Probing Marine Biogeochemistry with *in situ* Mass Spectrometry

Daniel Hoer

Harvard University

Underwater Mass Spectrometry and Marine Biogeochemistry

- Underwater Mass Spectrometry Primer
- Strengths, Weaknesses, and Field Experiences
- Overcoming Weaknesses: Technological Future Directions
- Future scientific applications

Why *in situ* Mass Spectrometry?

- Why *in situ*?
- Field-Tested Systems
  - *Technical University Hamburg - Harburg*
  - *USF - COT*
  - *MIT/WHOI*
  - *AWI*
  - *University of Hawaii*
  - *Harvard/MBARI*
- >25 publications since 1999

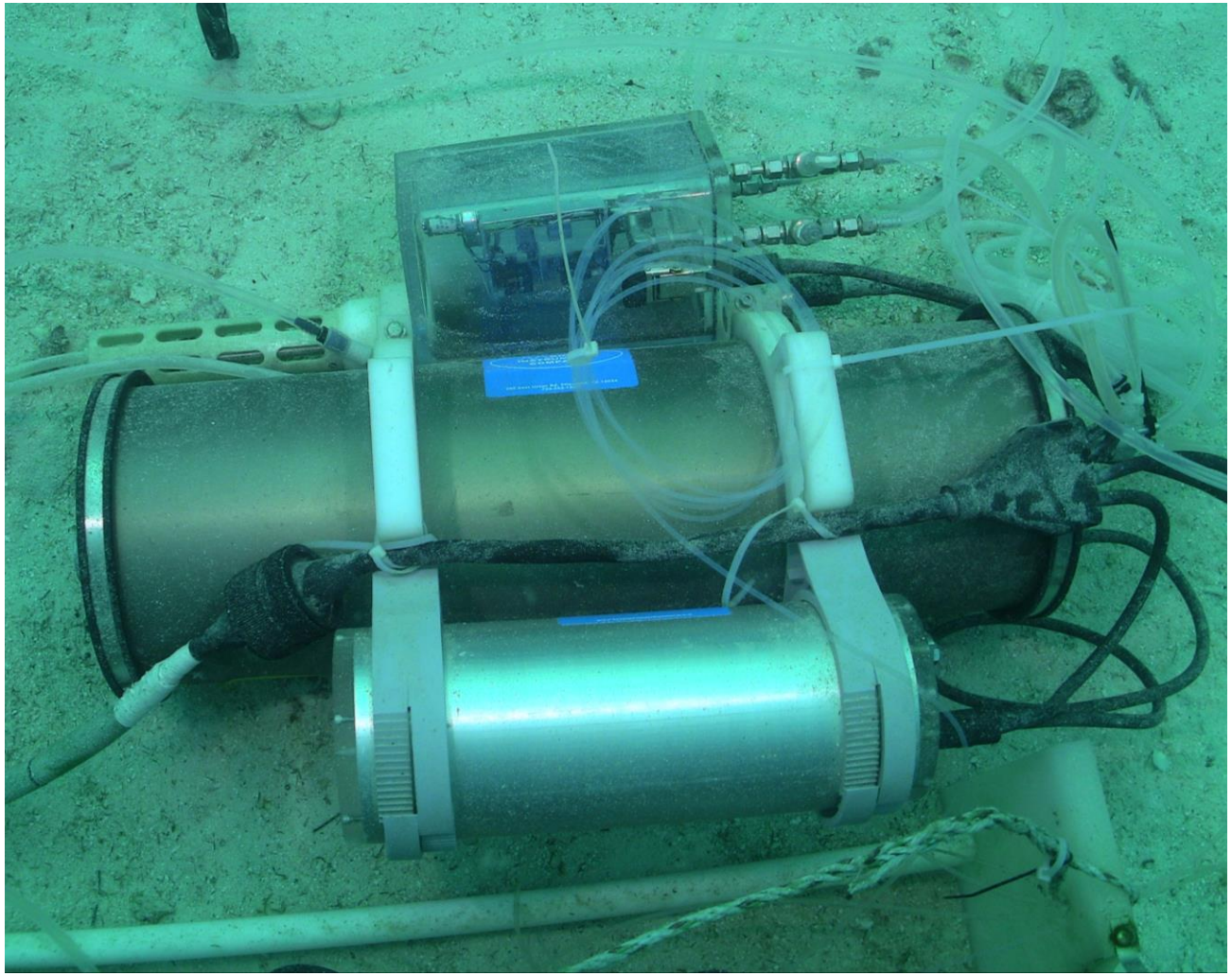
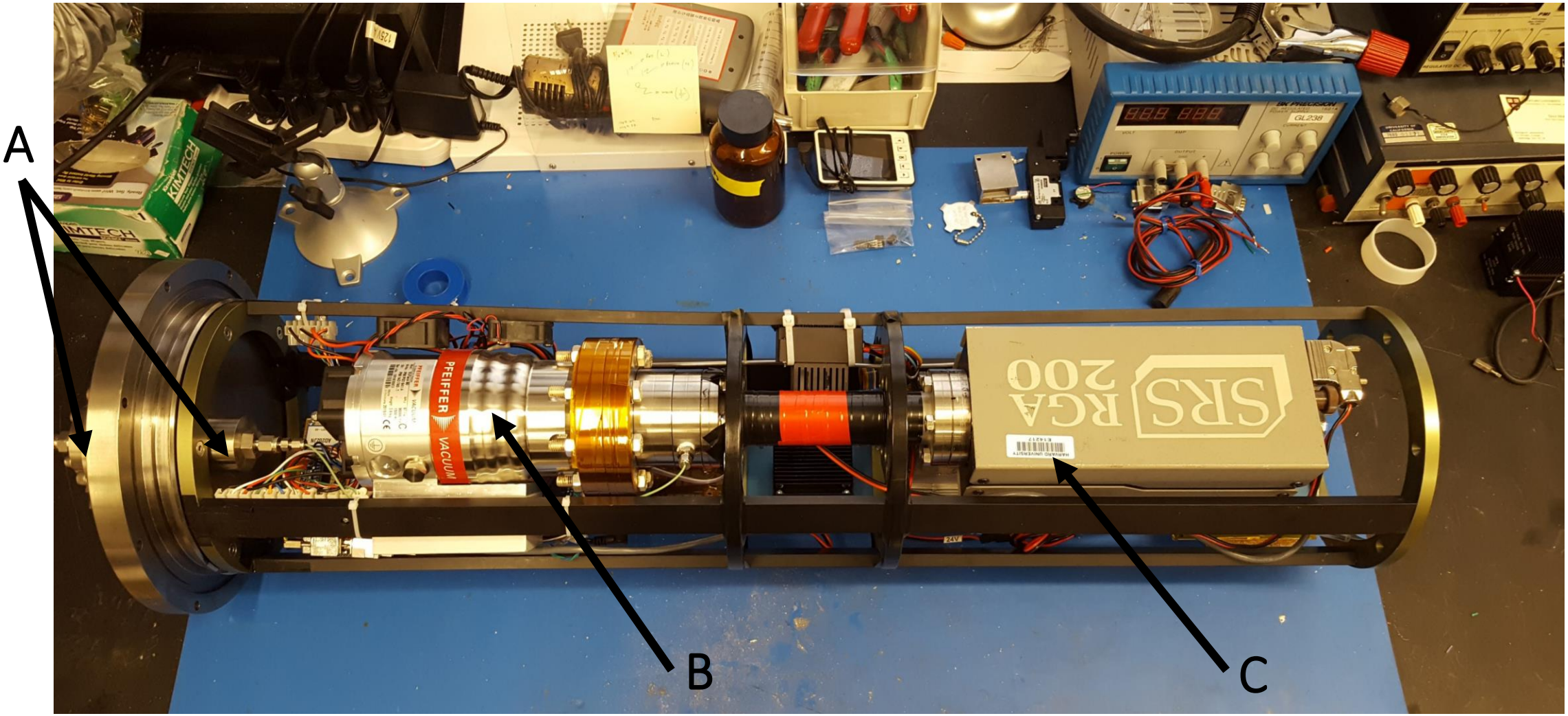


