Field-Portable Helium Isotope Detector for Continuous Monitoring of Volcanic Unrest and Large Earthquakes: a Development Update

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Status of Earthquake & Volcanic Eruption Prediction
(current arrows in our quiver)

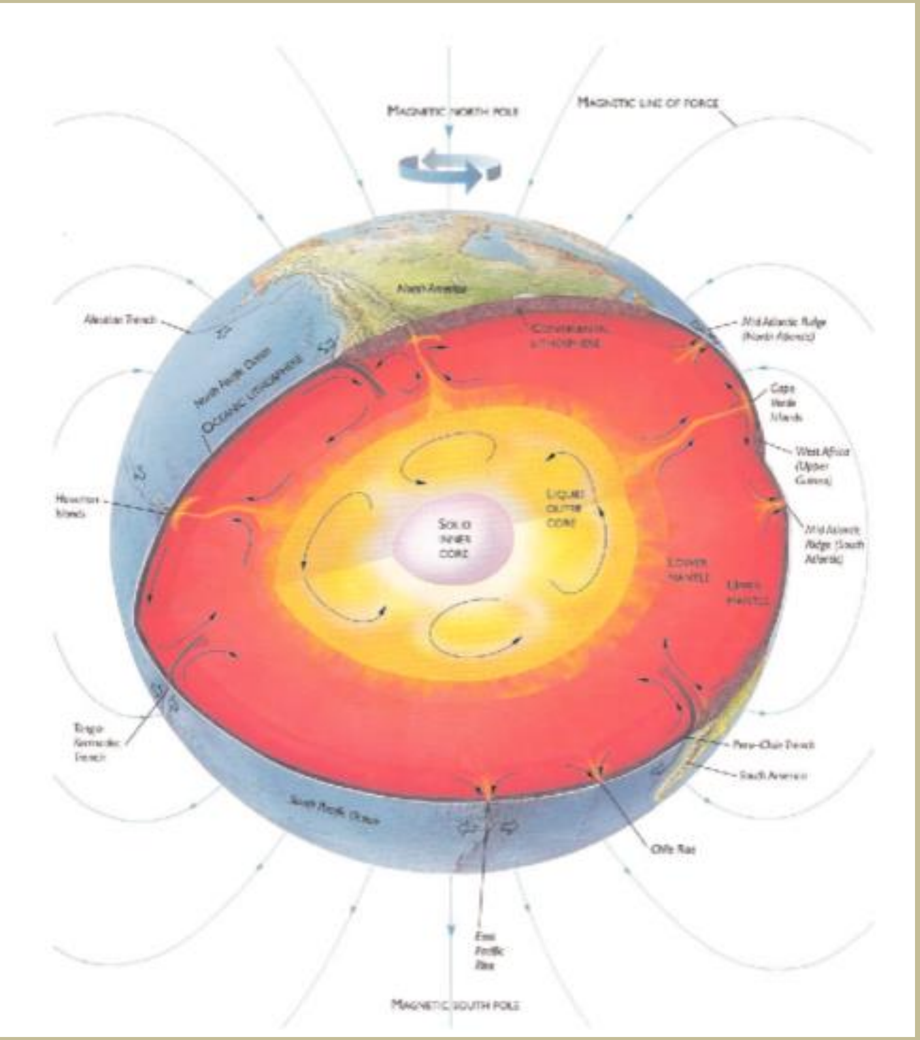
- **Seismology** -- sometimes premonitory. Most heavily relied upon method.
- **Inflation** -- sometimes premonitory. Effective by satellite altimetry.
- **Heat (IR)** -- sometimes premonitory. Effective by satellite IR sensors.
- **Radon** -- sometimes premonitory. Measures local, crustal stress only.
- **Helium (^{4}He)** -- sometimes premonitory. Measures crustal stress only.
- **$^{3}He/^{4}He$** -- Effective as a <u>mantle or magma monitor => premonitor</u>.

* Black = geophysical technology; blue, red = geochemical technology.

$^{3}He/^{4}He$ Systematics

- $^{3}He/^{4}He$ ratios reported as **R/R_a, where R_a = air** $^{3}He/^{4}He$ **= 1.4×10^{-6}**

- ocean water = **0.5 – 1.0**
- ocean crust = **0 – 8** (age & mixing dependent)
- arc volcanic crust = **5 – 8**
- continental crust = **<0.05** (radiogenic ^{4}He)
- upper mantle (MORB) = **8 ± 1**
- lower mantle (via hotspots) = **10 – 35**
- inner & outer core = **>35?**
- IDPs (interplanetary dust particles) &
- Moon's regolith = **100+**



Rationale for a New $^3He/^4He$ Detector

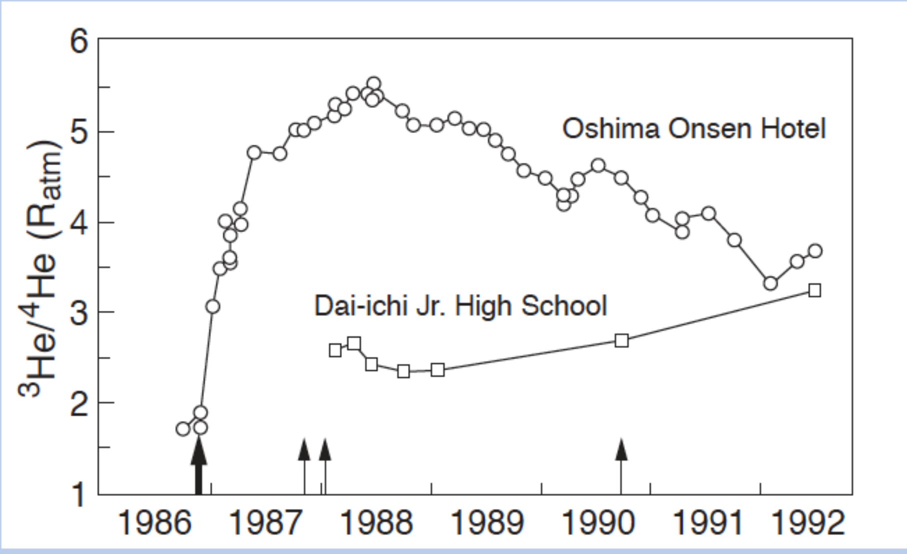
- **Need for quasi-real-time, remote, in-the-field analysis and monitoring of this important ratio as:**

- **Volcanic (magmatic) unrest & eruption monitor/predictor.**
- **Large earthquake monitor/predictor.**
- **In-field sampling guidance for conventional He isotopic analysis (sample return).**
- **Isotopic enrichment (process) monitor.**

- **Del $^3He/CO_2$ ratio is an important additional magmatic evolution guide, and <u>can be done with the same instrument</u> (as well as Ne, Ar, CO, CH_4).**

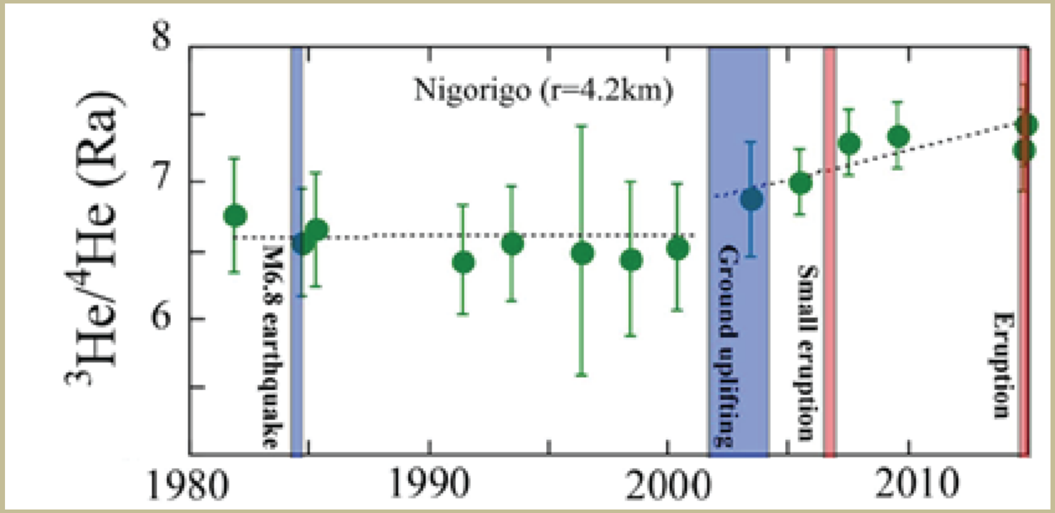
Change in ^3He-^4He ratio with Volcanic Eruptions

