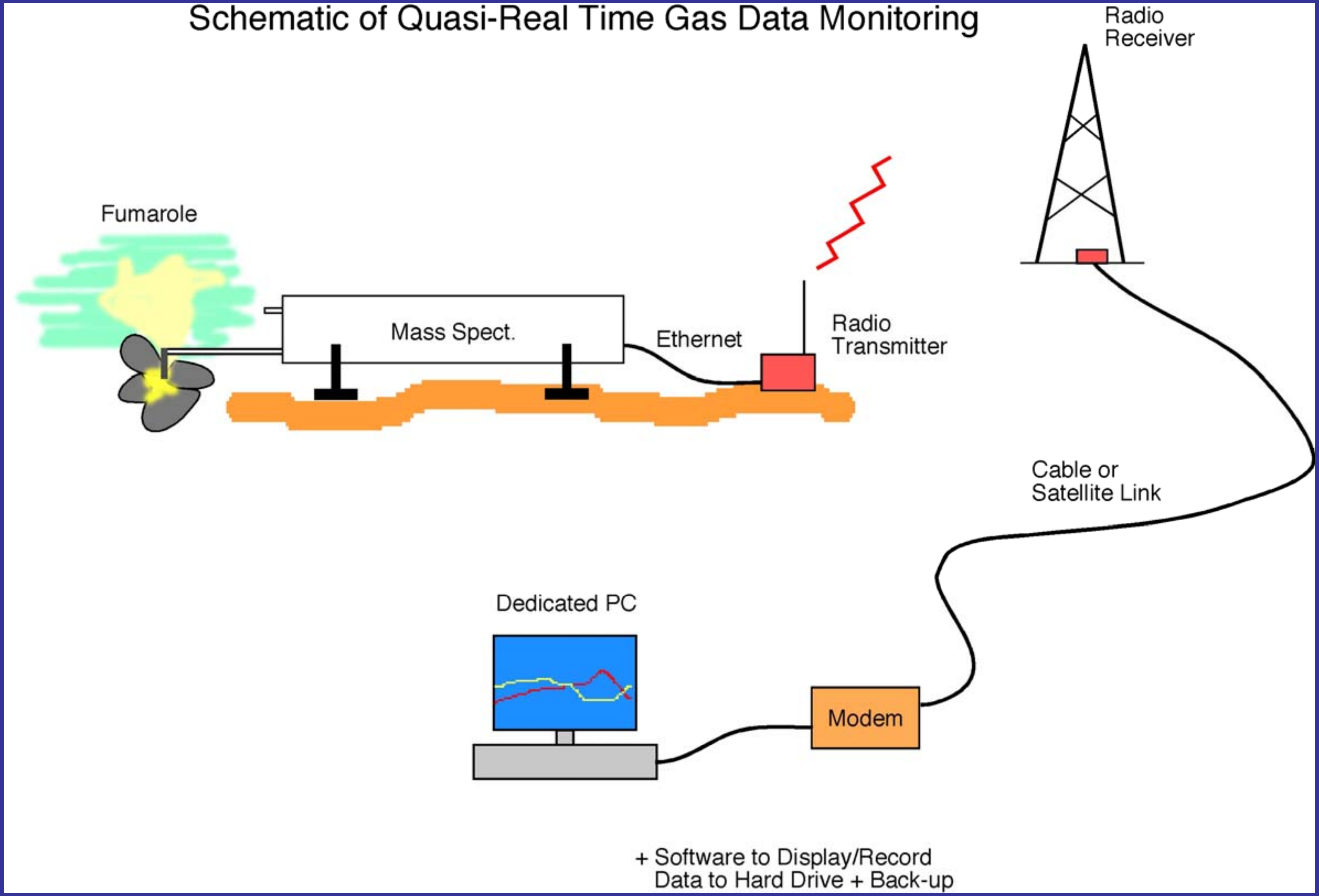
Programming Sequence:

