Development of Mass Spectrometer-based Instrumentation for Monitoring Deep-Ocean and Terrestrial Processes

Gary M. McMurtry
Dept. of Oceanography
School of Ocean & Earth Science & Technology
University of Hawaii

CEROS - National Defense Center of Excellence for Research in Ocean Sciences

National Science Foundation
WHERE DISCOVERIES BEGIN

Research Team

- Gary McMurtry, PI, Oceanography Dept., SOEST
- Lloyd French, project engineer, Hawaii Institute of Geophysics & Planetology
- Gindi French, technical assistant, Oceanography Dept.
- Arnaud Bossuyt, graduate student, Ocean Resources & Engineering Dept.
- Bernhard Chapligin, student trainee, University of Karlsruhe, Germany
- Technical support from SOEST Engineering Support Facility

  David Copson, ME

  James Jolly, EE

  Michael Cole, machinist

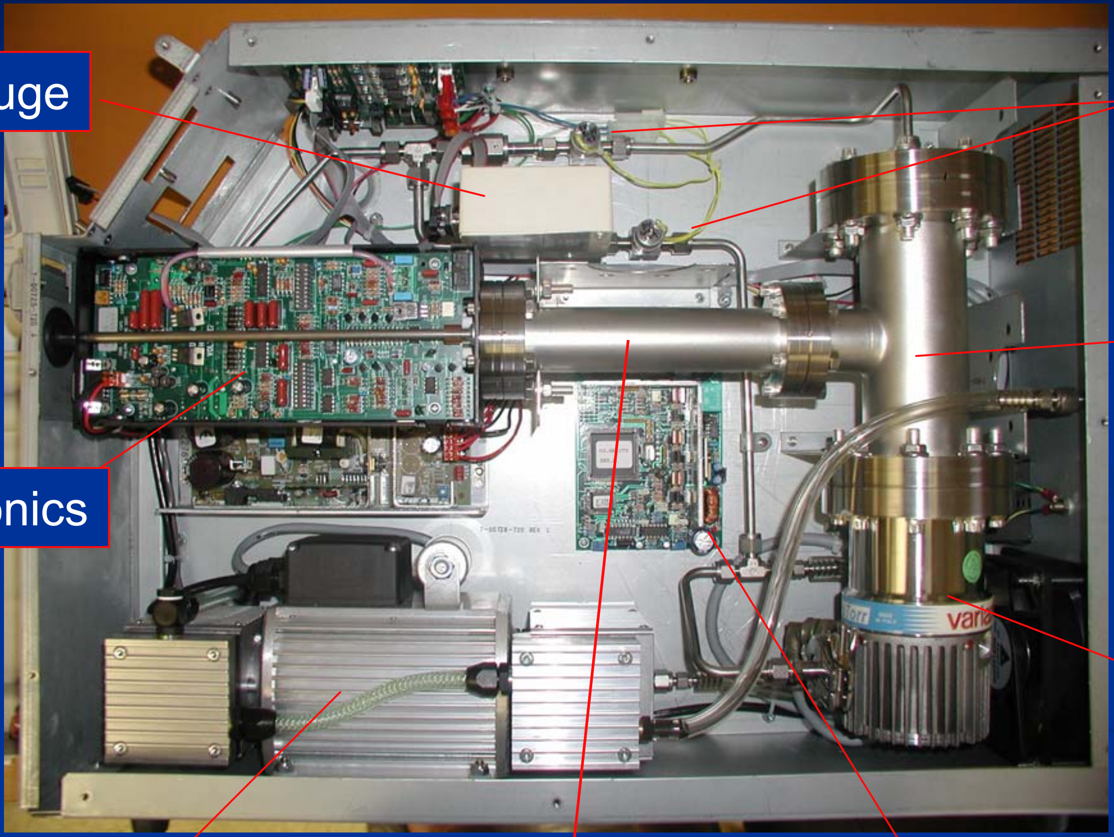
Goals of Research

- *In situ* analysis of a variety of dissolved gases and volatile organic compounds, using MIMS
- An extended presence in the deep ocean for monitoring long-term seafloor processes, with several months to a year deployment, using battery power
- High sensitivity, simultaneous chemical analysis with only modest power consumption
- Reasonably high precision and accuracy via lab MIMS calibration and *in situ* T, P corrections
- Make instrument as compact and light as possible
- Investigate volcanic gas monitoring with similar instrumental approach

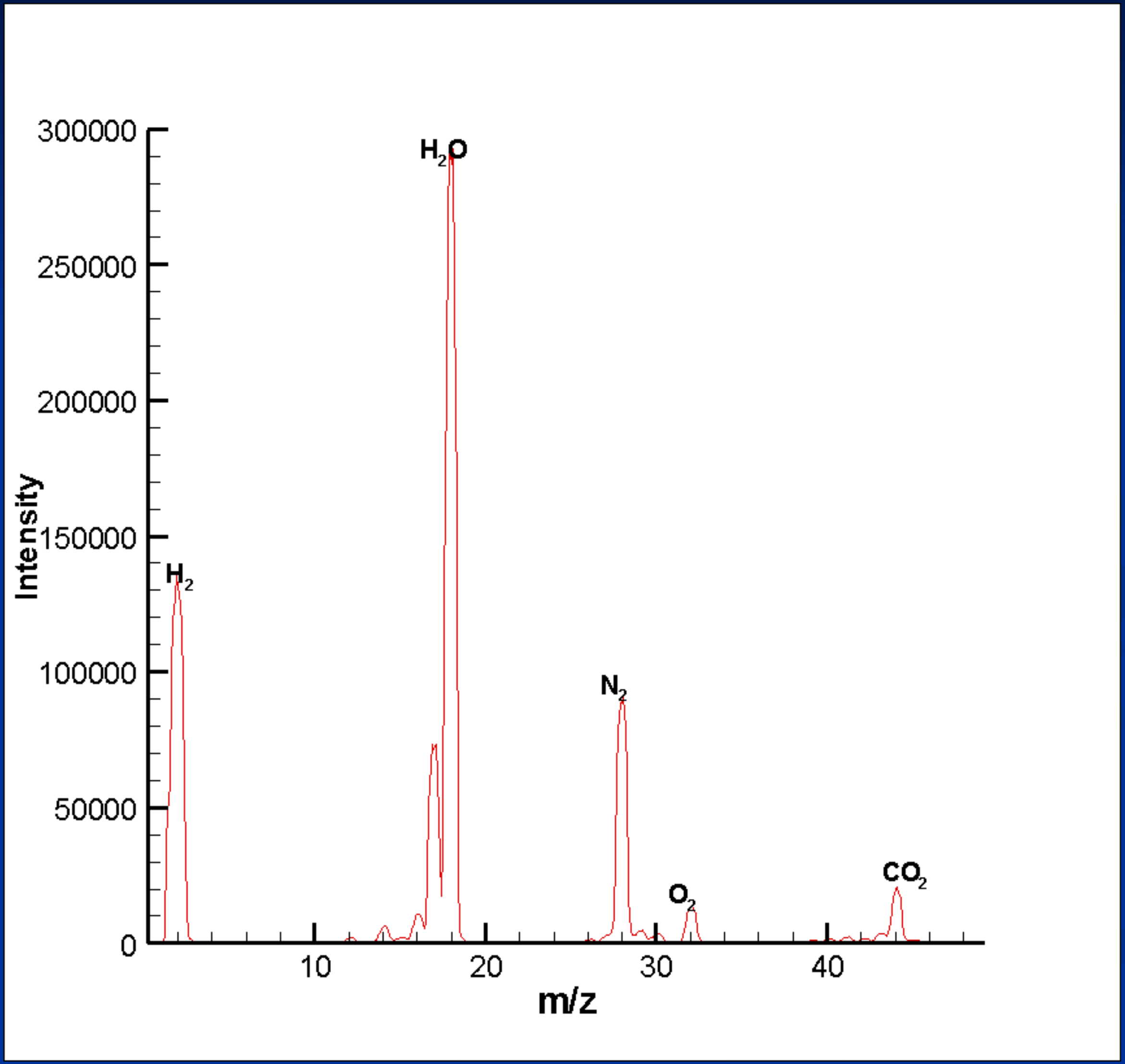
Mass Spectrometer Pros & Cons

- 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?
  - => High precision requires frequent calibration
  - => Expensive, unless self-made