Oshima Volcano



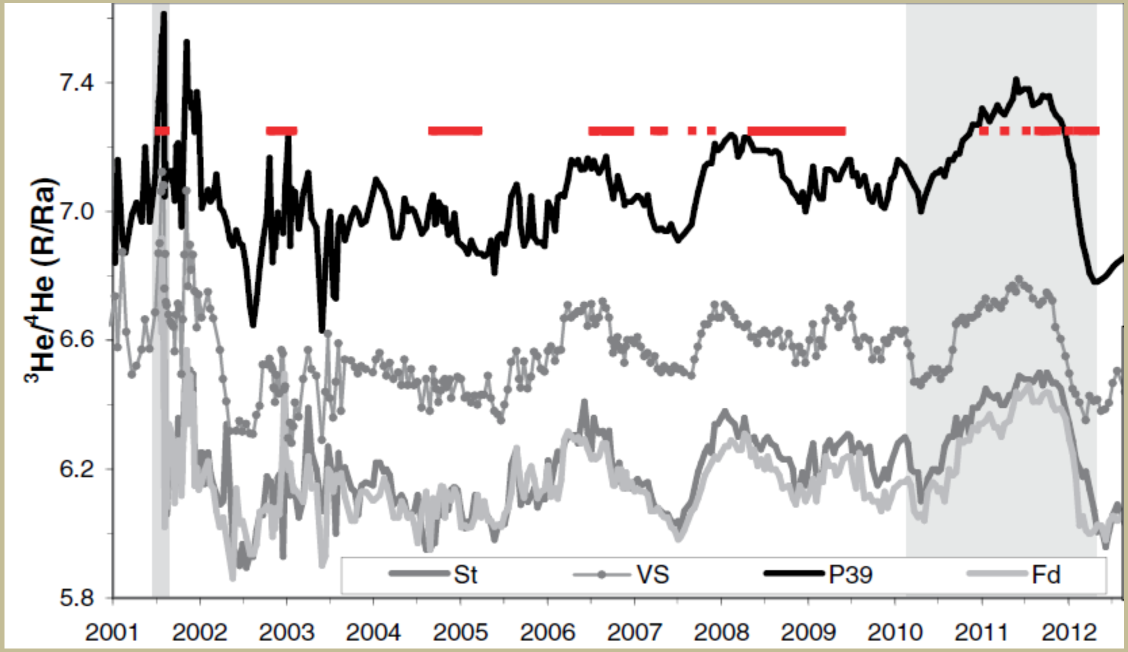
*Change in 3He/4He following magmatic activity at Oshima Volcano, Japan. Note the gradual decrease in 3He/4He following the main active period. Arrows indicate earthquakes (from **Sano et al., 1995**).*

Precursory Signals of Eruptions

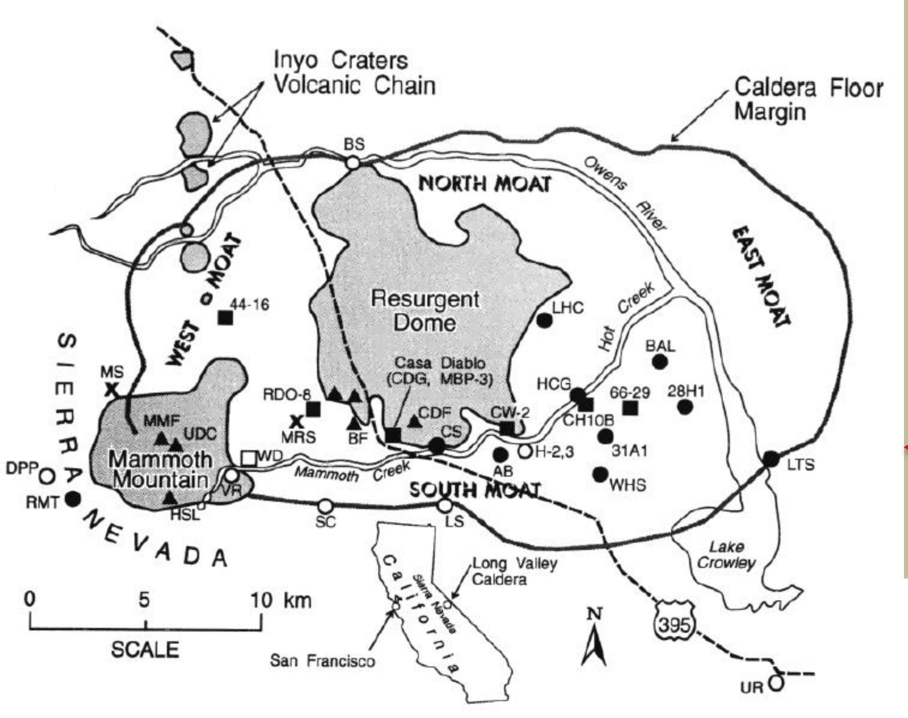


Temporal variations of $^3He/^4He$ measured at Nigorigo Hot Spring 4.2 km from the summit of Mount Ontake in Japan between 1980 and 2014 (**Sano et al., 2015**)

Temporal variations of $^3He/^4He$ measured at several gas vents on Mount Etna in Italy between 2001 and 2012 (horizontal red lines indicate the eruptions) (**Paonita et al., 2016**)