Photo: C. Martens (UNC-CH)

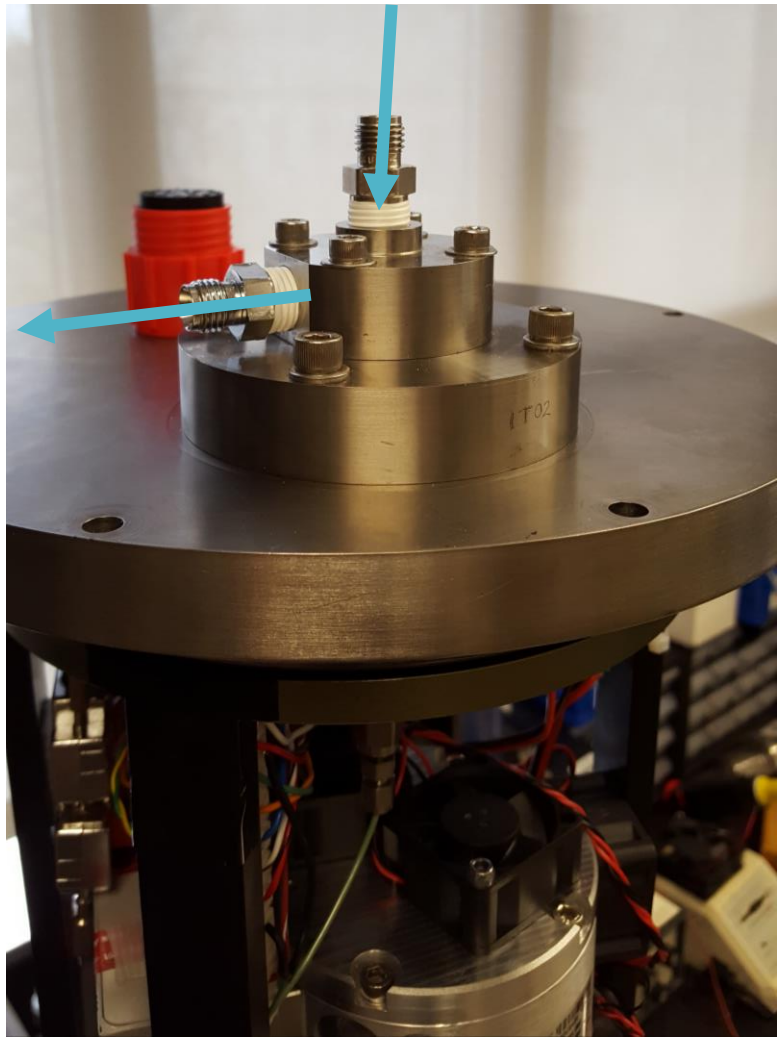
Underwater Mass Spectrometry Primer



Harvard ISMS System

Underwater Mass Spectrometry Primer

- Membrane Inlet Mass Spectrometry
  - *Membrane Diffusion*
  - *Dissolved Volatiles*
- Wide Range of Target Analytes
  - *Analytes < 300 amu*
  - *Common Dissolved Gasses*
  - *Volatile Organic Compounds (VOCs)*