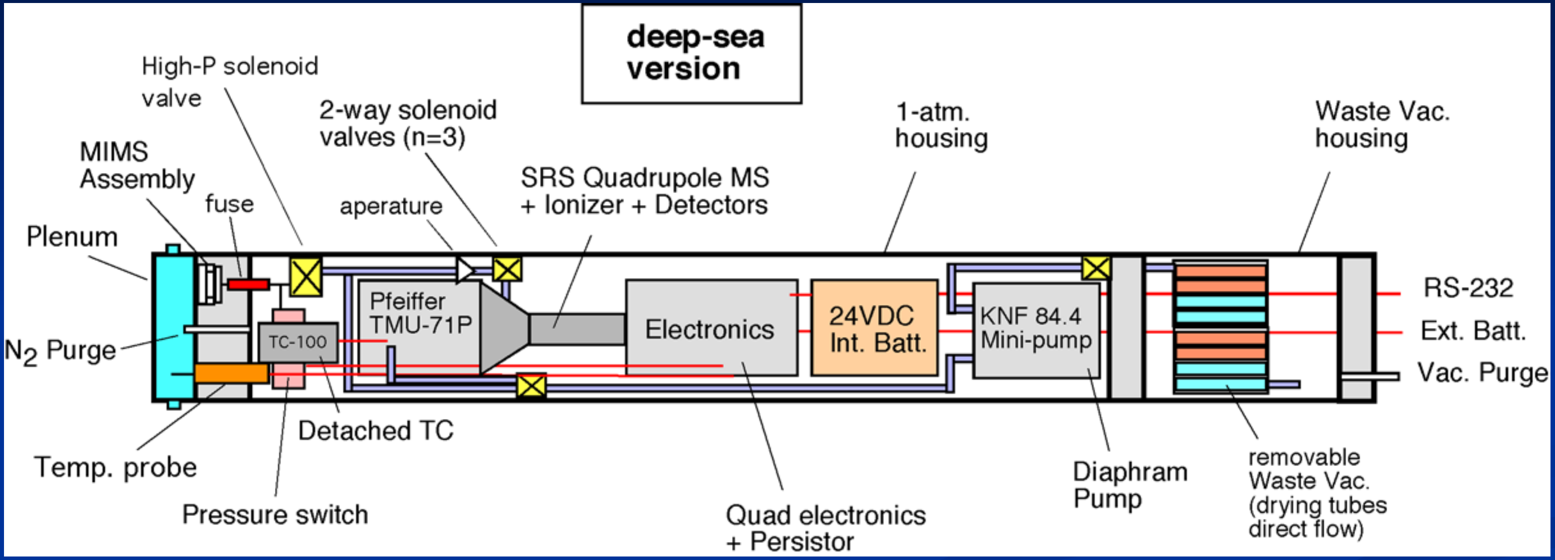
SRS QMS-200 Bench-Top Quadrupole MS



Quad mass spectrum--moist air



Deep-Ocean Mass Spect. (DOMS)



Features:

- MIMS tested to 400 bar (4,000 m water depth equivalent)
- Capable of deployments of months to a year on batteries
- Capable of real-time data via acoustic or light telemetry
- Capable of simultaneous multi-molecular monitoring of dissolved gases & volatile organic compounds

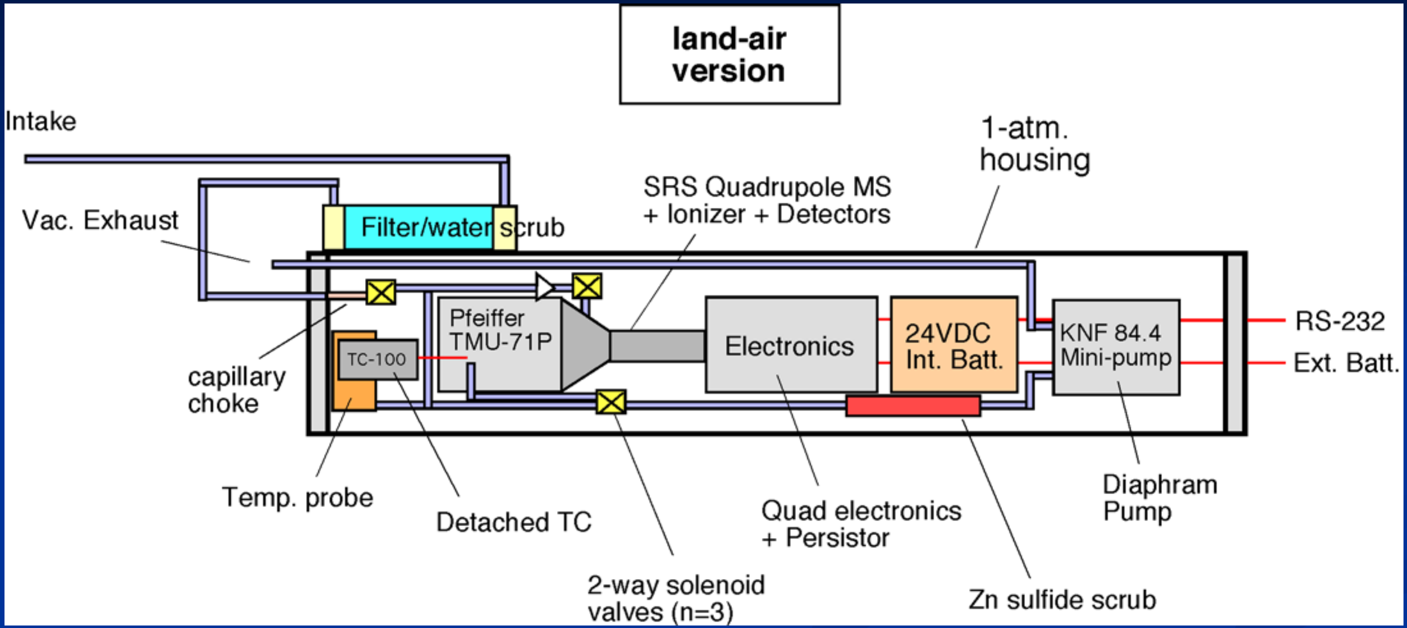
Volcanic fumarole sampling - the old fashioned way

Iwodake Volcano, Satsuma Iwojima, Japan
700° C fumarole

People Die Doing this Stuff!

Galeras Volcano, Colombia
225° C fumarole

Volcano Mass Spect. (VMS)