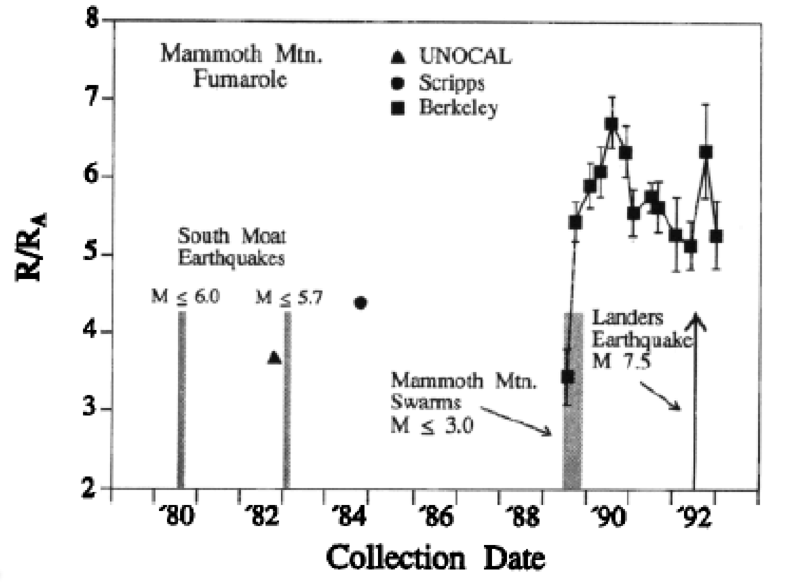


Change in ^3He-^4He ratio with Seismic Unrest



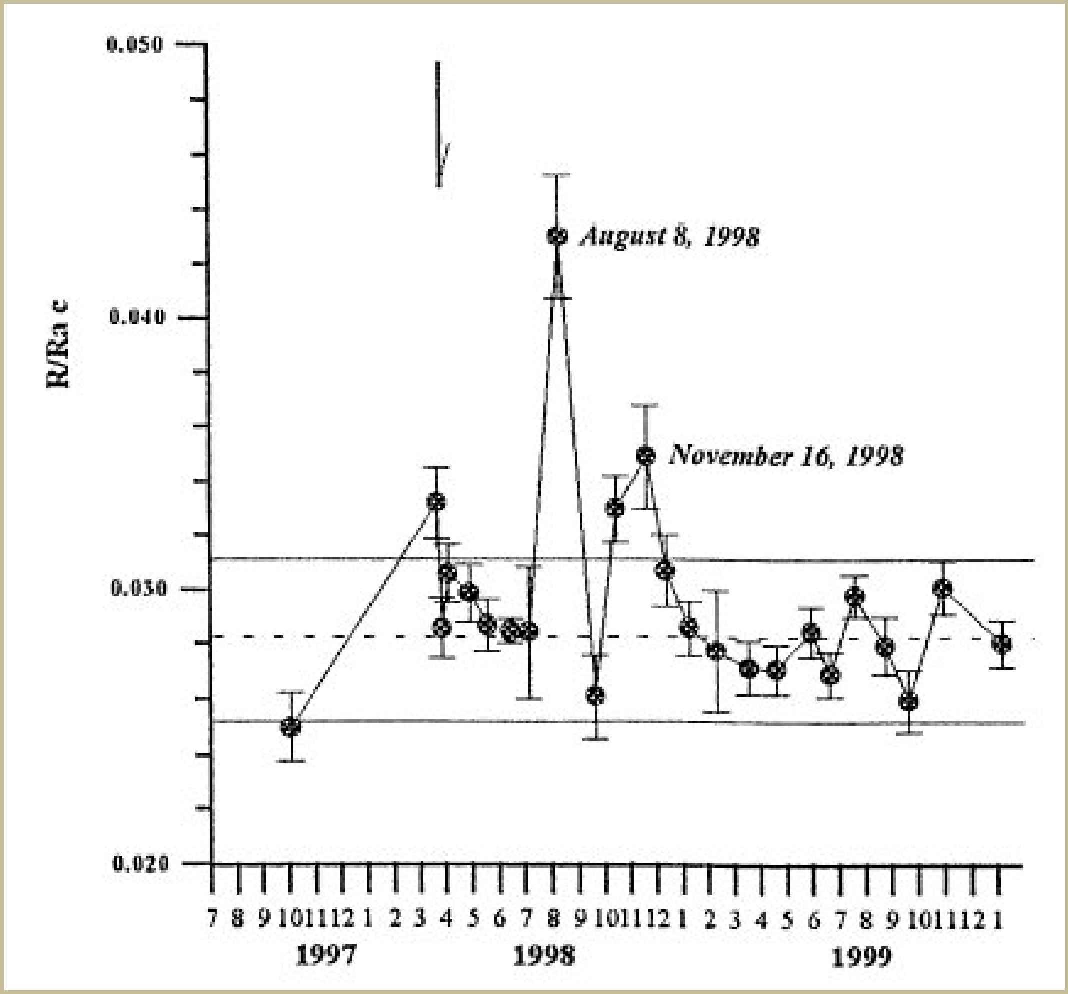
Map of Long Valley caldera area showing selected thermal springs (solid circles), fumarole (triangles), cold springs (open circles), thermal wells (solid squares), and cold wells (open squares).

Temporal variation in the air-corrected helium isotopic composition (R/R_A) for steam vent MMF on the north side of Mammoth Mountain. Periods of seismic swarm activity beneath Mammoth Mountain in1989 and beneath the south moat in 1980 and 1983 are indicated by the stippled regions (from **Sorey et al., 1993**).



Change in ^3He-^4He ratio with Non-Volcanic Earthquake Activity

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



State-of-the-Art for $^3He/^4He$ Monitoring

Automated syringe pump and copper coil crimper:

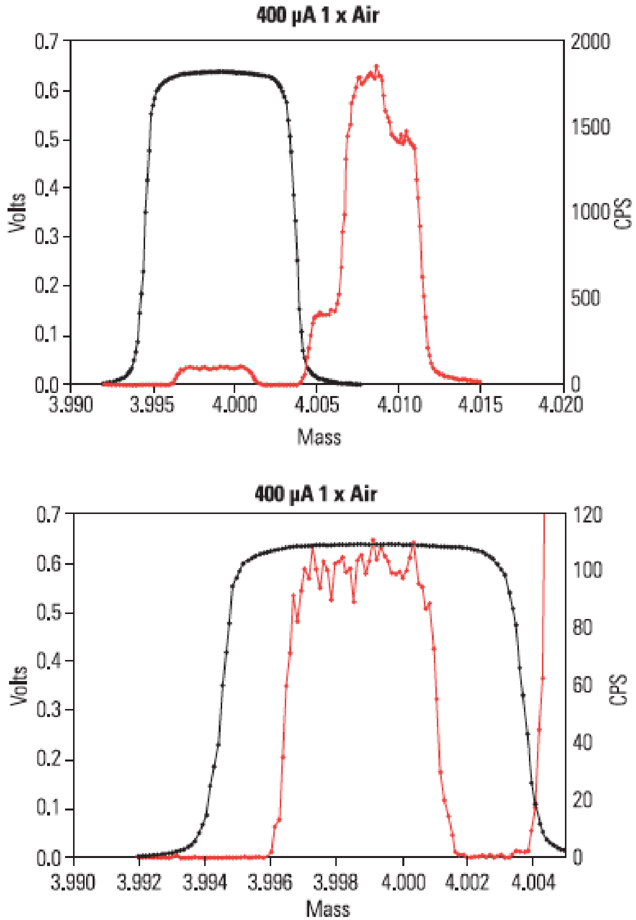
Barry, P.H., et al., 2009, A New Syringe Pump for the Retrieval and Temporal Analysis of Helium (SPARTAH) in groundwaters and geothermal fluids, G-cubed (Technical Briefs).

Figure 1. (top) The Harvard syringe pump apparatus with stainless steel syringe along with sectioned Cu tubing of 12.7 cm (500) length. Note the sectioned Cu coil with two refrigeration clamps and Ultratorr fitting attached to one end.

(bottom) Deployment of SPARTAH at the San Bernardino wellhead. The Pelican case houses the syringe pump apparatus and one Cu coil. One end of the coil is attached to the syringe, and the other leads through a hole in the case to the wellhead.

$^3He/^4He$ as Measured in Laboratories

Thermo Scientific noble gas isotope ratio mass spectrometer (Helix SFT)



Scans taken with the HELIX SFT showing He³ resolved from HD (upper) and typical peak shapes (lower)[1]

Standard Specification of the HELIX SFT

Mass range	1 to 150 Daltons
Background	Equal or better than 5e^{-14} cc STP at mass 36
Sensitivity	Helium - greater than 2 x 10^{-4} amps/Torr at 800 µA trap current. Argon - greater than 1x10^{-3} amps/Torr at 200 µA trap current.
Resolution	For Faraday detector resolution > 400 For multiplier detector resolution > 700
Peak side stability	Drift to be less than the equivalent of +/- 25 ppm in mass over 30 minutes at mass 40.