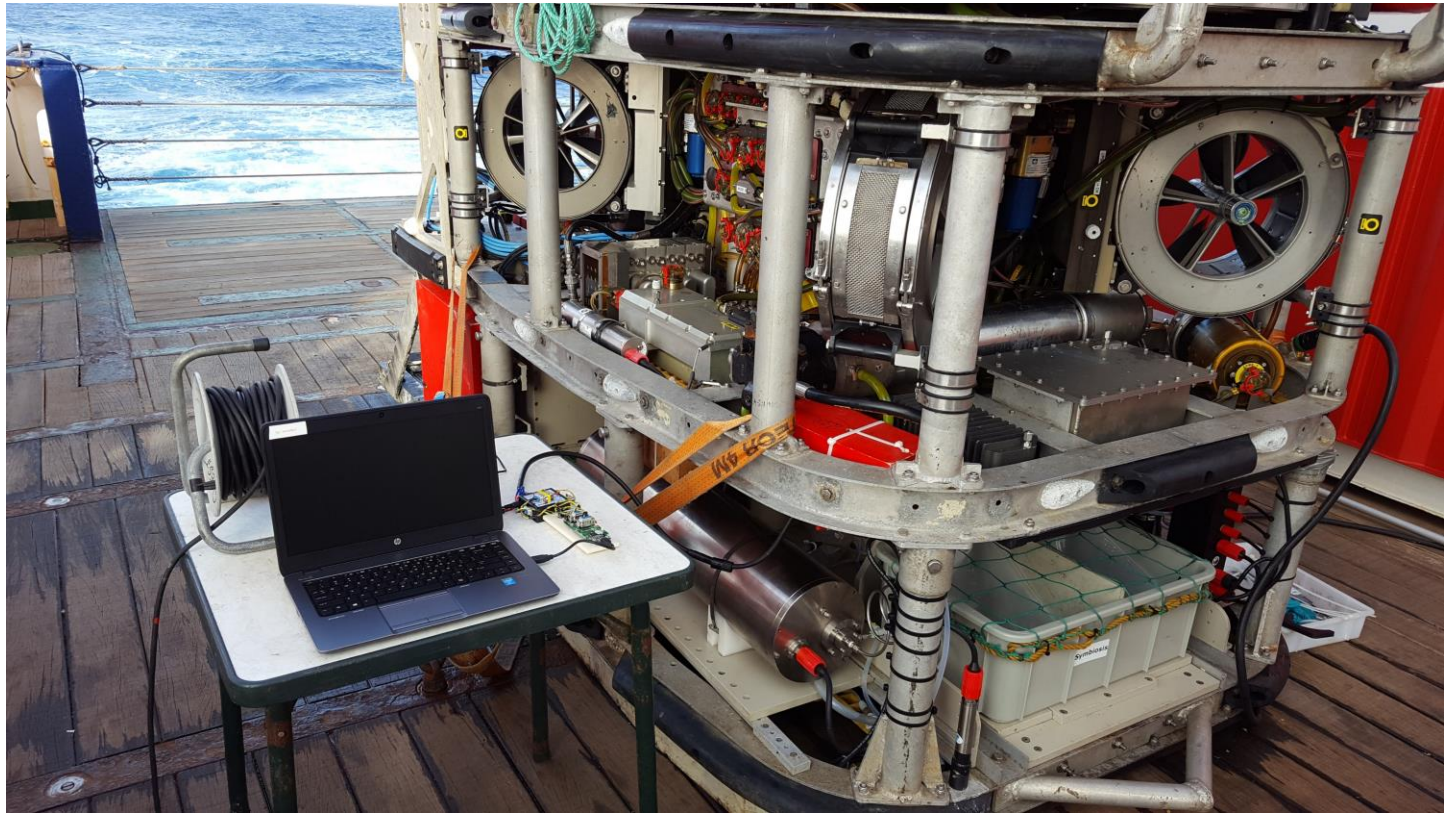


Harvard ISMS Sample Inlet

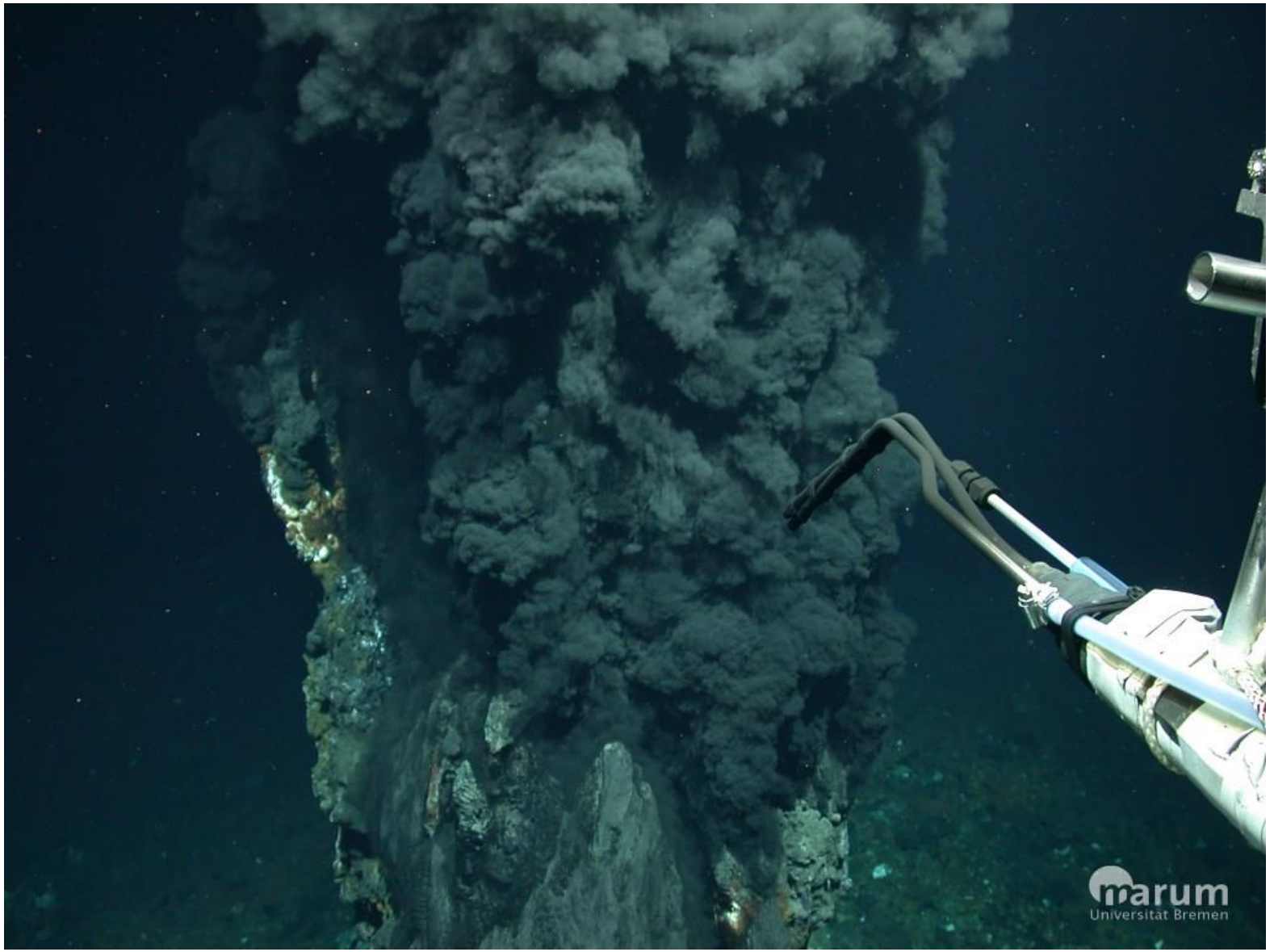
Deploying an *in situ MS*

Photo: U. Washington Regional Scale Nodes

Deploying an *in situ MS*