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

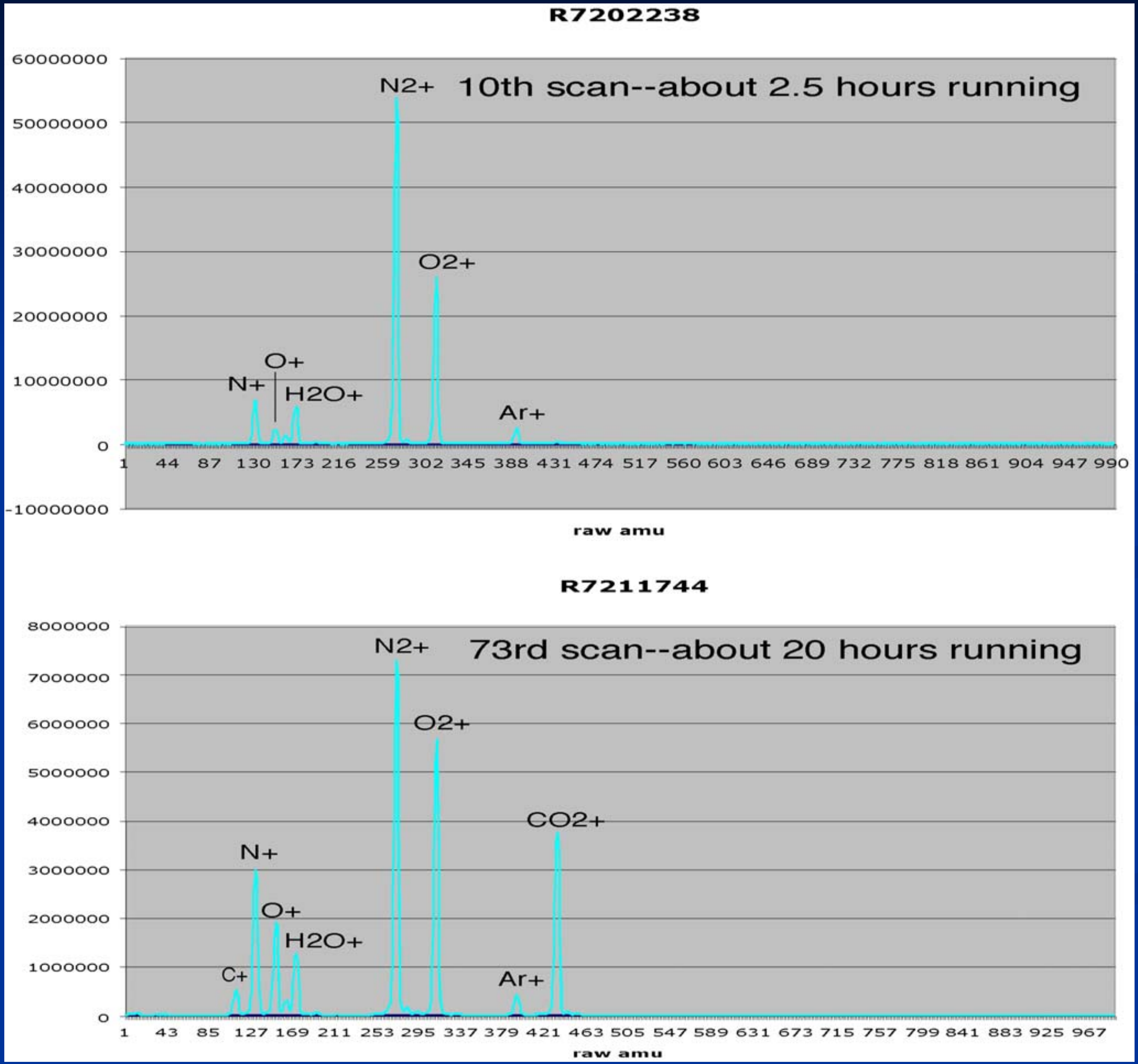
Ti corrosion-resistant housing

Bench test - VMS

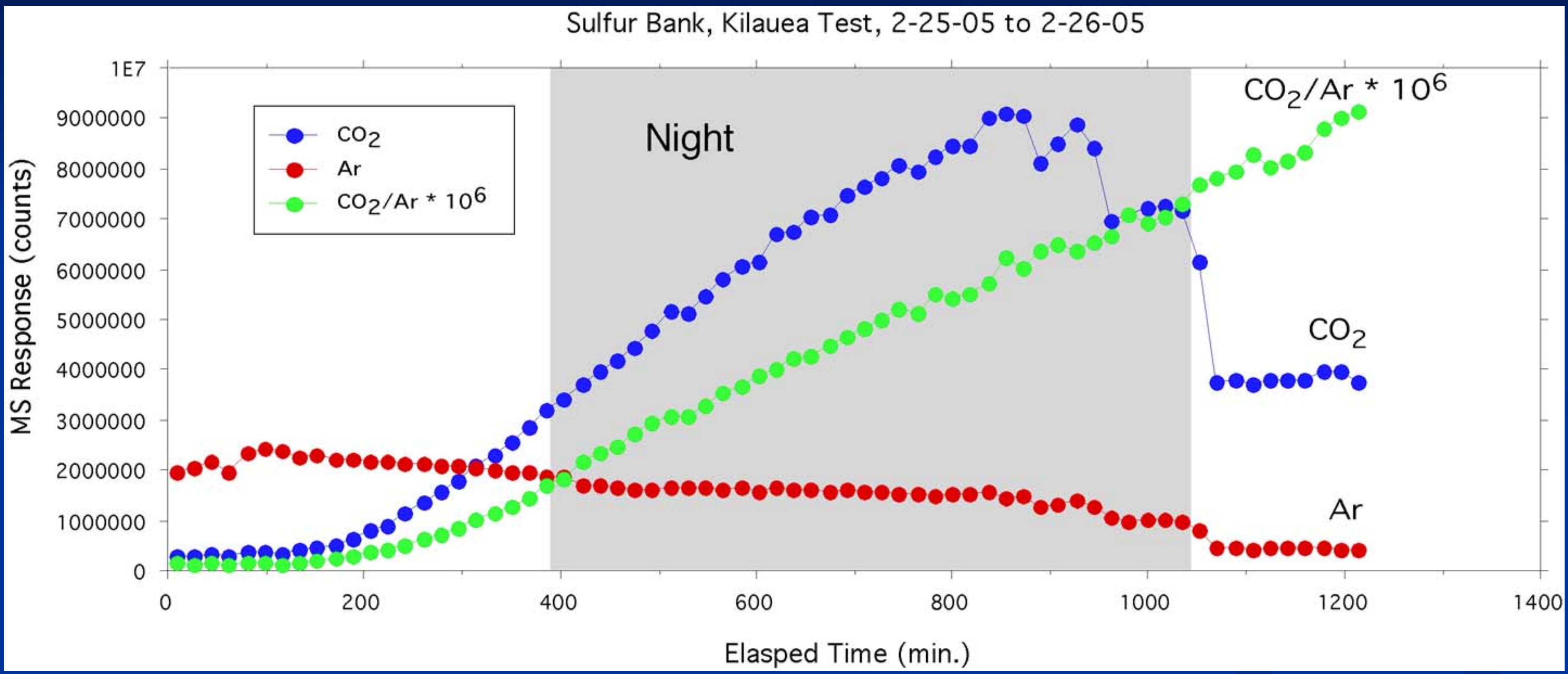
Sulphur Bank, Kilauea test

97°C fumarole

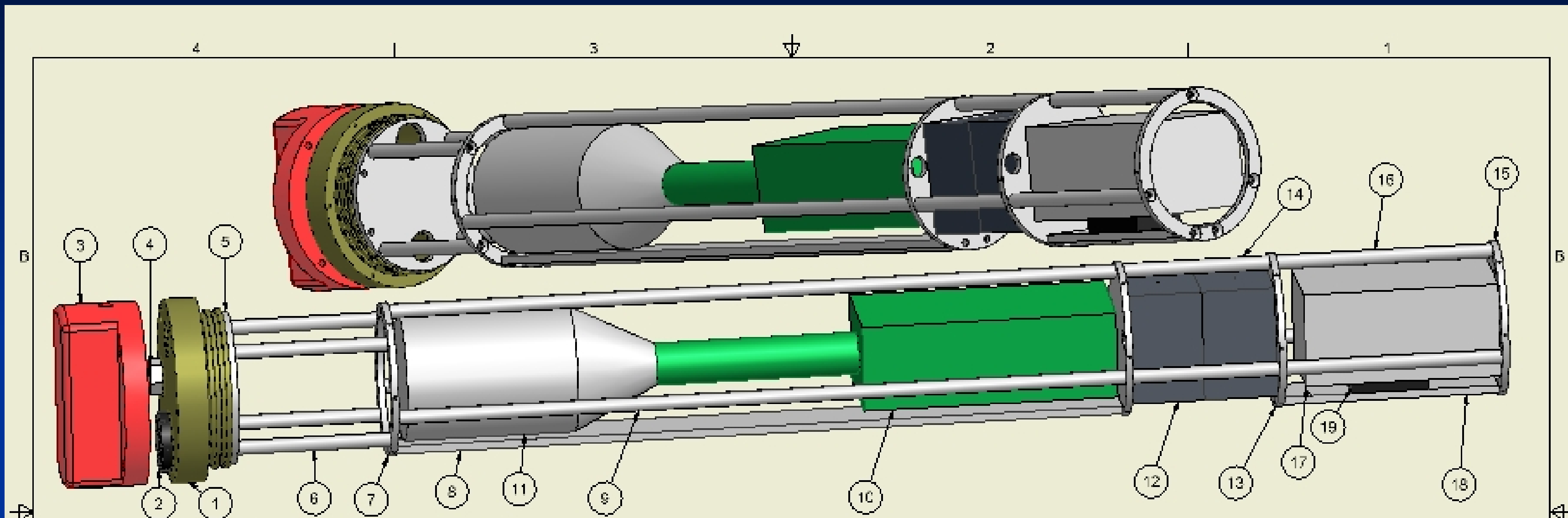
Mass scans, Sulphur Bank



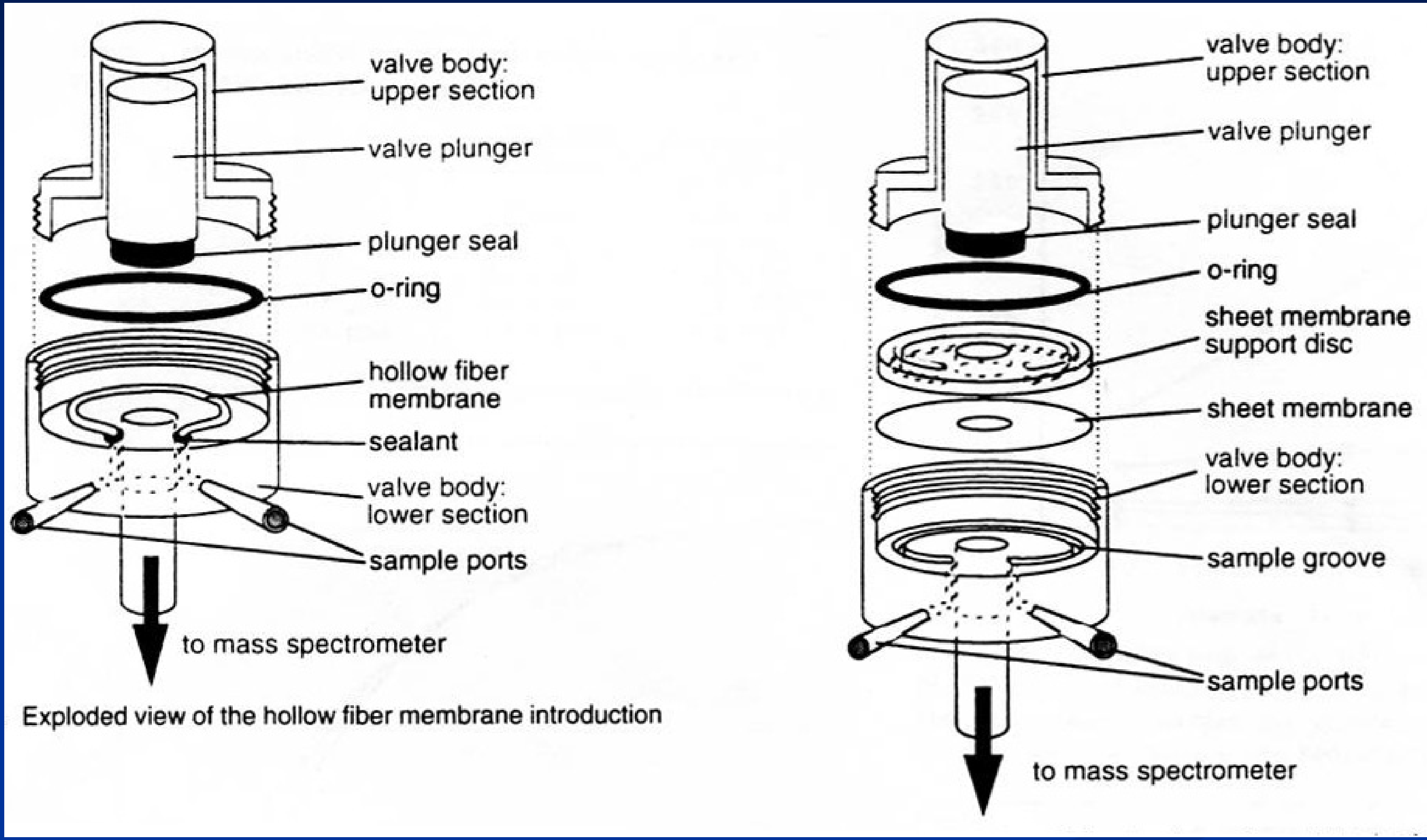
Preliminary results, Sulphur Bank



CAD Layout & Result- DOMS



Membrane Introduction Mass Spectrometry (MIMS)



Hollow Fiber versus **Sheet Membrane**