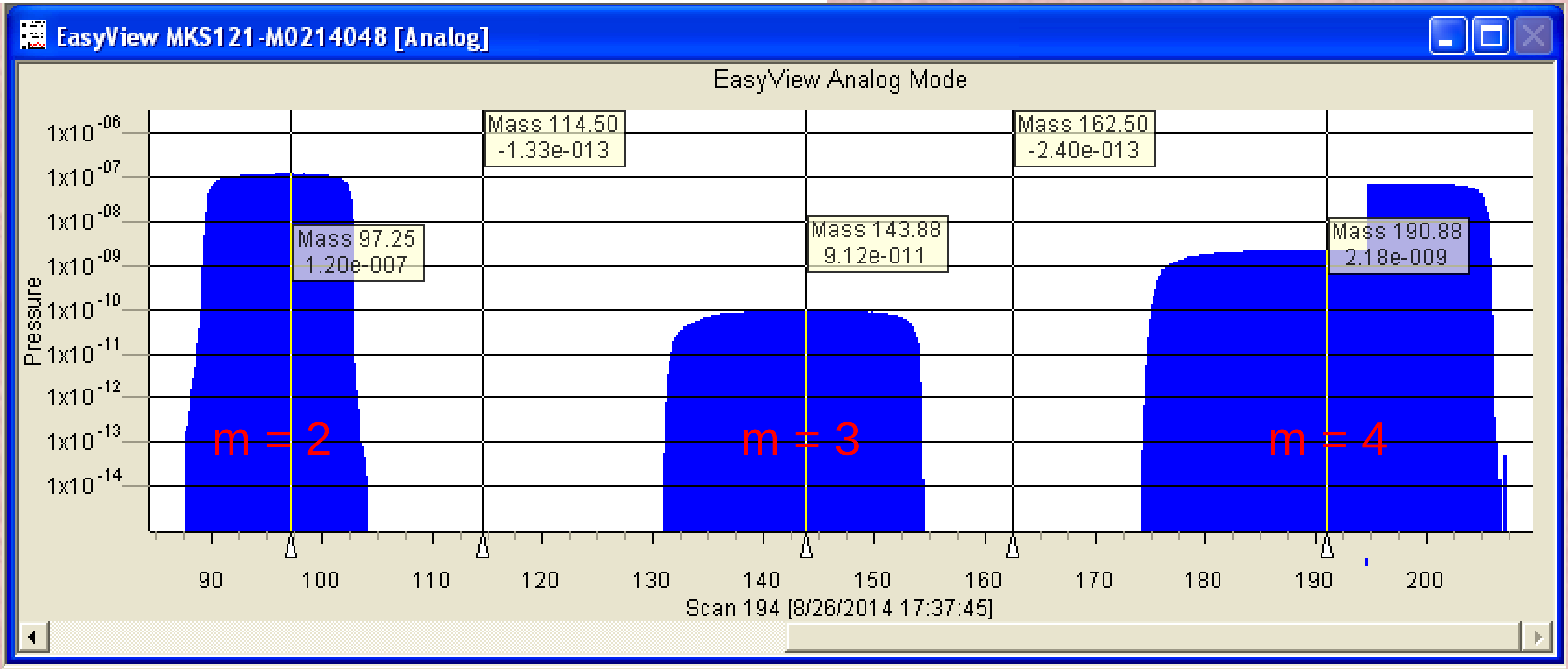
High-Resolution Quadrupole RGA

Mass Range: 1 to 6 amu

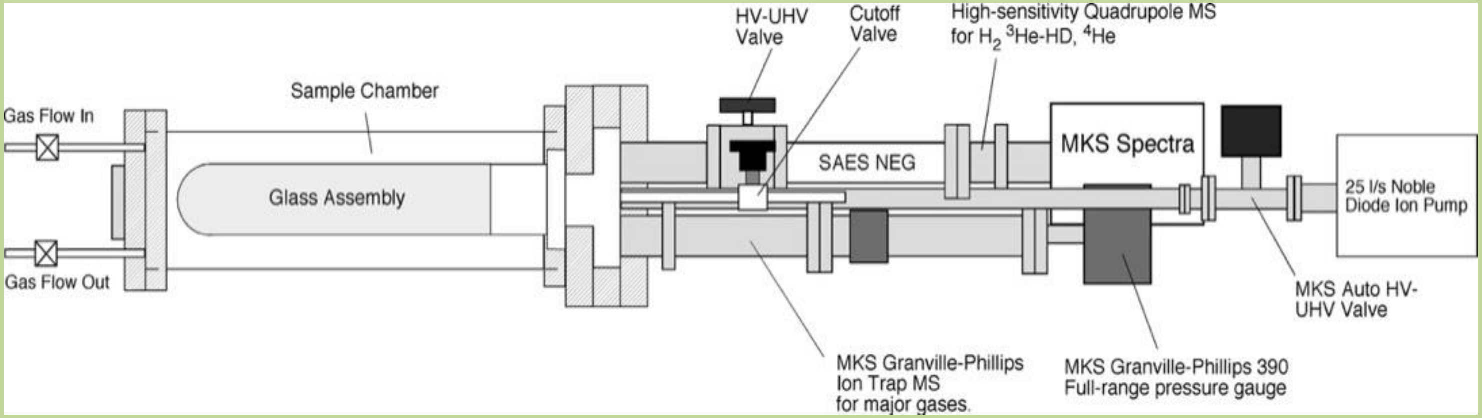
Dynamic Range: 10^7

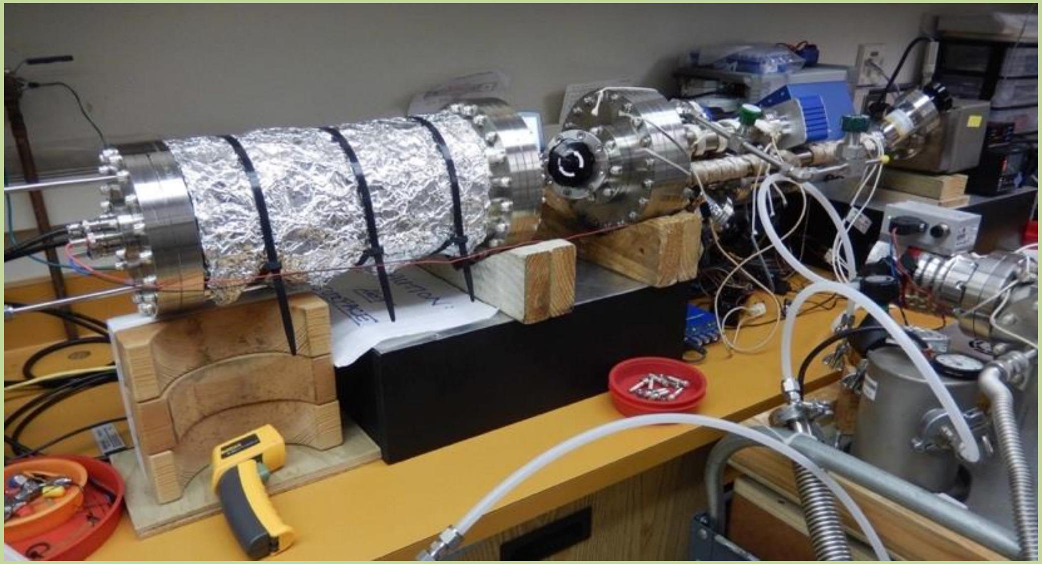
Selectable Peak Detection Mode

Can Adjust Filament Emission Current on the Fly



Bench-Top Experimental Prototype: Albert





<u>Analytical Challenges:</u>

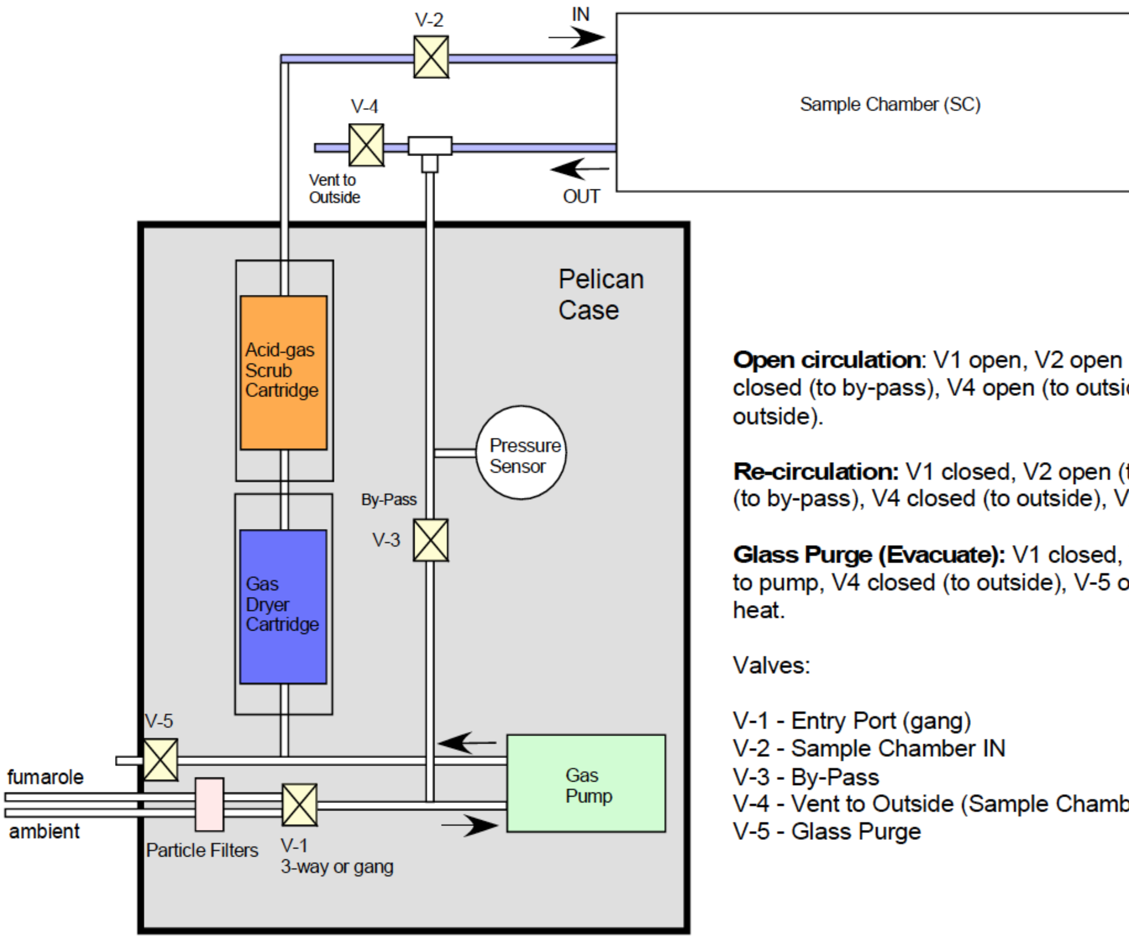
Detect 1 part in 10^{12} or better (pico to femto-molar).