Deploying an *in situ* MS

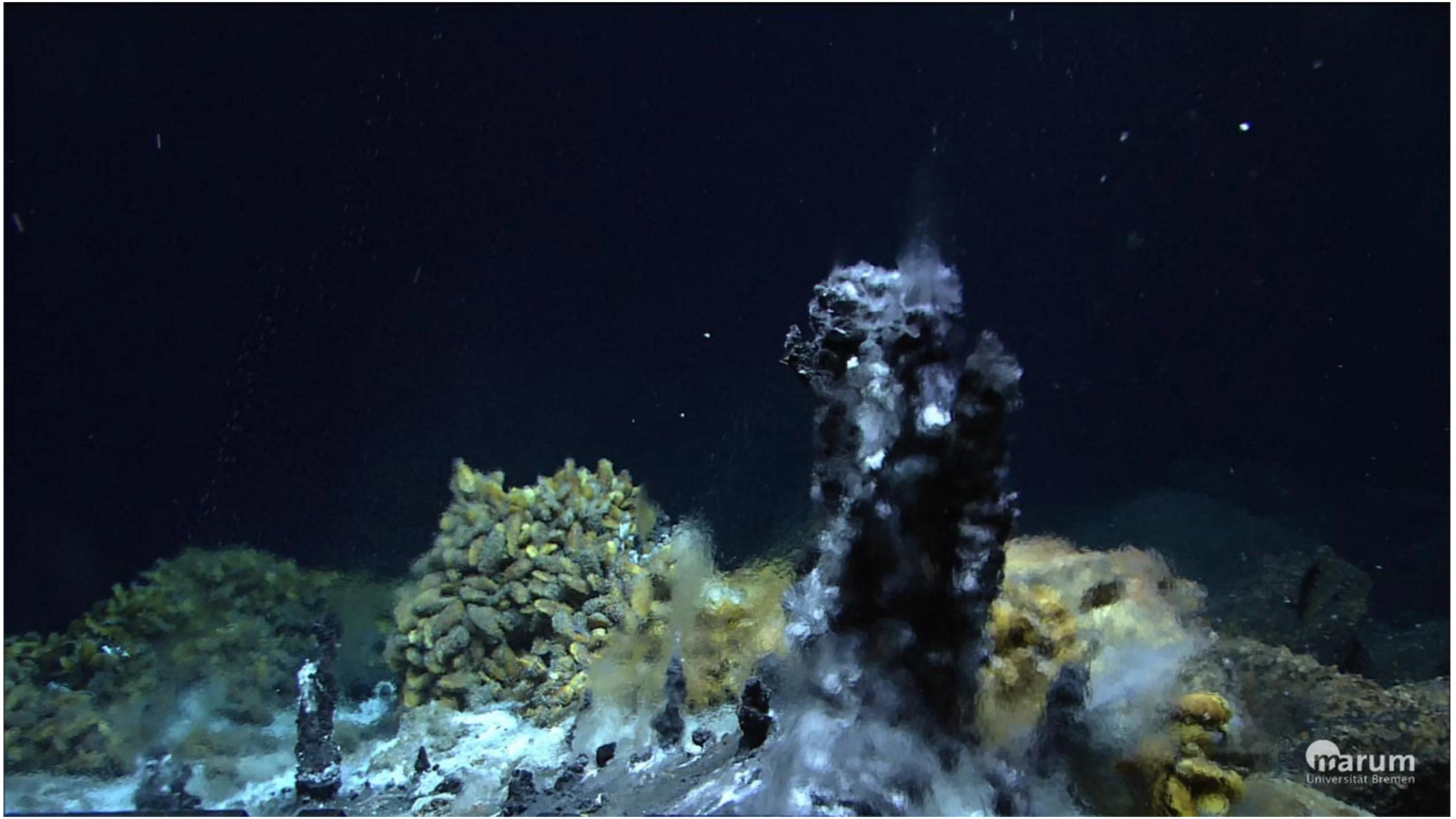


Harvard ISMS Sampling a Hydrothermal Chimney; Photo: ROV Quest

Strengths of the Harvard ISMS

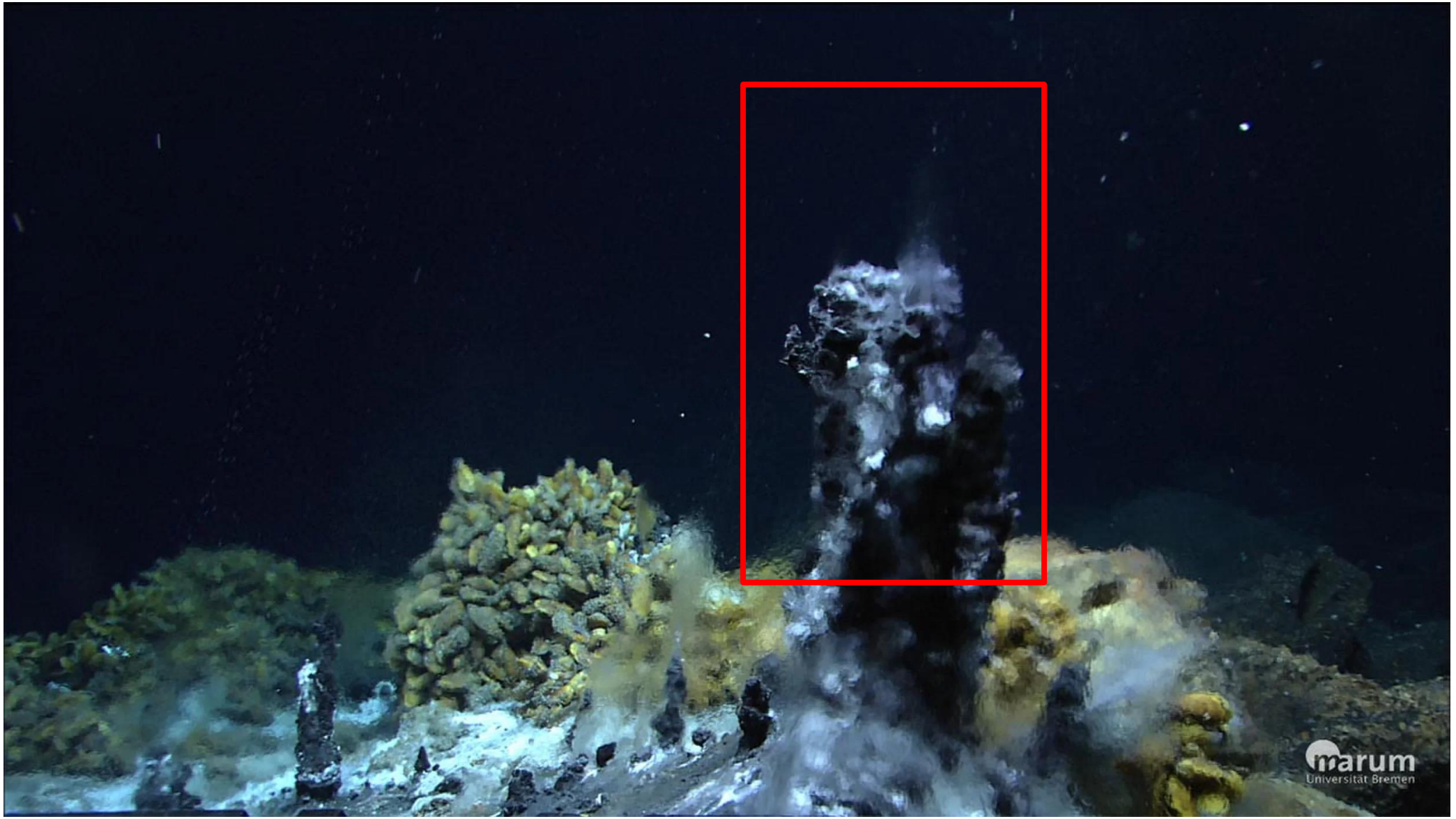
- Strengths of the *in situ* MS (ISMS)
  - *Ease of use*
    - Simple Operation
    - Robust
    - Field Tested
  - *Open Access*
  - *Broad Applicability*
    - Environmental
    - Analytical
  - *Real-Time Data*