LaPack et al. (1996)

METS Methane Sensor

ASD Sensortechnik GmbH

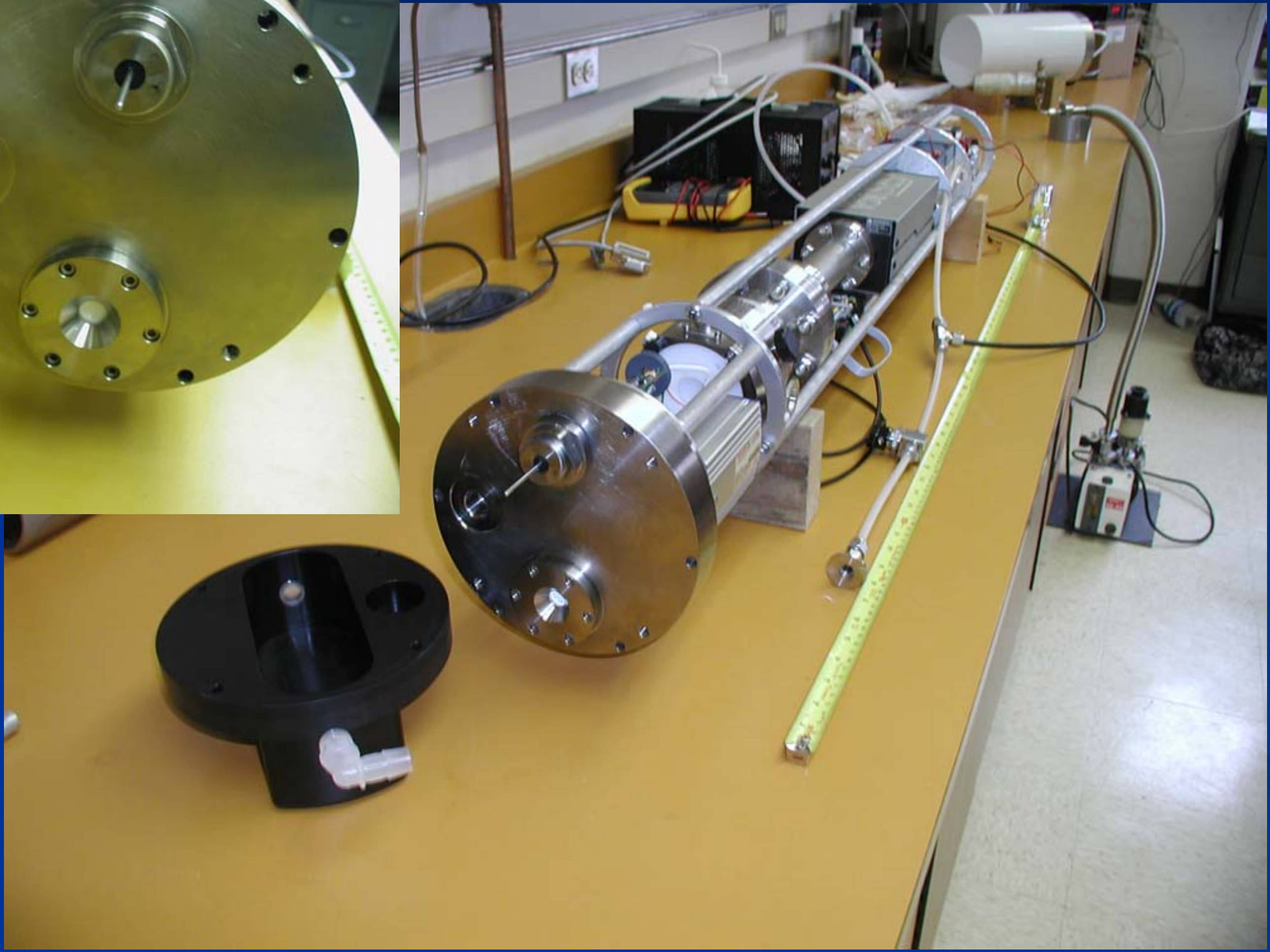
METS sensor specification:

Measuring range: 20 nmol/l to 10 µmol/l
other ranges on request between 20 nmol/l and 1 mmol/l
Resolution: at 50 nmol/l approx. 4 to 5 nmol/l
Response time: 3 to 30 min, conditionned to turbulences
Pressure range: 200 bar (other ranges on request)
Operational range: +2 to +20°C (other ranges on request)

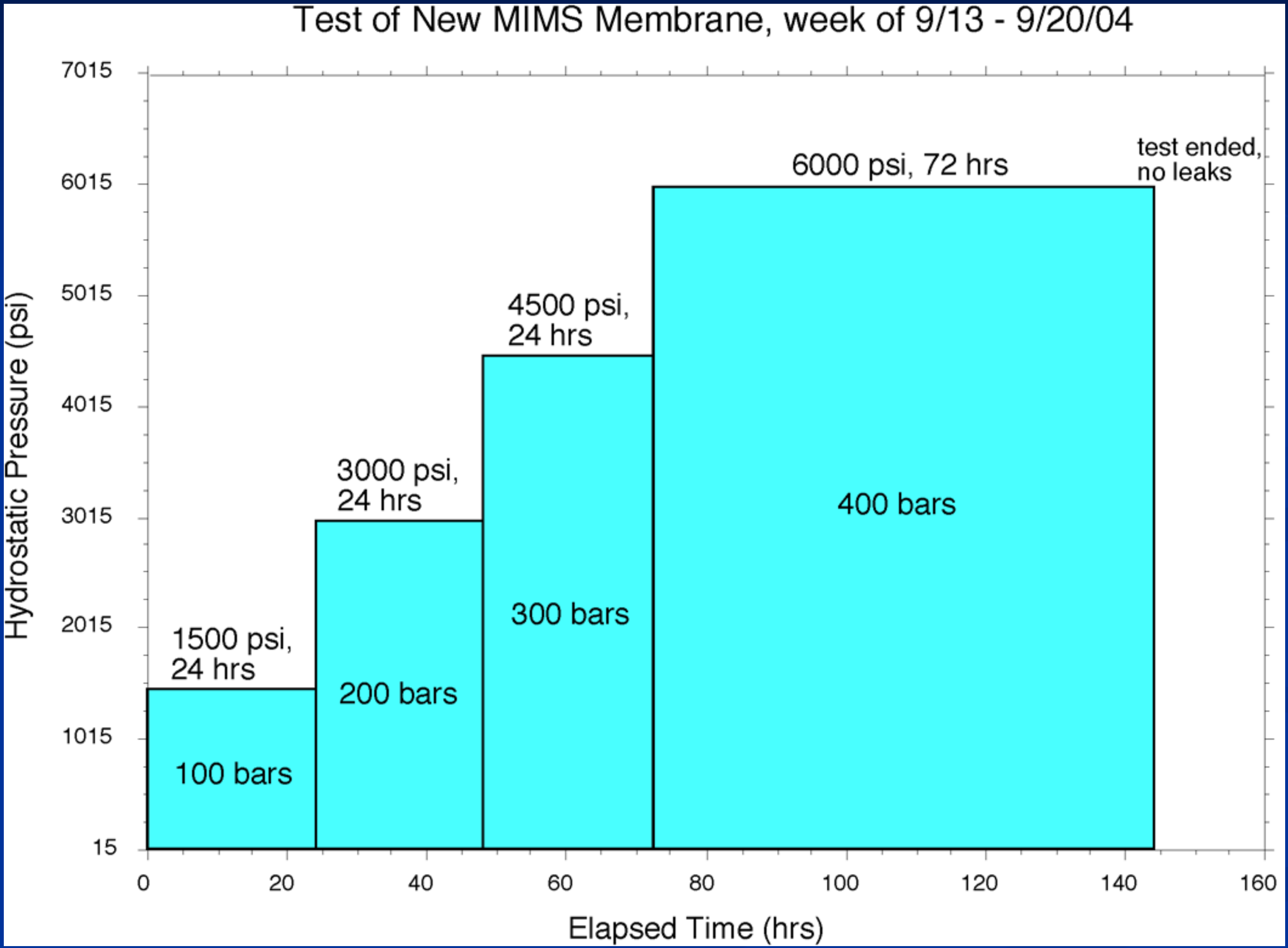
Electrical data:

Power supply: 12 V (9 to 36 VDC)
Power consumption: 230 mA (switch-on peak 400 mA)
Analogue output: 0 to ~ 5 V for methane, temperature and humidity

MIMS and chassis layout



High-Pressure Test of MIMS Membrane



Energy Budget-DOMS

instruments (in order of operation)	Voltage (V)	Current (A.)	Power (W) peak	time(sec) peak	Watt/sec peak	Power (W) steady	time(sec) steady	Watt/sec steady	Watt/sec total
Seabird (temperature probe)	9	0.01	0.09			0.09	10	0.9	0.9
By pass SV (vacuum valve)	24	0.50	12.00			12.00	600	7200	7200
Hi. Vac. SV (behind aperture)	24	0.50	12.00			12.00	600	7200	7200
Waste SV (vacuum valve)	24	0.50	12.00			12.00	600	7200	7200
Diaphragm Pump	24	0.63	15.00			15.00	600	9000	9000
Turbo Pump	24	3.90	93.60	150.0	14040.0	21.60	390	8424	22464
RGA (quadrupole MS)	24	2.50	60.00			60.00	360	21600	21600
								60624.9	74664.9
							Watt/hr.		**20.7**
						total battery	Watt/hr.	**alkaline**	3000.0
						7" dia. X 24"	# samples		144.6
								lithium	6000.0
							# samples		289.3

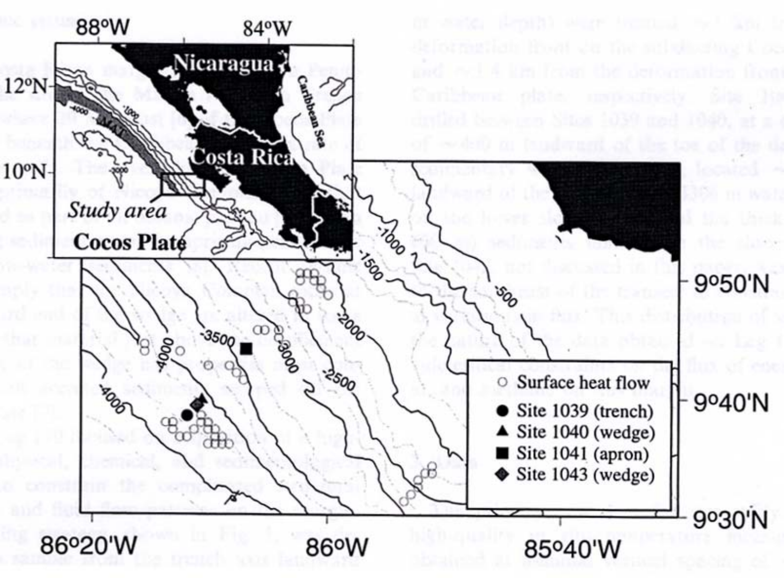
Ten minute sample period @ 1/day = 145 days (4.5 months) alkaline, 289 days (>9 months) lithium

Waste Vacuum Experiment

About 7+ days of continuous sampling…may not be a problem.

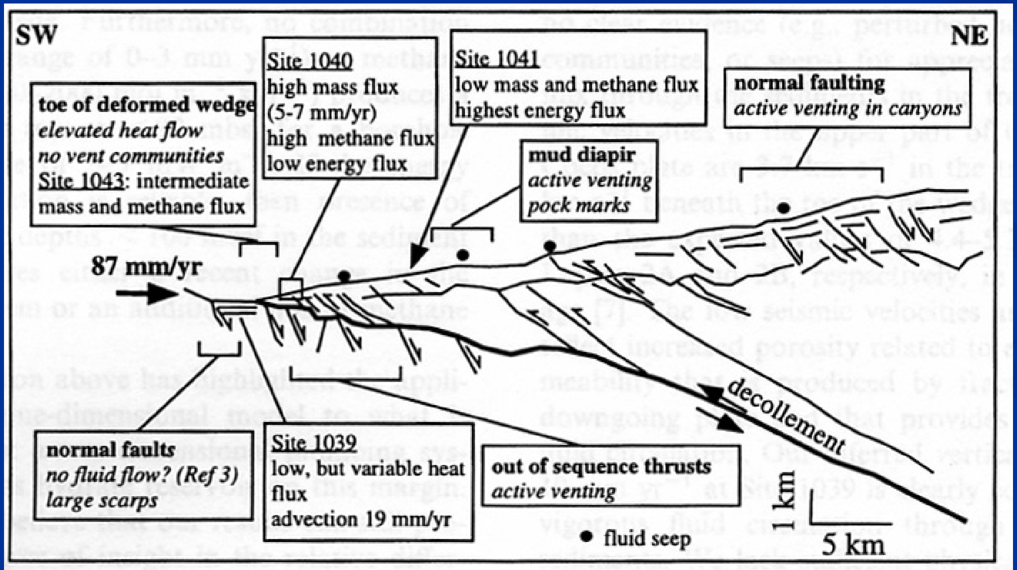
Carbon Flux from Margins-
Chemical Oceanography Program, NSF