Resolve ^{3}He from HD isobar.

Compact & low power for the field.

Rugged & reliable.

Gas Purification System (GPS)



Open circulation: V1 open, V2 open (to sample), V3 closed (to by-pass), V4 open (to outside), V-5 closed (to outside).

Re-circulation: V1 closed, V2 open (to sample), V3 open (to by-pass), V4 closed (to outside), V-5 closed (to outside).

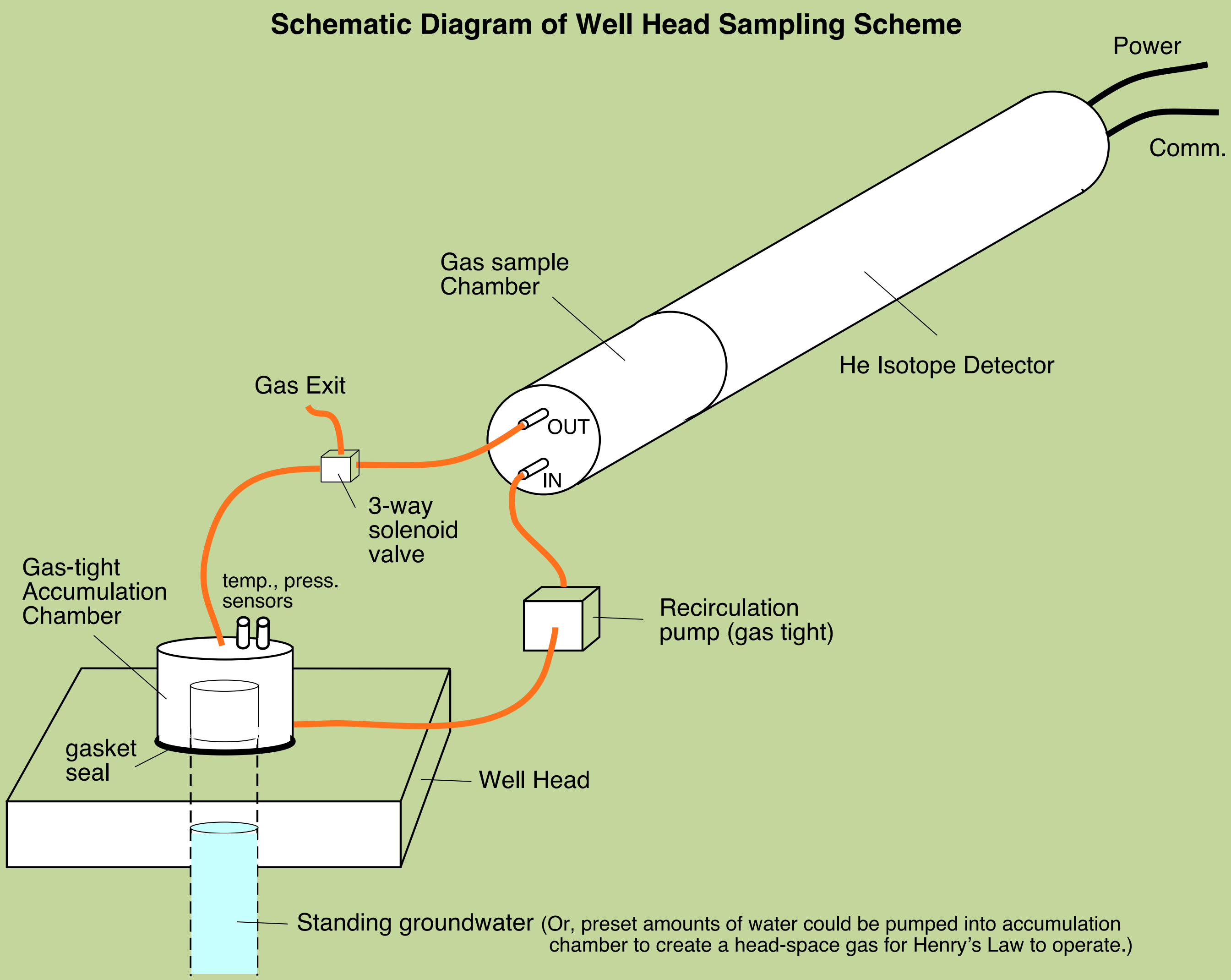
Glass Purge (Evacuate): V1 closed, V2 closed, V3 open to pump, V4 closed (to outside), V-5 open (to outside), then heat.

Valves:

V-1 - Entry Port (gang)
V-2 - Sample Chamber IN
V-3 - By-Pass
V-4 - Vent to Outside (Sample Chamber OUT)
V-5 - Glass Purge

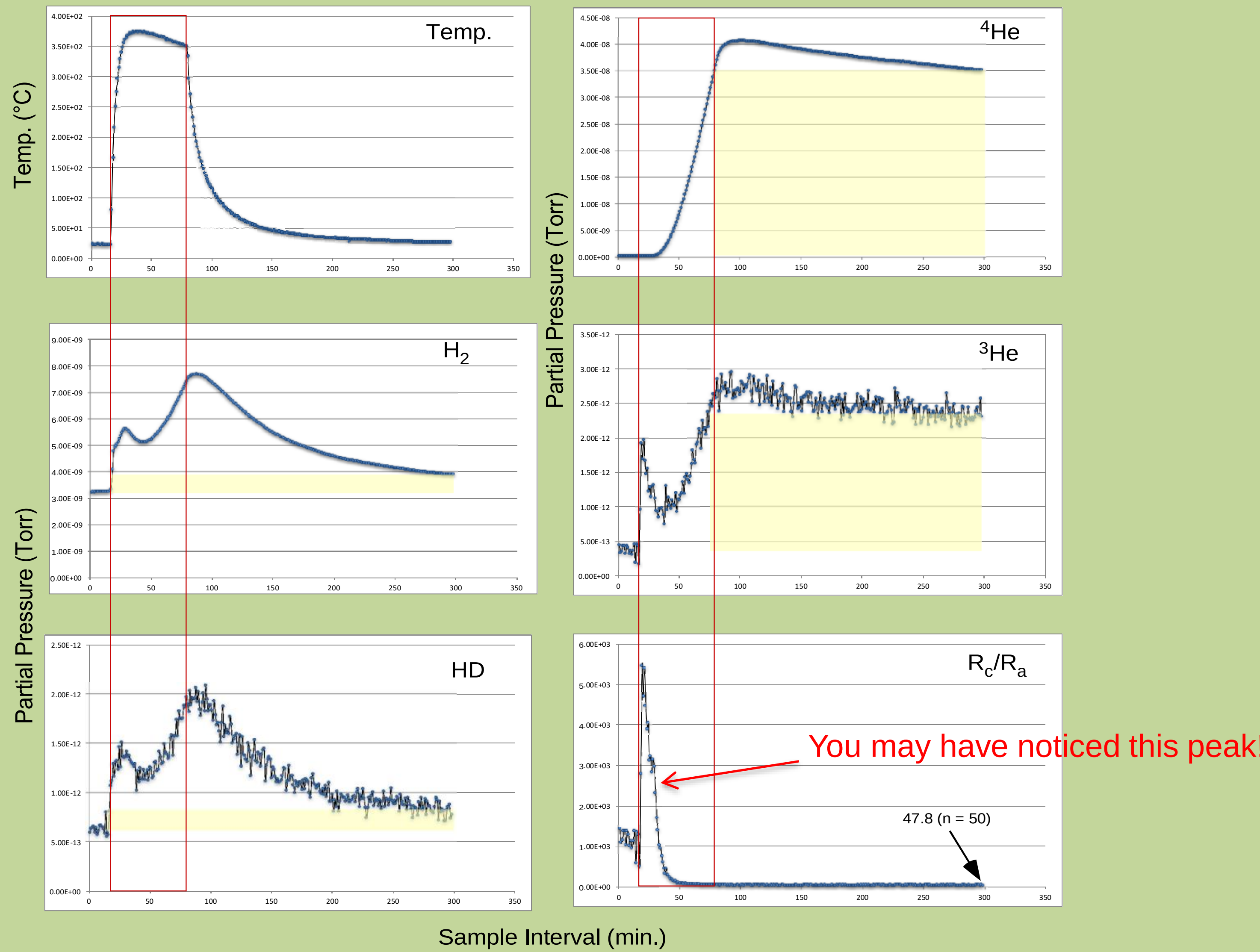
Helps to eliminate most water, CO_2 and other acid gases to concentrate signal, protect inlet & conserve high vacuum.