1. Y-5 ON (RP on) 1 min.
2. Y-2 ON (Sample line flush) 1 min.
3. Y-2 OFF
4. Y-3 ON (Capillary open)
5. JP-22 (TC record (2) + TT record)
6. Y-6 ON (TP on) 4 min.
7. Y-7 ON (RGA on, filament on) 1 min.
8. Y-1 ON (Sample solenoid)
9. RGA faraday scan (1), EM scan (1) 3 min.
10. JP-14 (RGA Comm.)
11. Y-1, Y-3, Y-7, Y-6 OFF 1 min.
12. Y-5 OFF (RP off)
13. Rest (time = ## min.)

Terms:

RGA = Residual Gas Analyzer
Faraday = Faraday cup detector
EM = Electron Multiplier detector
Capillary = capillary line flow (press.) reducer
Aperture = aperture flow (press.) reducer

Remote Communications



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

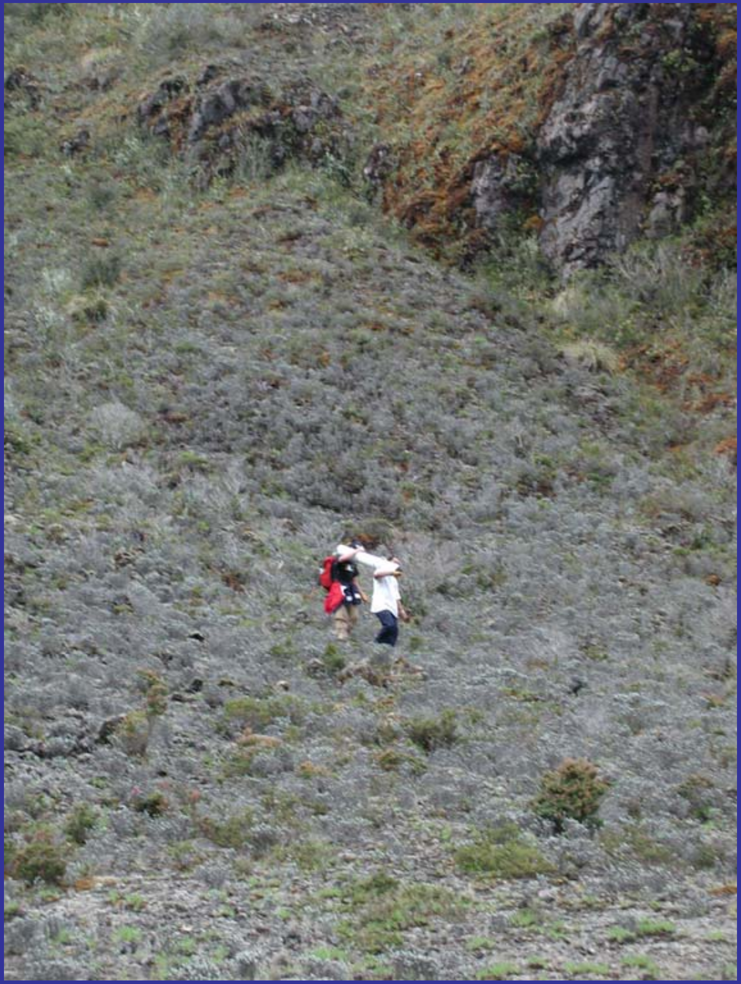
Turrialba, Costa Rica, 2005

Turrialba Summit

Four-wheel drive
Recommended…

Inside Turrialba

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

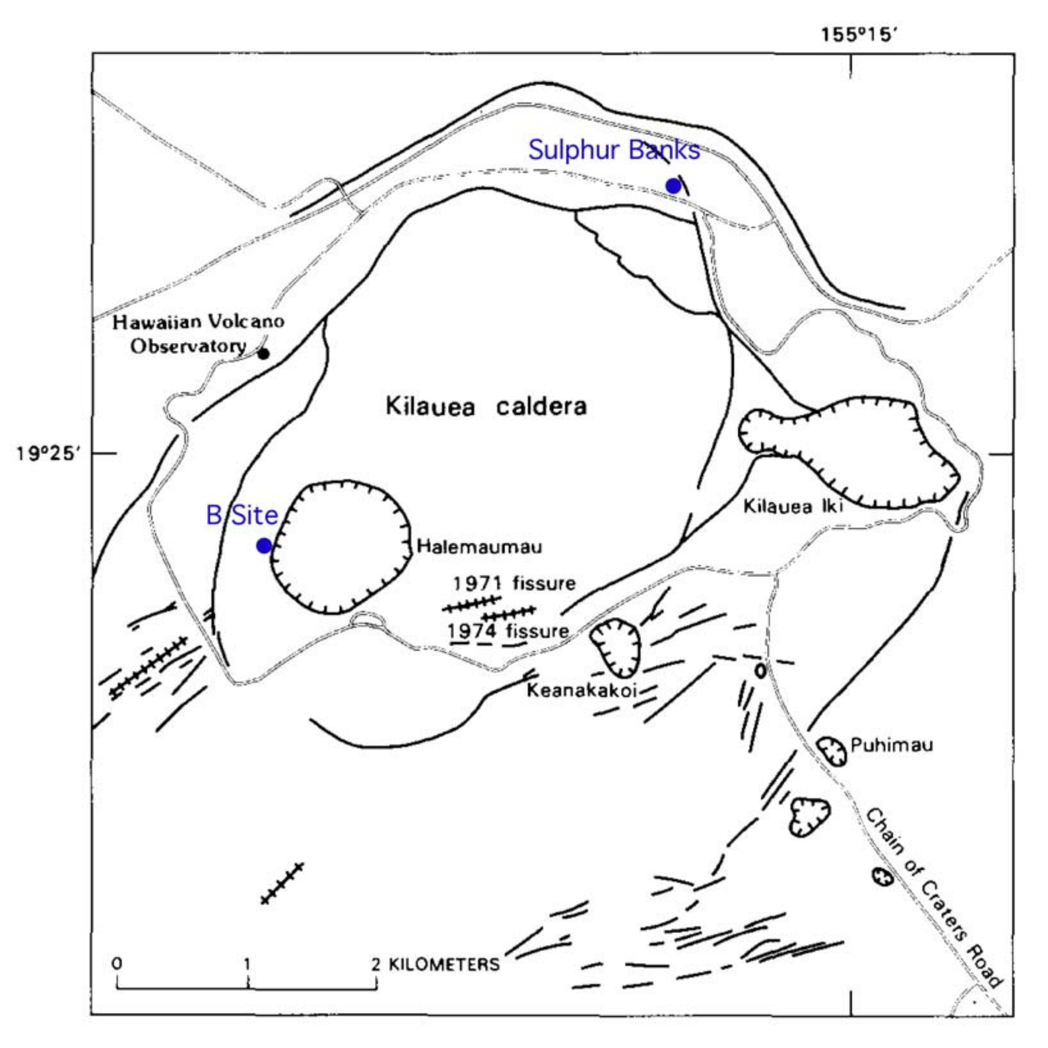
Camouflage!