Costa Rica margin seeps

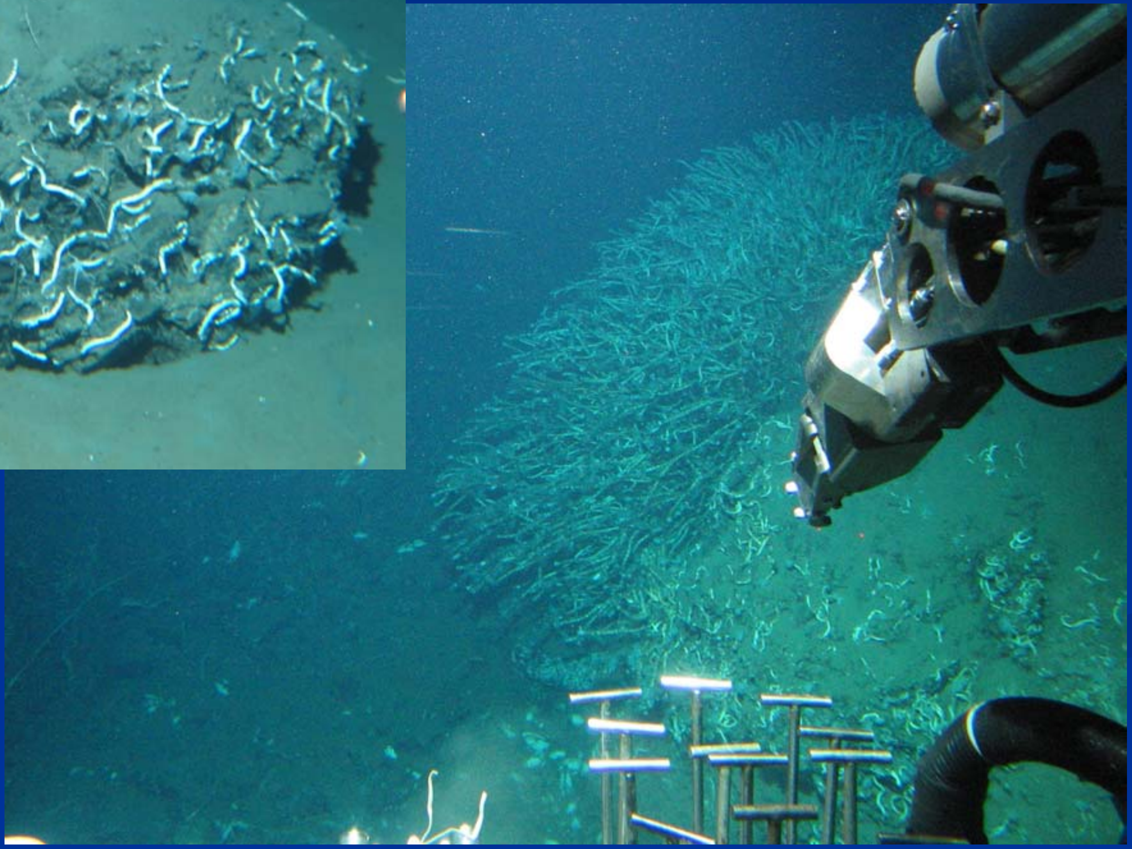


Active Margin Gas Hydrate Province
ODP Leg 170 results

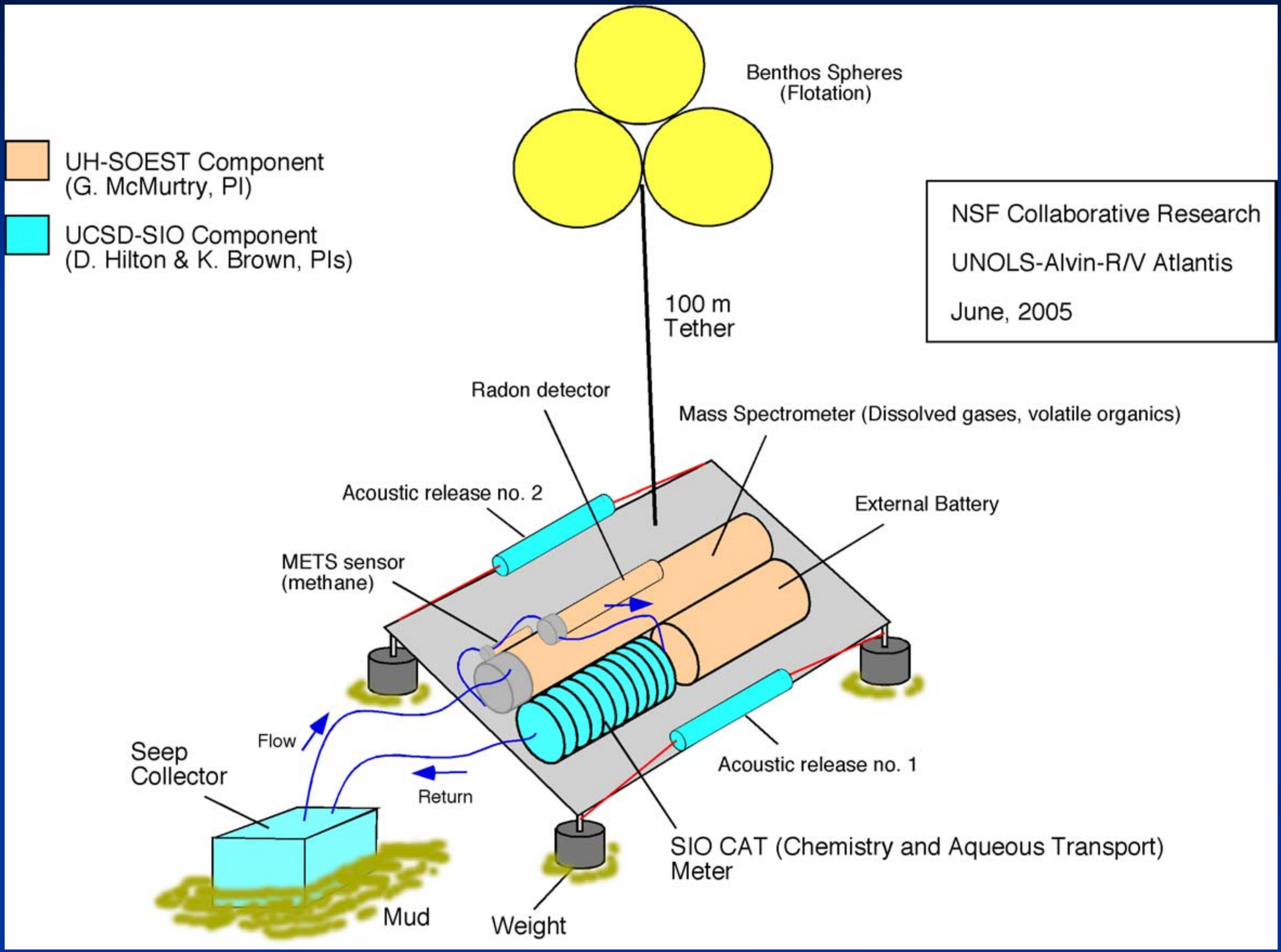
Ruppel & Kinoshita (2000)



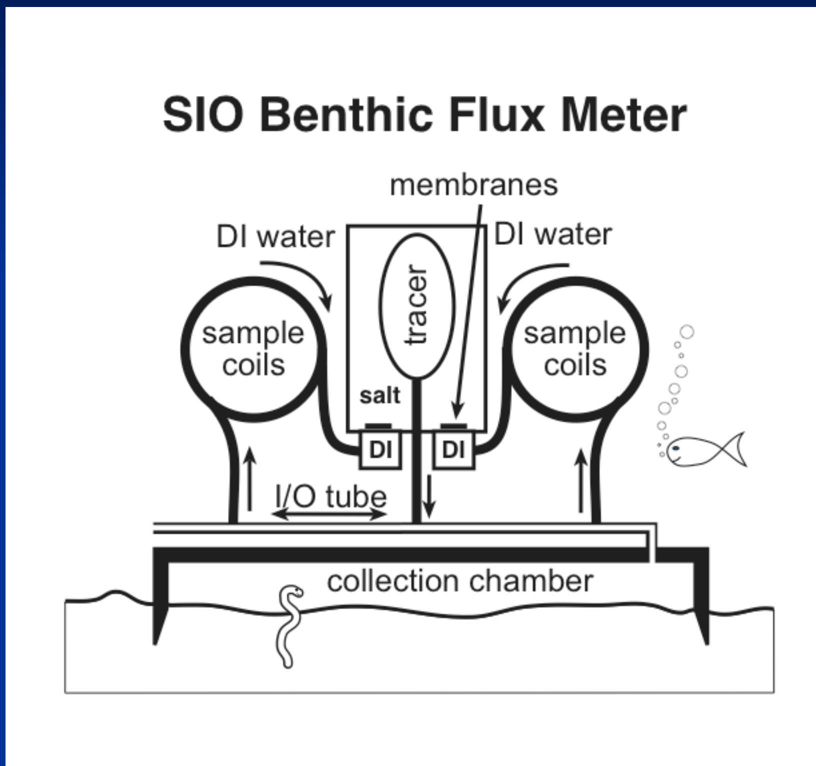
Costa Rica Cold Seep Mounds



Costa Rica Margin Deployment



SIO Chemical and Aqueous Transport (CAT) Meter



Clever method for long-term chemical monitoring at minimal power--
The major drawback is “after-the-fact” sampling approach.

CAT meter - Monterey Bay results

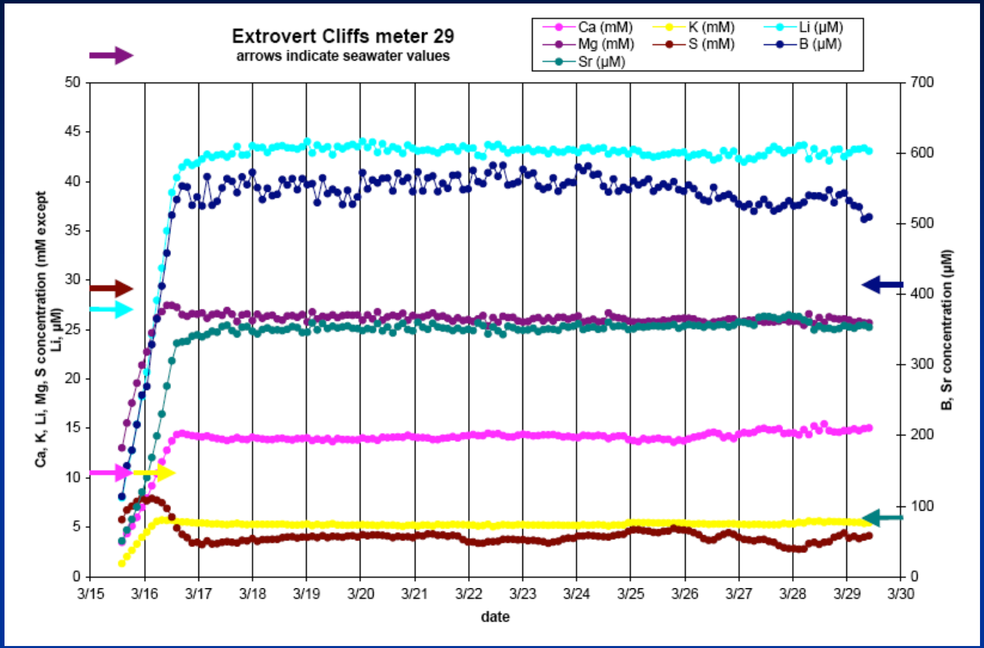


Figure 2. Fluid chemistry as a function of date for the March, 2004 CAT deployment at Monterey Bay.