One of several proposed field deployments: abandoned well head



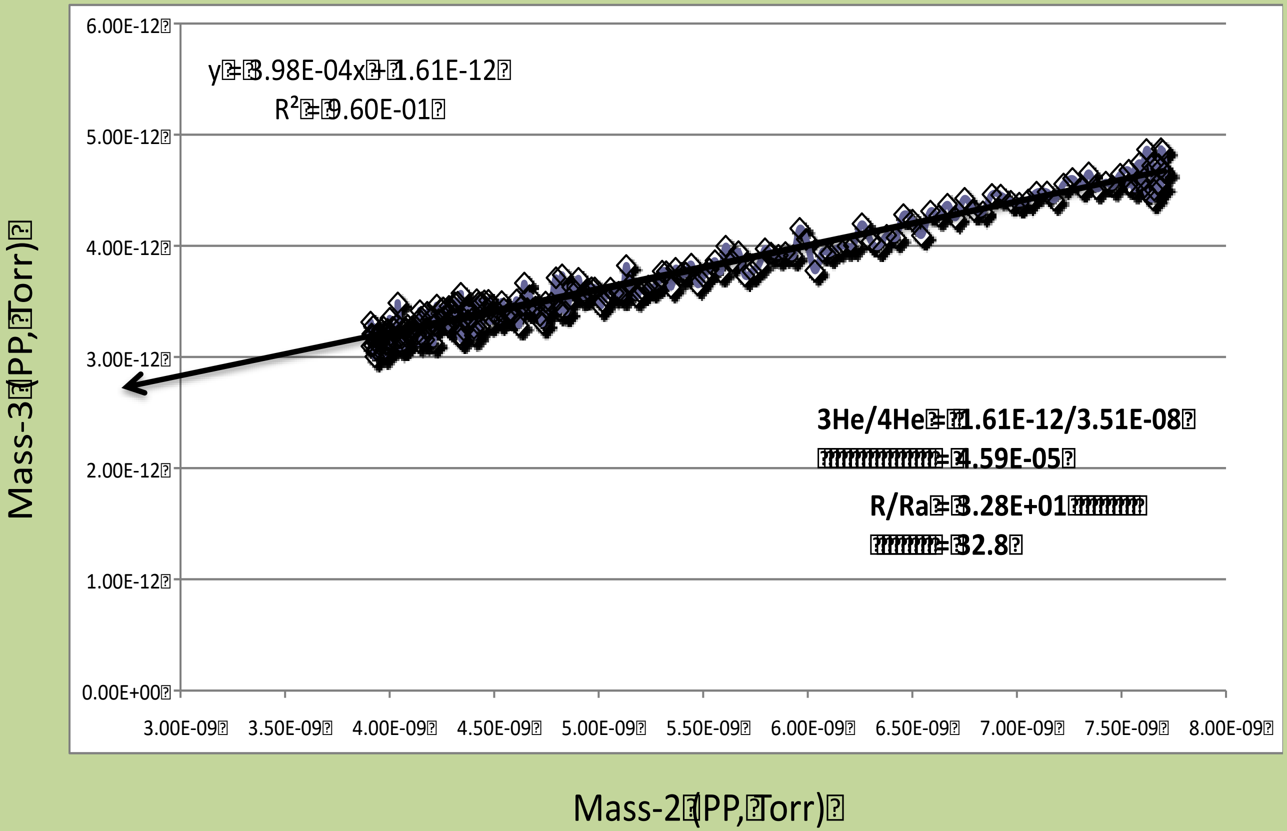
HD-^{3}He Isobar Separation – Method I

Adjusted Ionization MS (AIMS)