Field Experiences from Hydrothermal Vents



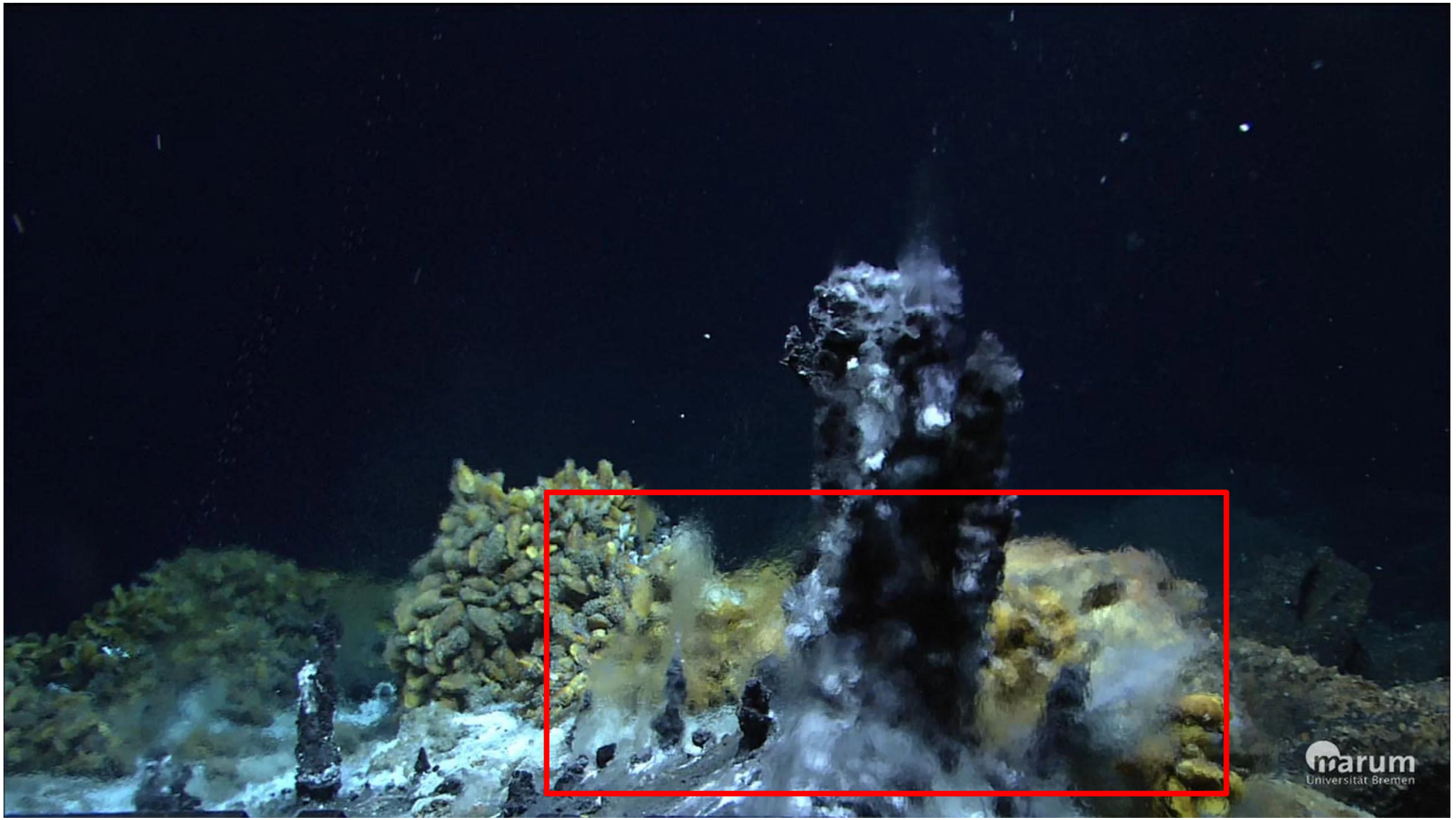
Diffuse Flows at the MAR: Photo: ROV Quest

Field Experiences from Hydrothermal Vents



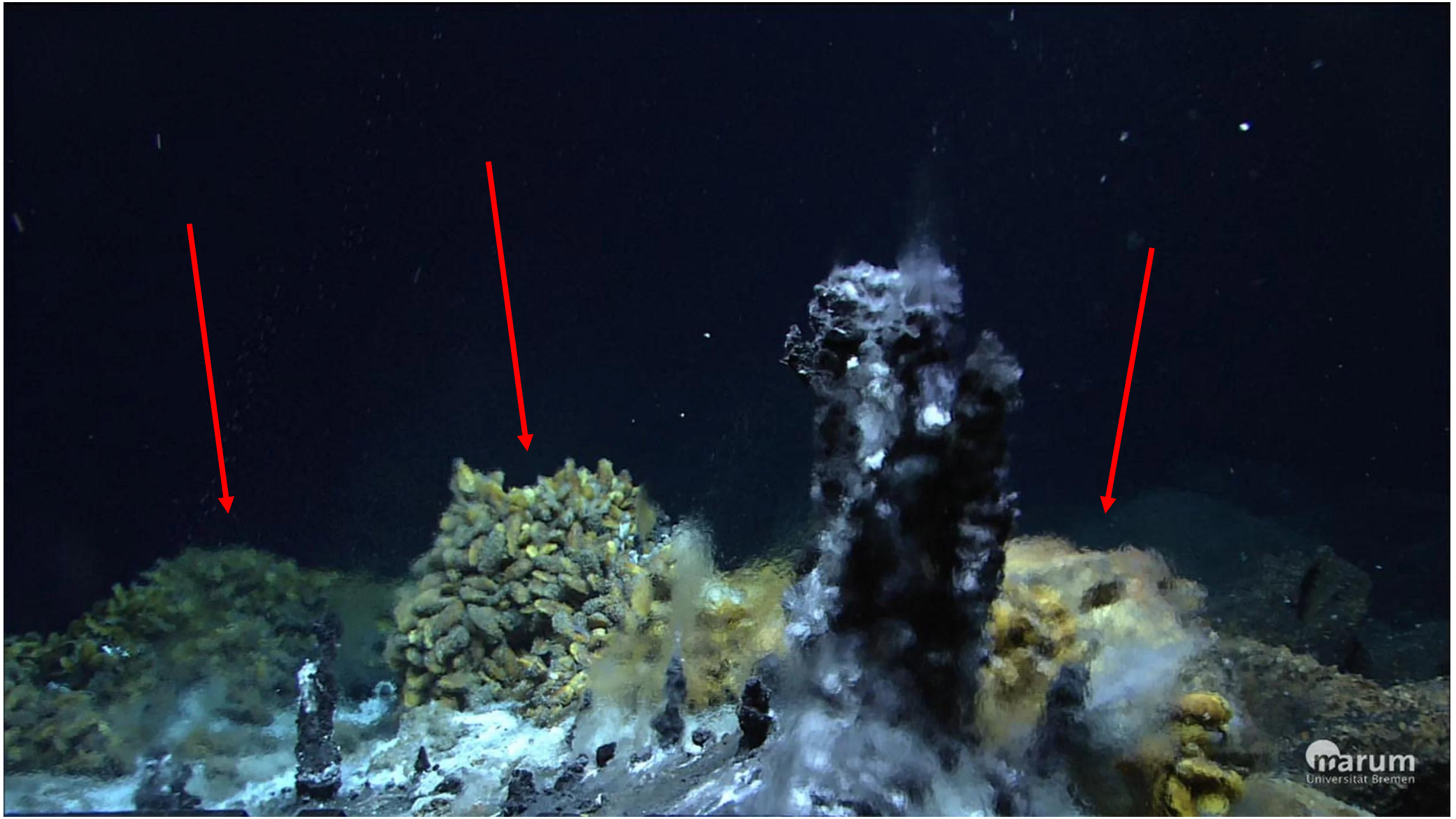
Diffuse Flows at the MAR: Photo: ROV Quest