⇒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

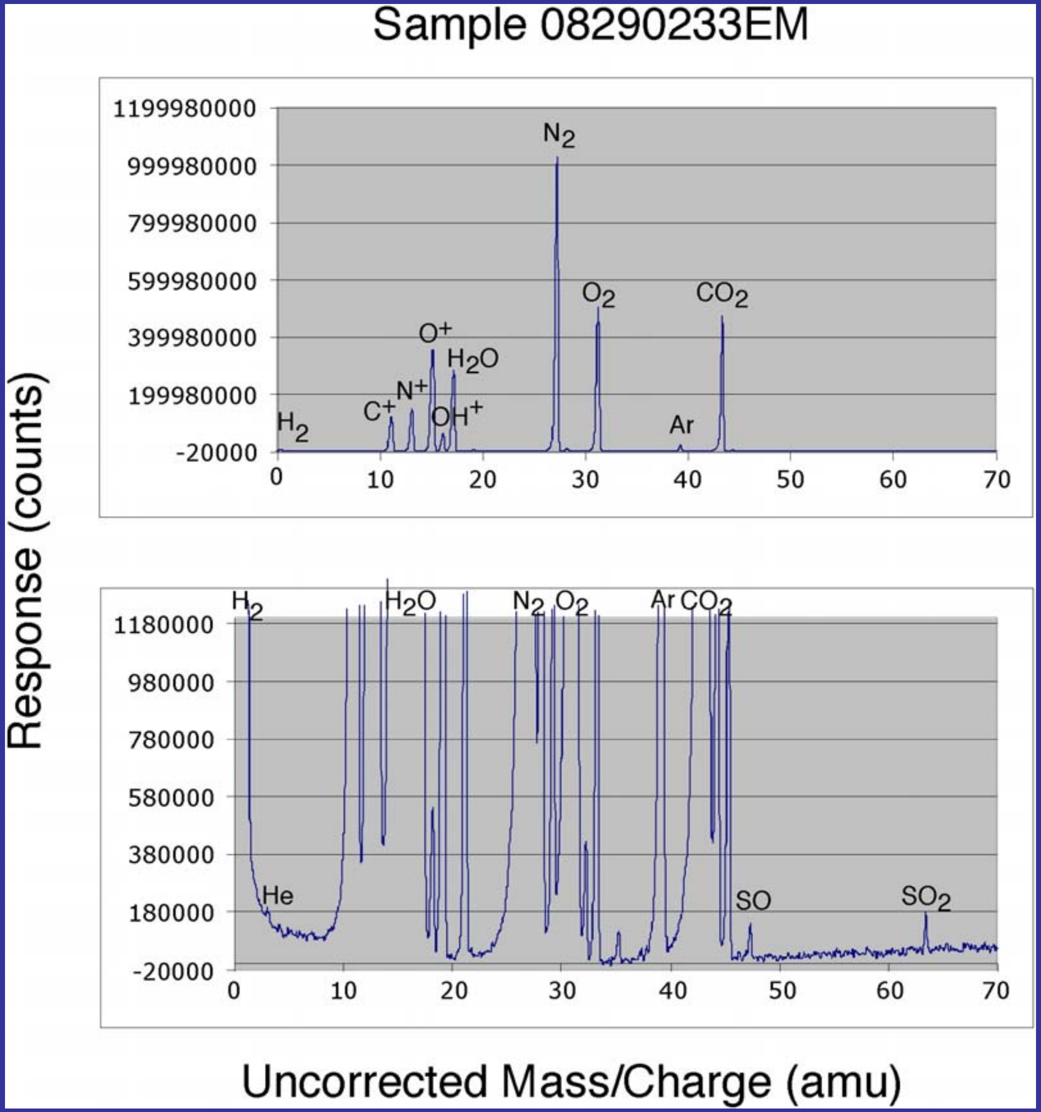
Twin 12V deep-cycle batteries

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

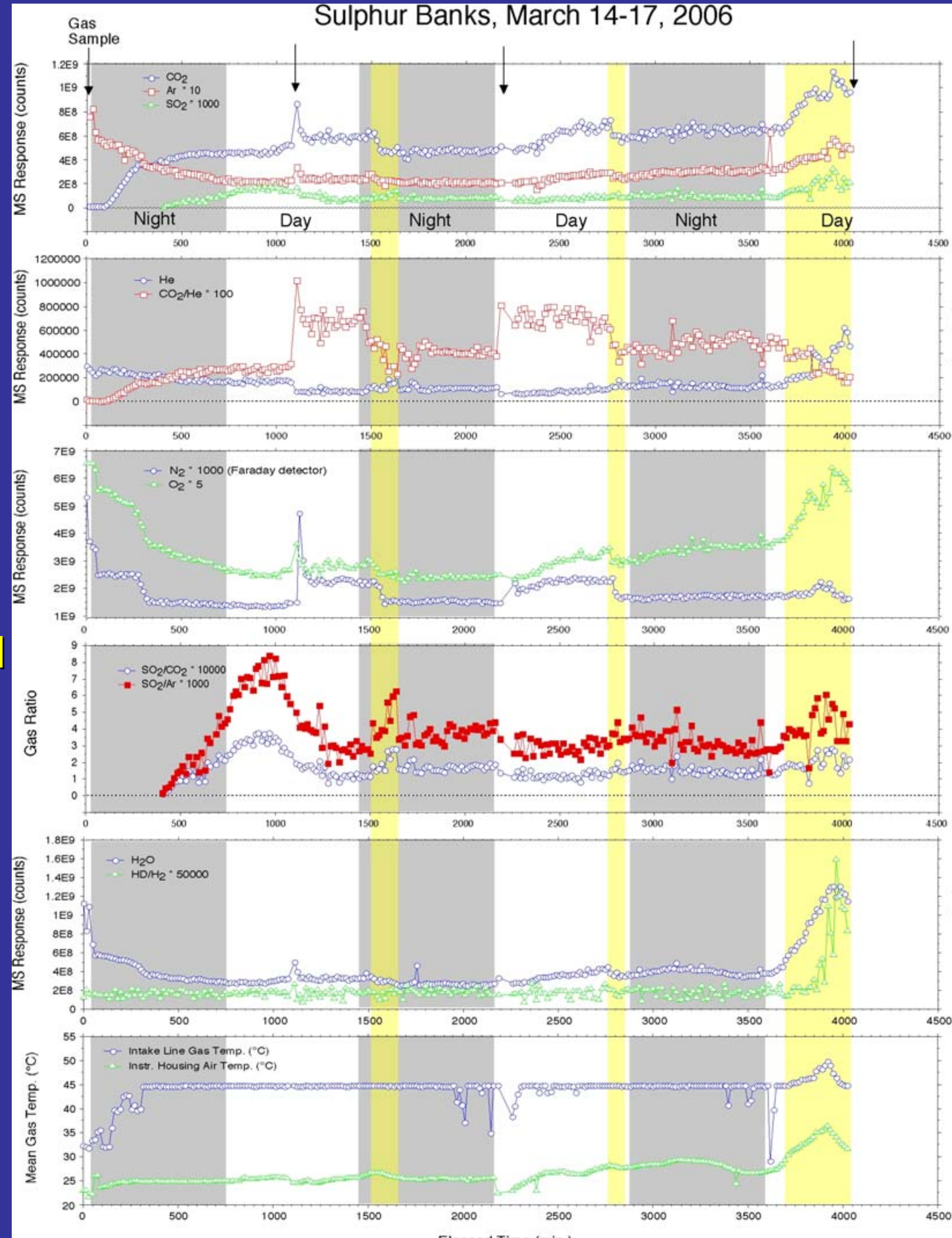
The major species peaks are truncated in the bottom, vertically expanded view

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.

Bottle ID	Collection Date/Time	Location	SO_2/CO_2*	SO_2/Ar	CO_2/Ar	CO_2/He	He/Ar
SB-2	3/15/06 1230 hrs	After condenser	0.02002	10.239	511.46	86,014	0.0059
QVMS	3/15/06 1230 hrs	---	0.00025	0.0060	24.0	3,000	0.0080
SB-4	3/16/06 0630 hrs	After condenser	0.02341	89.417	3,819.8	134,064	0.0285
SB-4	3/16/06 0630 hrs	Before condenser	0.03041	24.238	796.95	73,219	0.0109
QVMS	3/16/06 0630 hrs	---	0.00014	0.0034	24.3	8,090	0.0030

* *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 (SO_2, CO_2) 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.