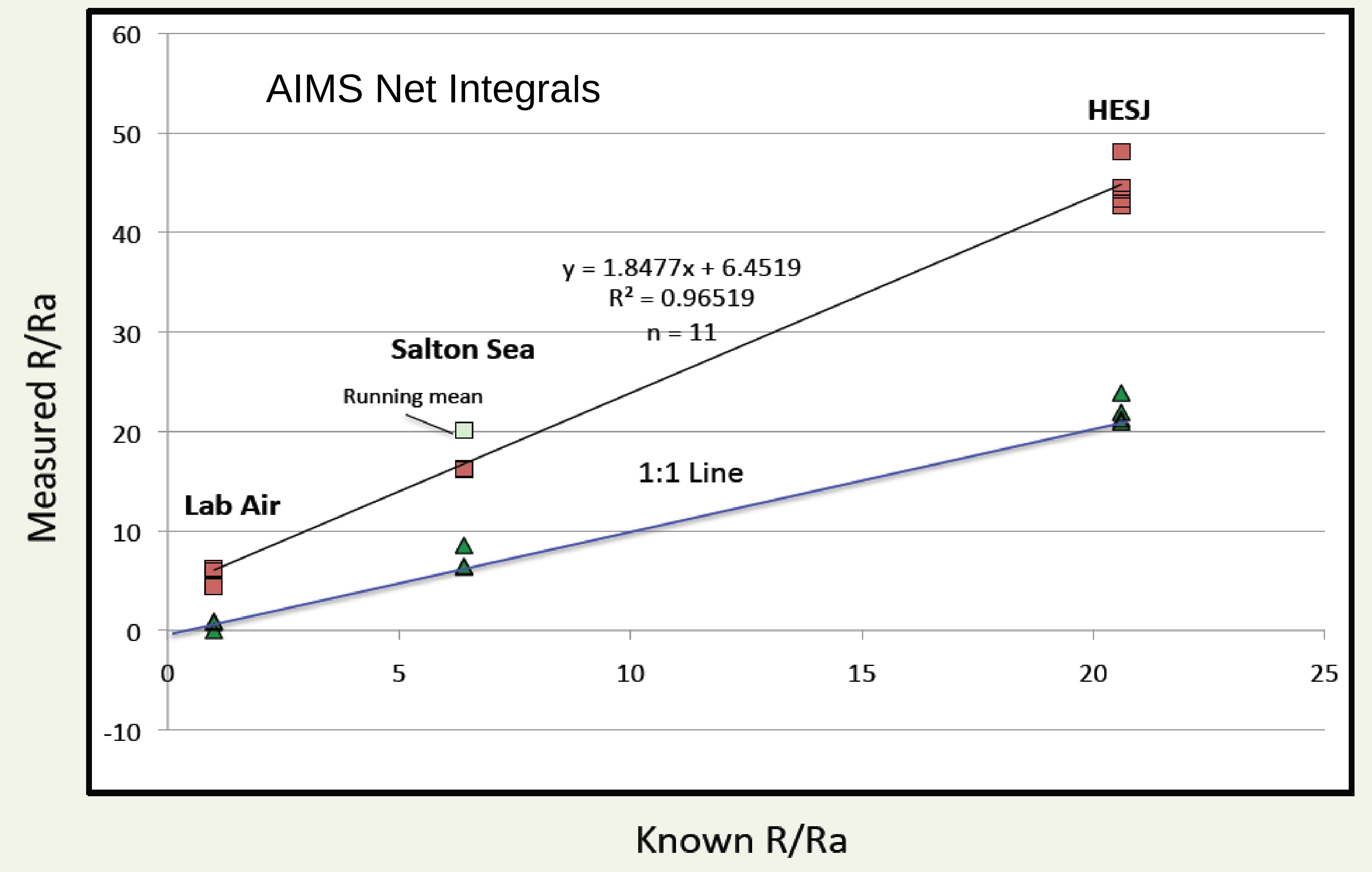


HD-^{3}He Isobar Separation- Method II

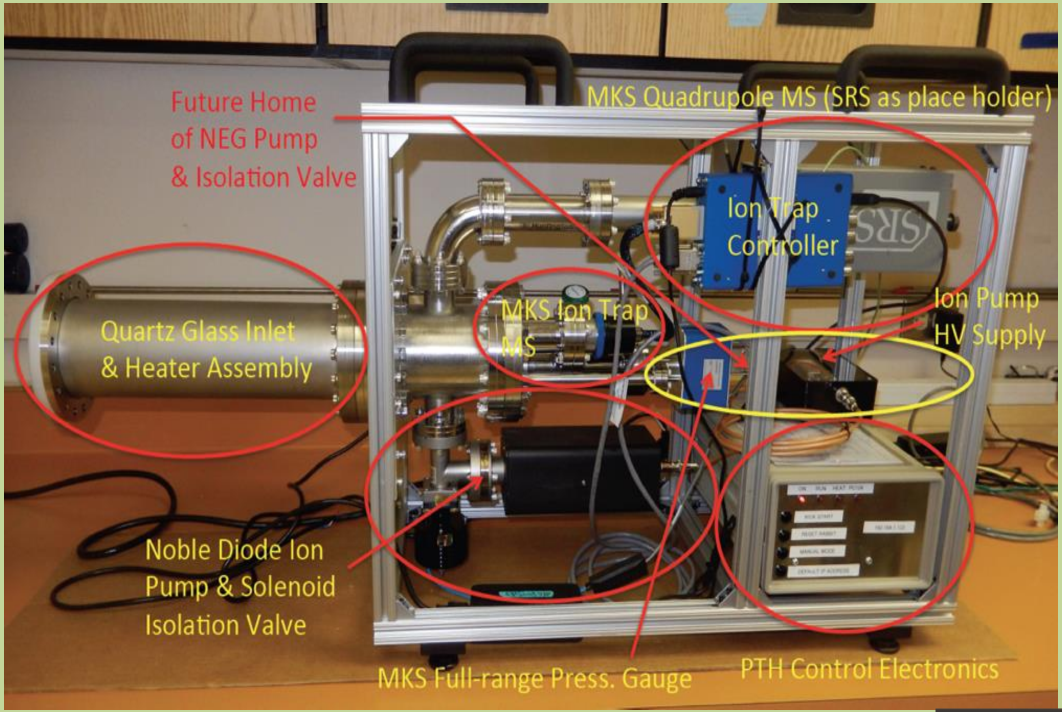
Mass-2 vs. Mass-3 Zero-Intercept



Standards Regression Plot



Field Prototypes – Edward & Lyle



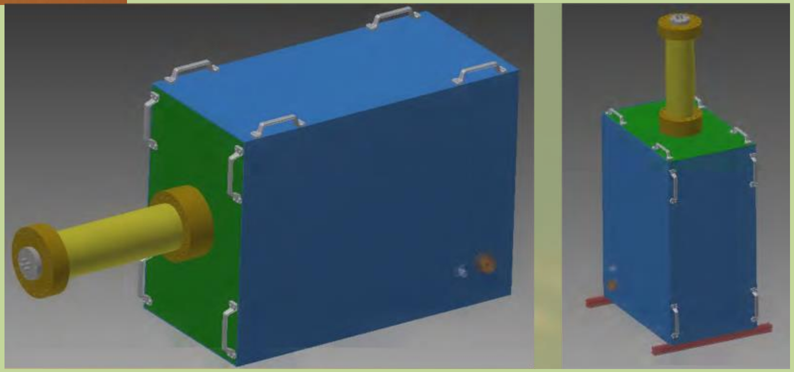
Weight: approx. 100 pounds (45.4 kg)

Dimensions: 43.5"L x 19"H x 13"W

Power: peak of 300 W @ 24V DC; 12.5 amps. (Rest of system electronics' power are trivial.) Average 135 W (no int. heater)

Sampling rate: $\geq$ 6 cycles per 24 hr day

- 1 hr or less collection @ max. temp.
- 2 hr or less glass clearing @ max. temp.
- 1 hr or less cool down, repeat.



Future Deployment Plans:

Edward => Mammoth Lakes, CA

Lyle => Kilauea, Hawaii

Instrument Advantages & Disadvantages

Advantages

- Allows real-time record for hazard mitigation.
- Eliminates costly, lengthy and labor-intensive lab analysis of this ratio.
- Allows temporal resolution of isotope ratio dependent mainly upon ^3He counting statistics.
- Can fulfill both science objectives and emergency warnings in a single portable, rugged field instrument.
- Instrument can be simply made at relatively low cost.
- Only one small mechanical pump (diaphragm pump in GPS unit).

Disadvantages

- ~~Risk that He accumulation, HD isobar suppression, and glass-MS combo dynamic range will not be sensitive enough to detect ^3He.~~ [Good to 1R/Ra; thinner glass should get below 1 R/Ra.]
- Cost will be greater than simple pumped Cu coil collectors.
- Power budget will be in sub-kW range, probably 3-400 W in cold weather.

Conclusions

- We have developed a method for a field-portable $^3He/^4He$ detector/monitor using a customized quadrupole mass spectrometer, NEG-Ion pumped vacuum, and custom electronics.

- HD-^3He isobaric interference is effectively handled by an Adjusted Ionization MS (AIMS) method. The mass-2 vs. mass-3 intercept method also works to separate ^3He from HD-^3He at mass-3.

- Diffusion of He and H isotopes through quartz glass is variable with time and temperature. We are continuing to investigate this variability with regard to increasing ^3He detection sensitivity.

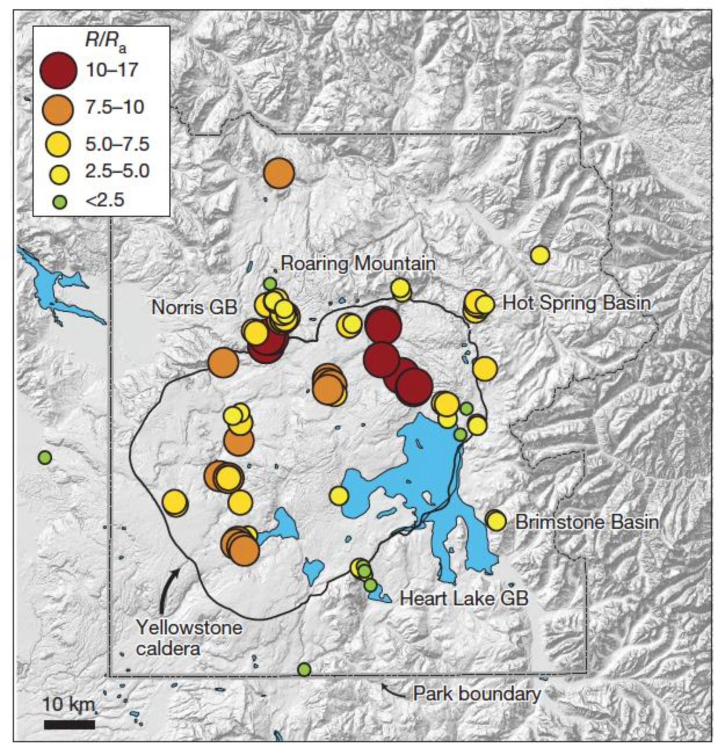
- ^4He, ^{20}Ne, and ^{40}Ar all diffuse through heated quartz glass. These isotopes allow an air contamination correction. A new custom quadrupole MS is being made to extend the mass range from 1-6 amu to 1-50 amu to include these gas species, plus CH_4, CO, CO_2.

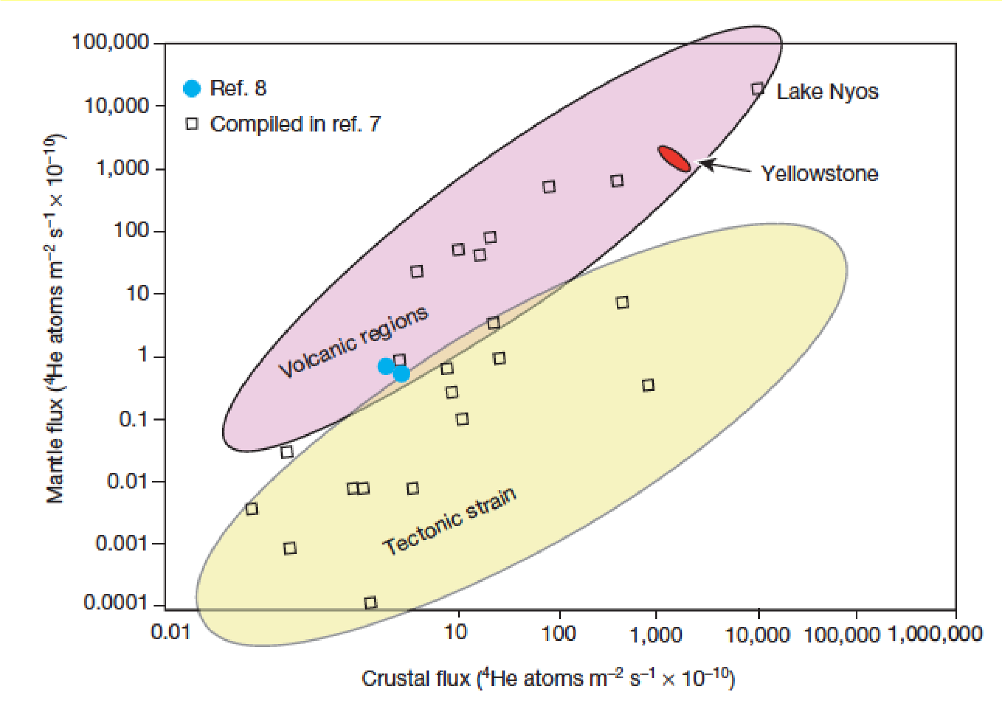
Acknowledgements

- Team collaborators: David R. Hilton, UCSD, James E. Blessing, MKS Instruments, Inc., James R. DeLuze, Fusion Energy Solutions of Hawaii.
- Engineering: James Jolly, David Copson, Mario Williamson, University of Hawaii, Manoa.
- Initial Funding: DCO DECADE Seed Grant to Gary McMurtry, UH, Manoa and David R. Hilton, UCSD.
- Current & Future Funding: USGS, NSF, and/or DCO to expand operations to active fault zones and active volcanoes globally.