Field Experiences from Hydrothermal Vents



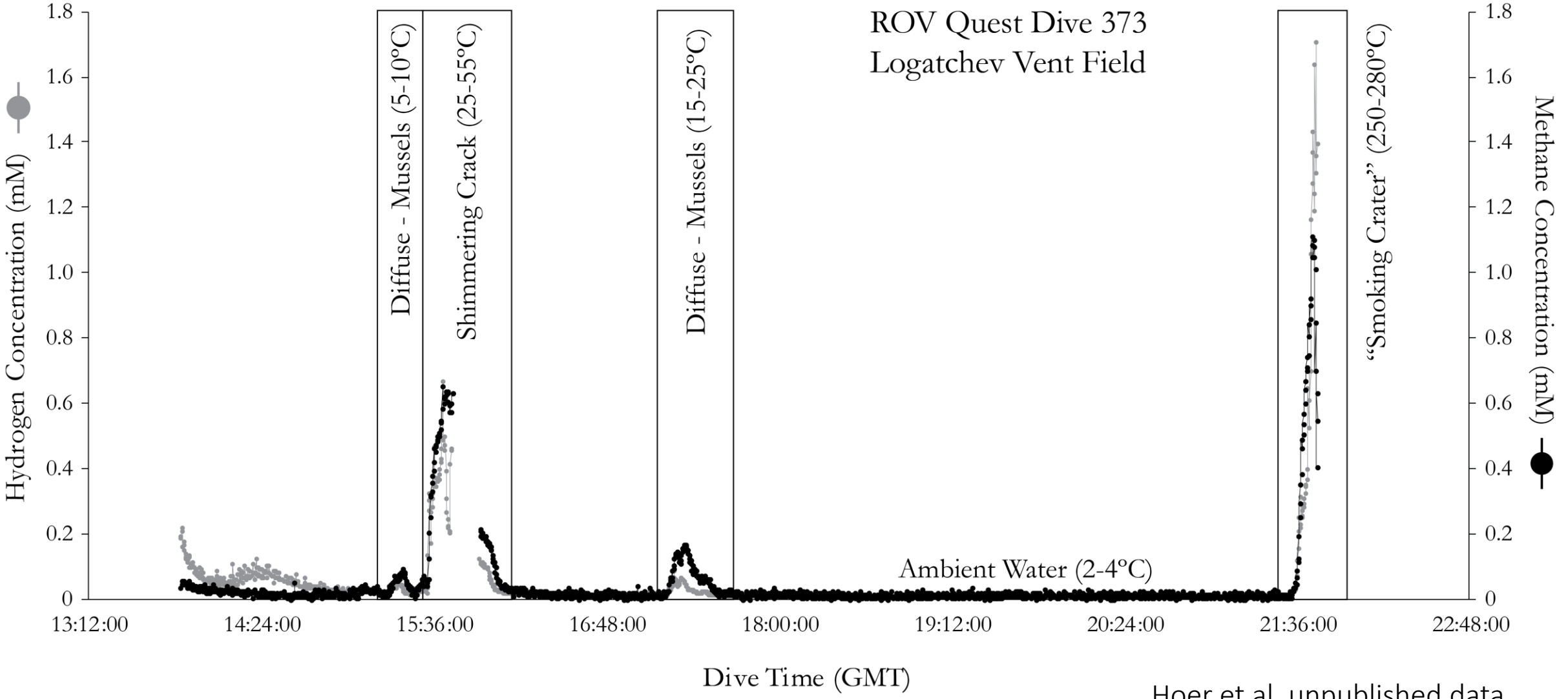
Diffuse Flows at the MAR: Photo: ROV Quest

Field Experiences from Hydrothermal Vents



Diffuse Flows at the MAR: Photo: ROV Quest

Mid Atlantic Ridge Deployment 2016



Hoer et al. unpublished data

Mid Atlantic Ridge Deployment 2016

Hydrogen Concentration (mM)

Methane Concentration (mM)

"Smoking Crater" (250-280°C)

Ambient Water (2-4°C)