D. Hilton & K. Brown, pers. comm., (2004)

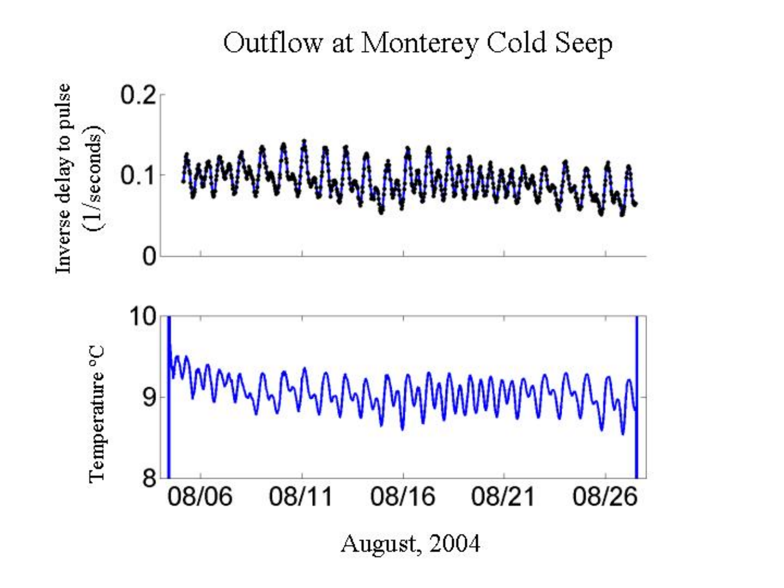
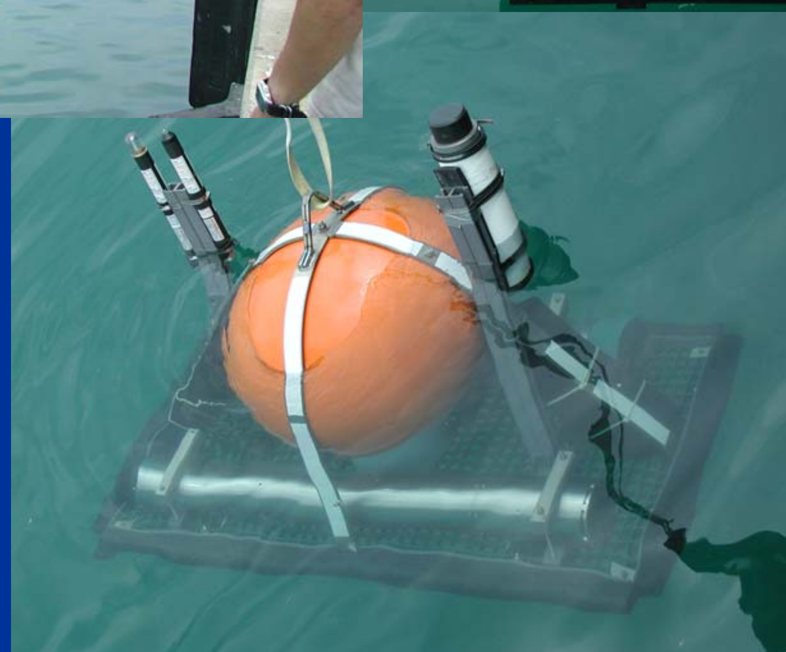
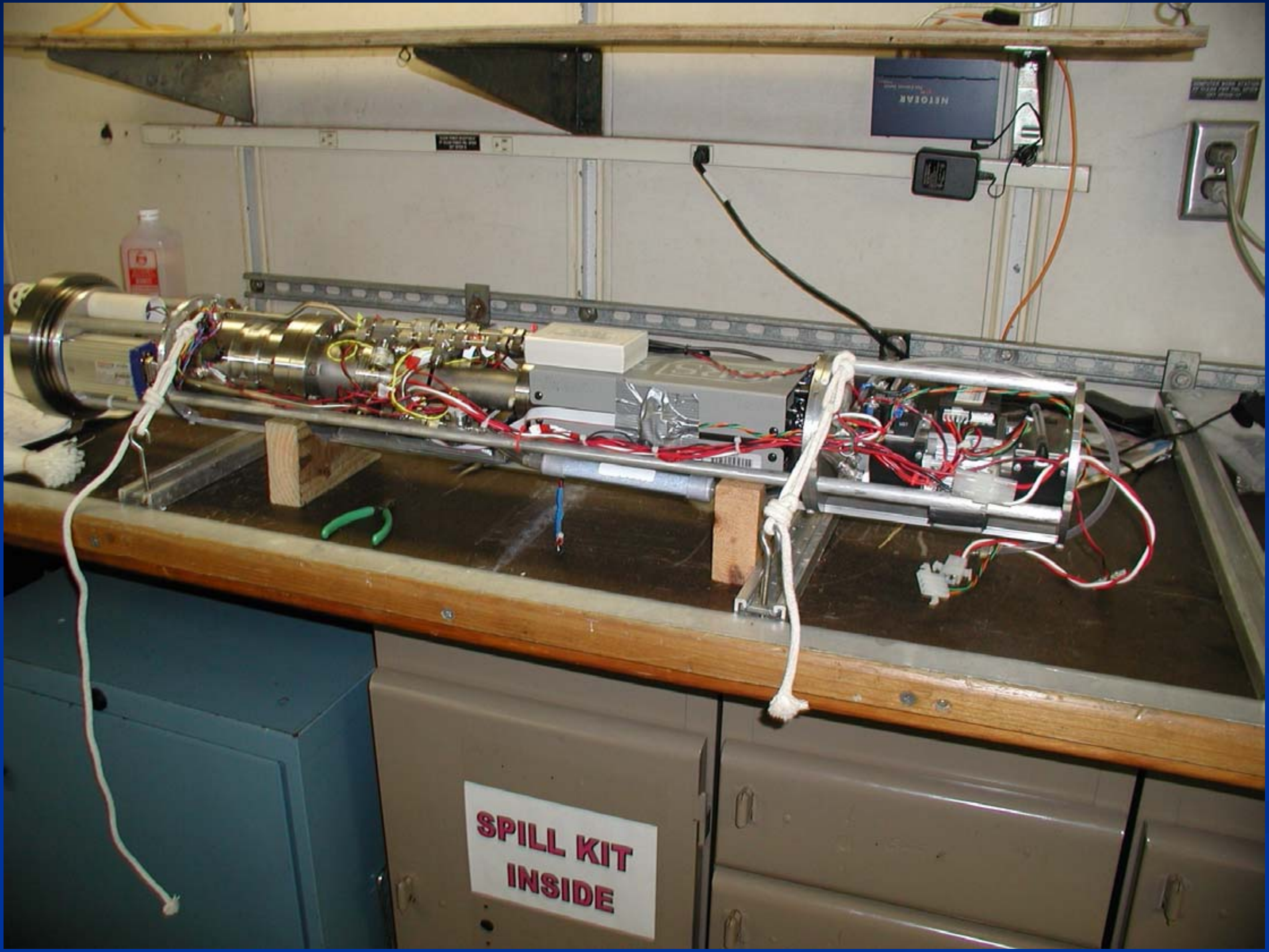


Figure 3: Relative changes in flow rate (upper) correlating with temperature fluctuations (lower). Both records show the influence of (deep) source fluids with an overprint of tidal loading.