Additional Slides

Prodigious degassing of a billion years of accumulated radiogenic helium at Yellowstone





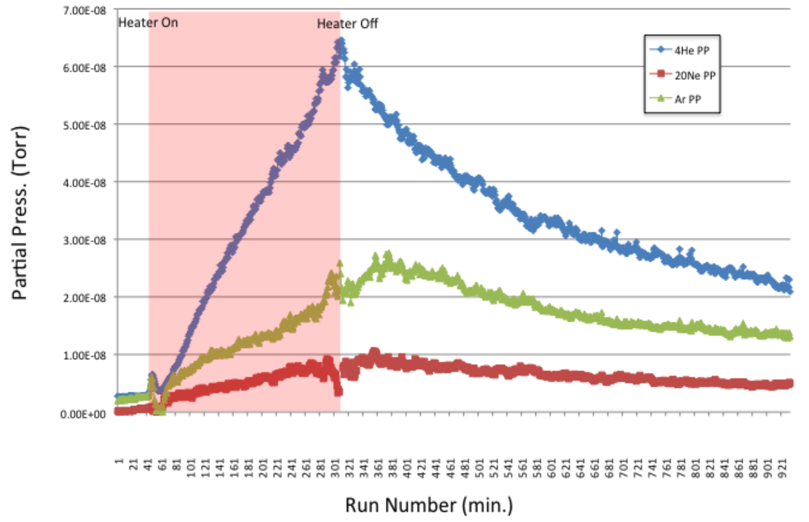
Lowenstern et al., Nature (2014)

Besides He and H_2, what diffuses through the glass?

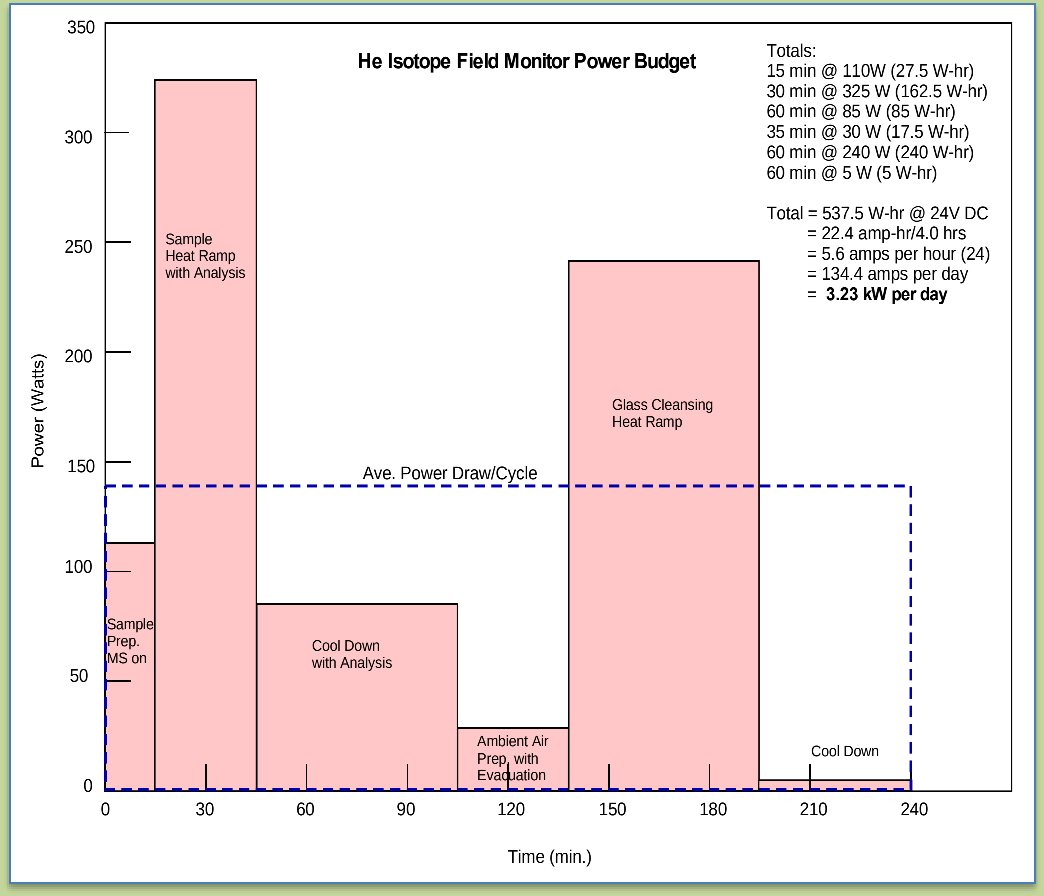
Gas	Chemical Symbol	Molecular Mass (kg/kmol)	Ratio compared to Dry Air (%)* By volume	By weight	Partial Pressure (Torr)	Qtz. Glass Inlet- Albert II prototype: Uptake 6/12/2015 1.5 hrs, T_{max}=309°C	Ratio (%)**	E. F. Air
Oxygen	O2	32.00	2.10E+01	23.2	159.22	0.00	0.0	0.00E+00
Nitrogen††	N2	28.02	7.81E+01	75.47	593.484	2.90E-09	4.5	5.98E-02
Carbon dioxide***	CO2	44.01	4.00E-02	0.046	0.304	1.35E-09	2.1	4.56E+01
Hydrogen	H2	2.02	5.00E-05	~ 0	0.00038	3.10E-09	4.8	9.64E+04
Argon	Ar	39.94	9.33E-01	1.28	7.0908	1.12E-08	17.4	1.87E+01
Neon	Ne	20.18	1.80E-03	0.0012	0.01368	4.80E-09	7.5	4.15E+03
Helium	He	4.00	5.00E-04	0.00007	0.0038	1.92E-08	29.9	5.97E+04
Krypton	Kr	83.80	1.00E-04	0.0003	0.00076	0.00	0.0	
Xenon	Xe	131.29	9.00E-06	0.00004	0.0000684	0.00	0.0	
Methane	CH4		2.00E-04		0.00152	4.80E-09	7.5	3.73E+04
Sulfur dioxide	SO2		1.00E-04		0.00076		0.0	
Carbon monoxide	CO		1.00E-04				0.0	
Water vapor	H2O		---			6.30E-09	9.8	4.51E+04
Ave. Total Press.						6.43E-08		
SUM†							83.4	

* From: The Engineering Toolbox <http://www.engineeringtoolbox.com/air-composition-d_212.html>
** Computed as ratio of VQM net partial pressure (PP) to net average total pressure uptake recorded by GP 390 gauge.
*** Enrichment factors (EF) relative to air generally follow the species molecular size (red) with the prominent exception of methane and CO (green). We suspect hydrocarbon contamination in the prototype as cause. Di-hydrogen EF is anomalously large for its size, suggesting a quantum tunneling effect or interaction with the glass. The EF of CO2 is also anomalously large for its size, suggesting hydrocarbon contamination.
† Missing PP from ca. 100% may be from unaccounted organics known to inhabit the prototype's high vacuum. The 10% lower sum for the 6/15/2015 run is likely from m/z 18 peak oversaturation for water vapor.
†† Assumed to be 100% di-nitrogen. However, CO is probably present and may be dominant at m/z 28. In that case, the E.F.'s are large (green) suggesting hydrocarbon contamination in the prototype as cause.

<u>Lab Air Runs</u>
Important because additional gases such as Ne, Ar, and perhaps CH_4, CO and CO_2 can be measured.



Instrument Power Budget



PLUS: the MS needs to be held within an Operable temperature range of 10° to 50°C! <u>Solution</u>: insulate box and add a space heater on thermostat control.