Deployment Mainframe Test



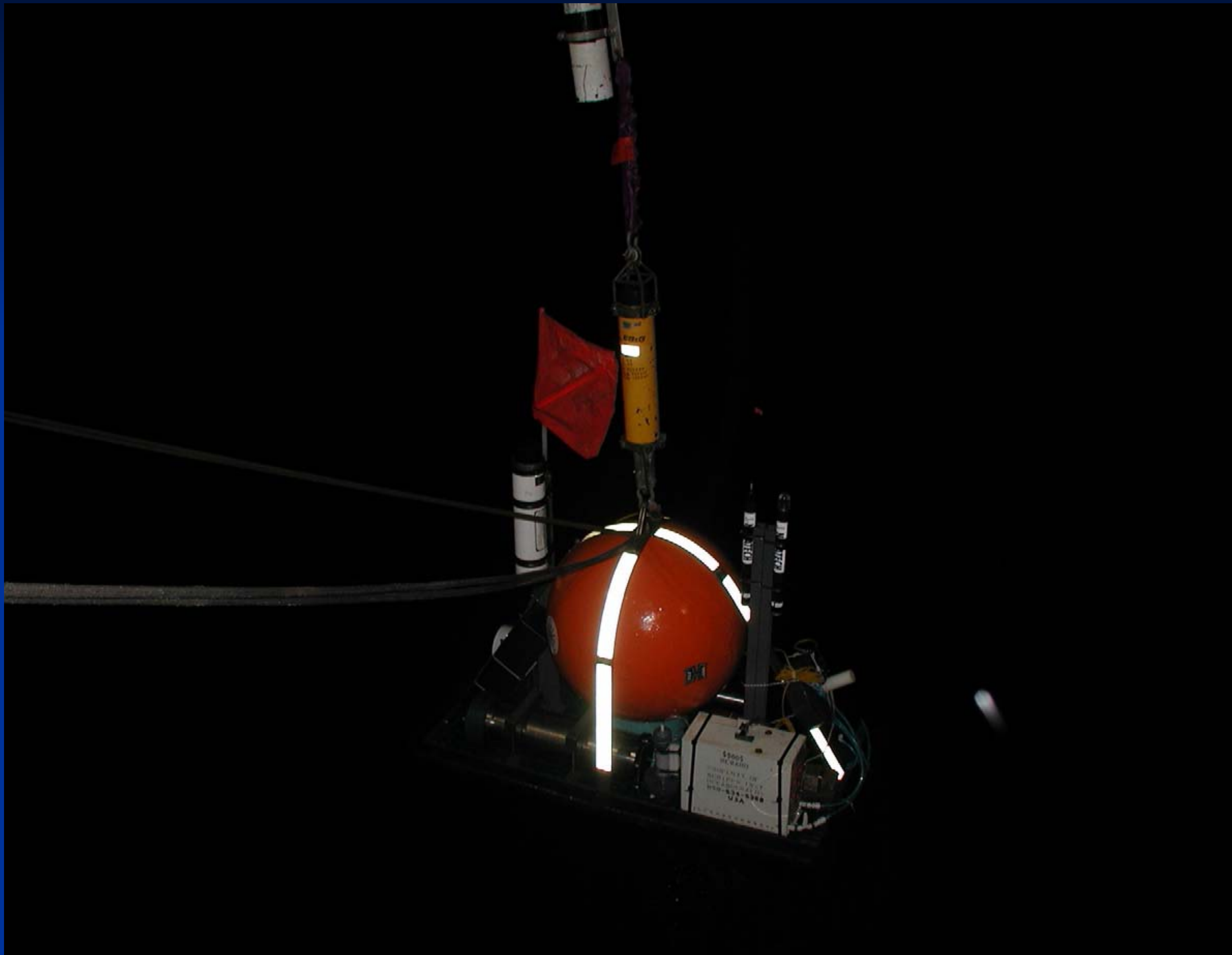
Final Assembly-DOMS



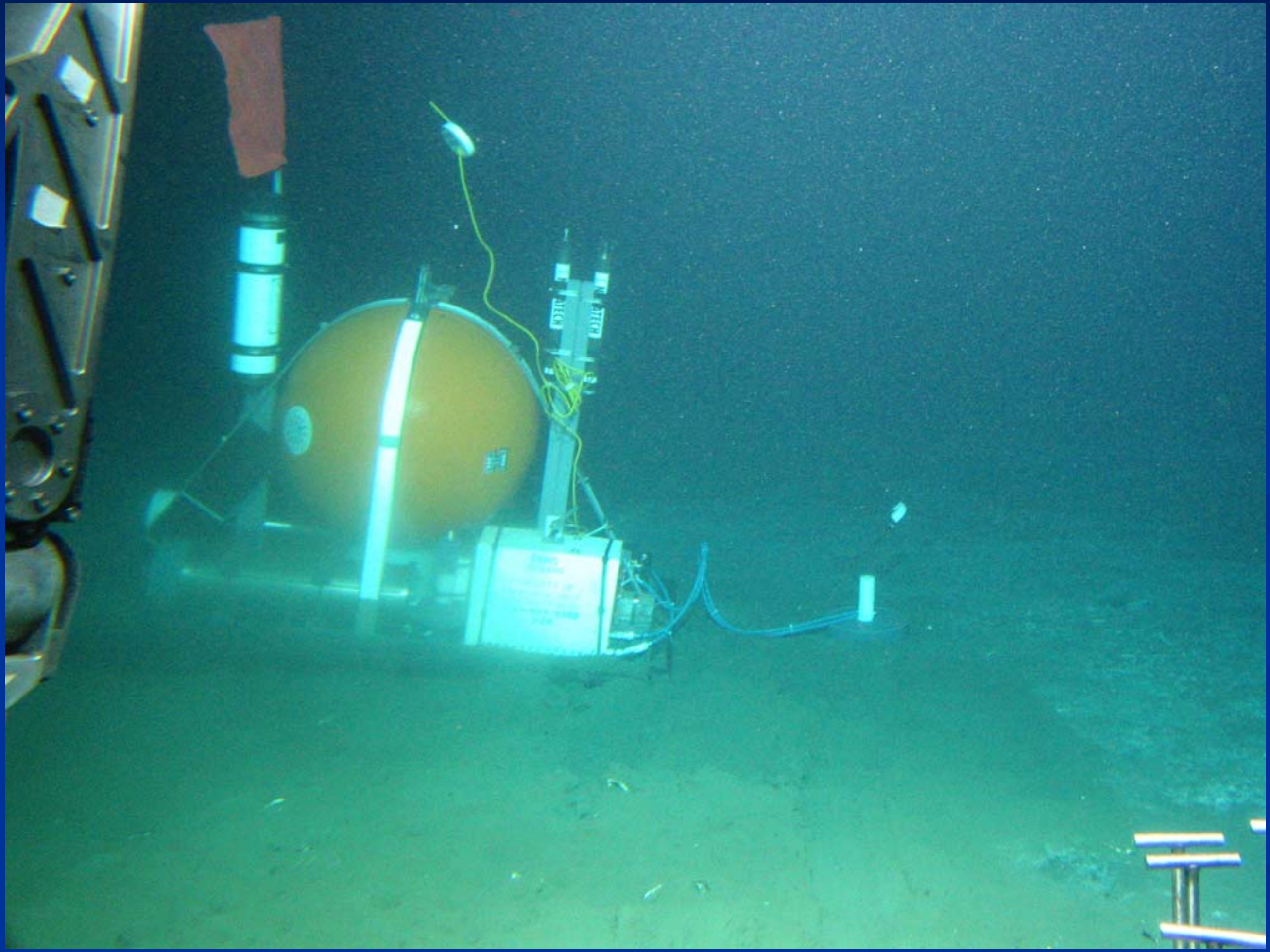
Attaching the Waste Vacuum Chamber

Final Shipboard Assembly & Test

Over the side--R/V Atlantis

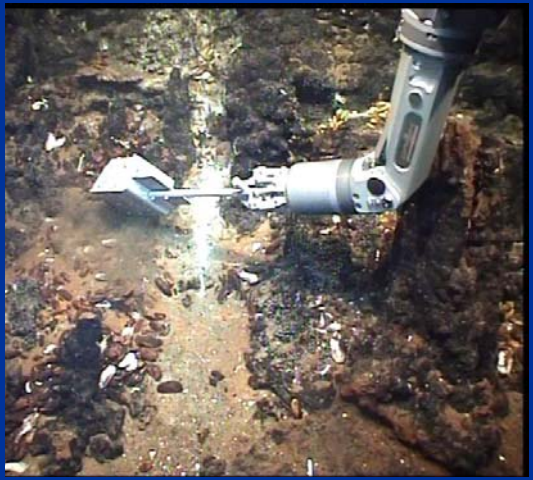


Alvin Deployment, 1000-m, Costa Rica Margin



METEOR M66

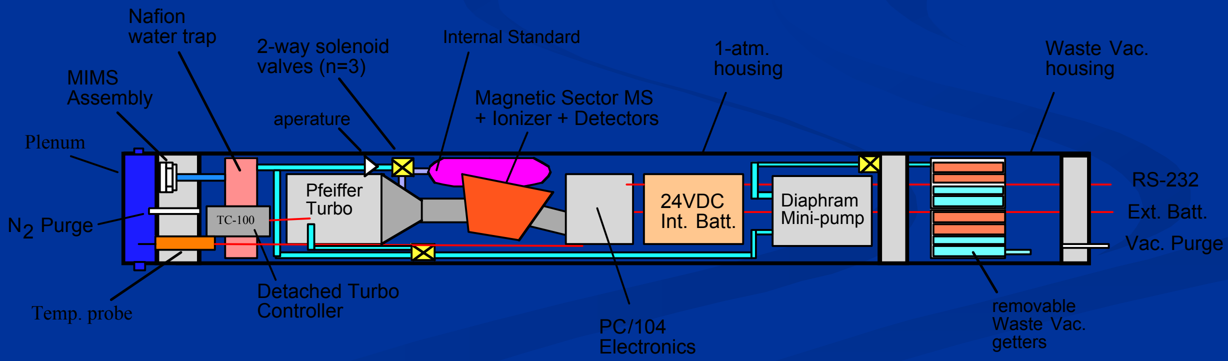
Leg 2b: ROV Quest (MARUM, Bremen)



Other & Future Research Directions

MassSURFER Aqueous Monitoring with RFMS

In situ Isotopic ^{16}O, ^{17}O, ^{18}O Analysis of O_2 by Sector/Cycloid MS



Conclusions

- We are on our way toward a long-term *in situ* analysis tool on the seafloor using MIMS. Real-time and long-term analysis in the field should be possible
- Power is still a problem, but can be overcome by additional batteries, fuel cells, or a power cable
- Waste vacuum appears not to be a big problem (at present rates)
- ASD membrane can go deep (> 4 km--a record), but 10 µm thickness has rapid diffusion characteristics under vacuum
- Volcano monitoring looks feasible, but water vapor is a major problem--will know more soon
- Costa Rica deployment in 2005 will offer *in situ* ground truths
- Other *in situ* MS approaches (aqueous and isotopic) are promising