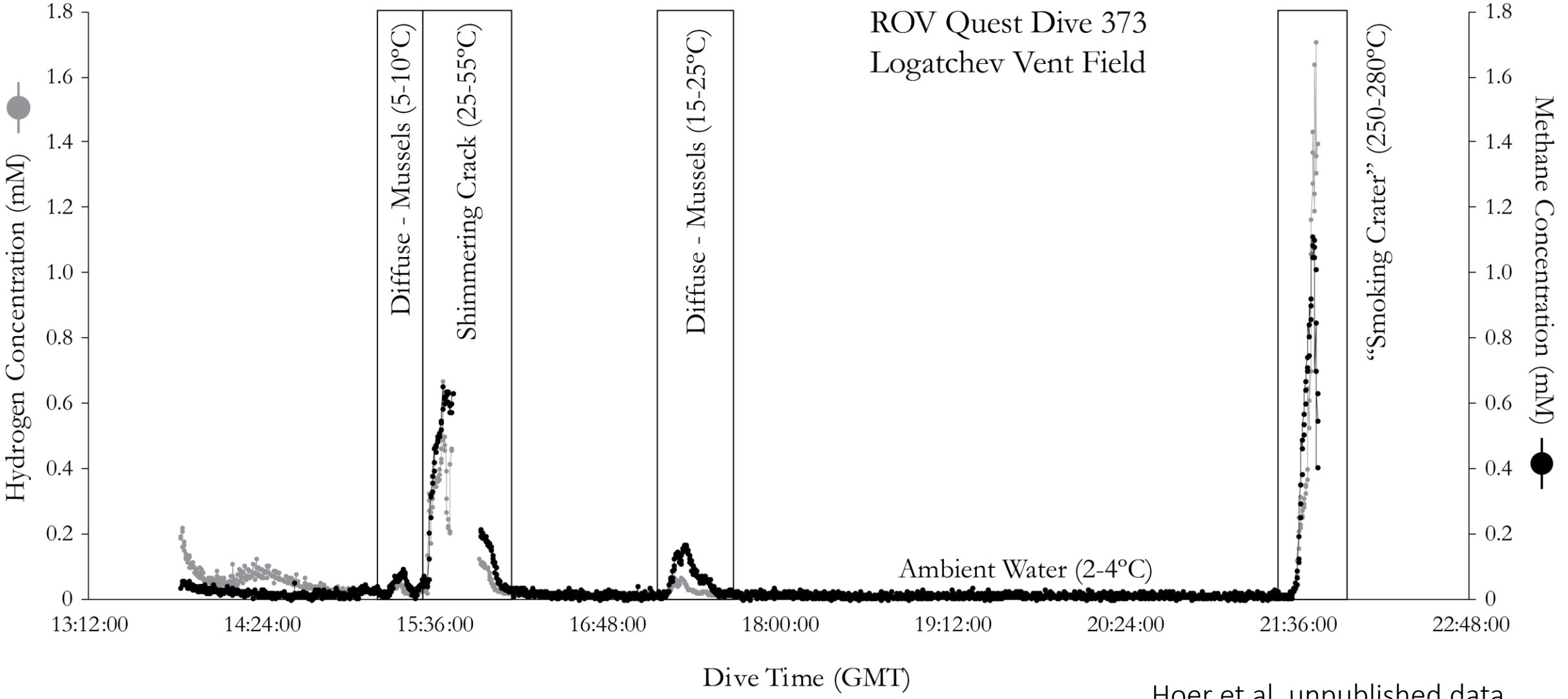
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8

13:12:00 14:24:00 15:36:00 16:48:00 18:00:00 19:12:00 20:24:00 21:36:00 22:48:00

Dive Time (GMT)

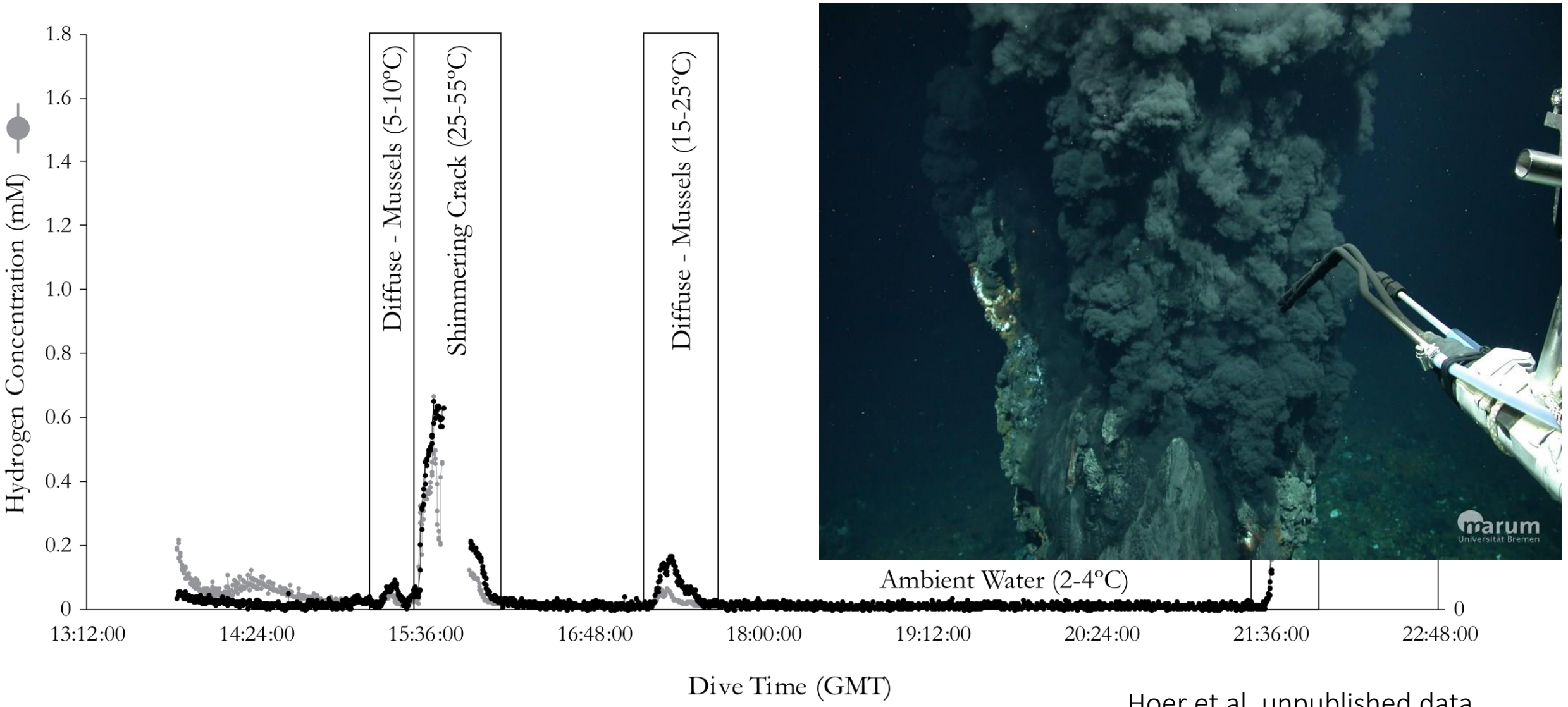
Hoer et al. unpublished data

Mid Atlantic Ridge Deployment 2016



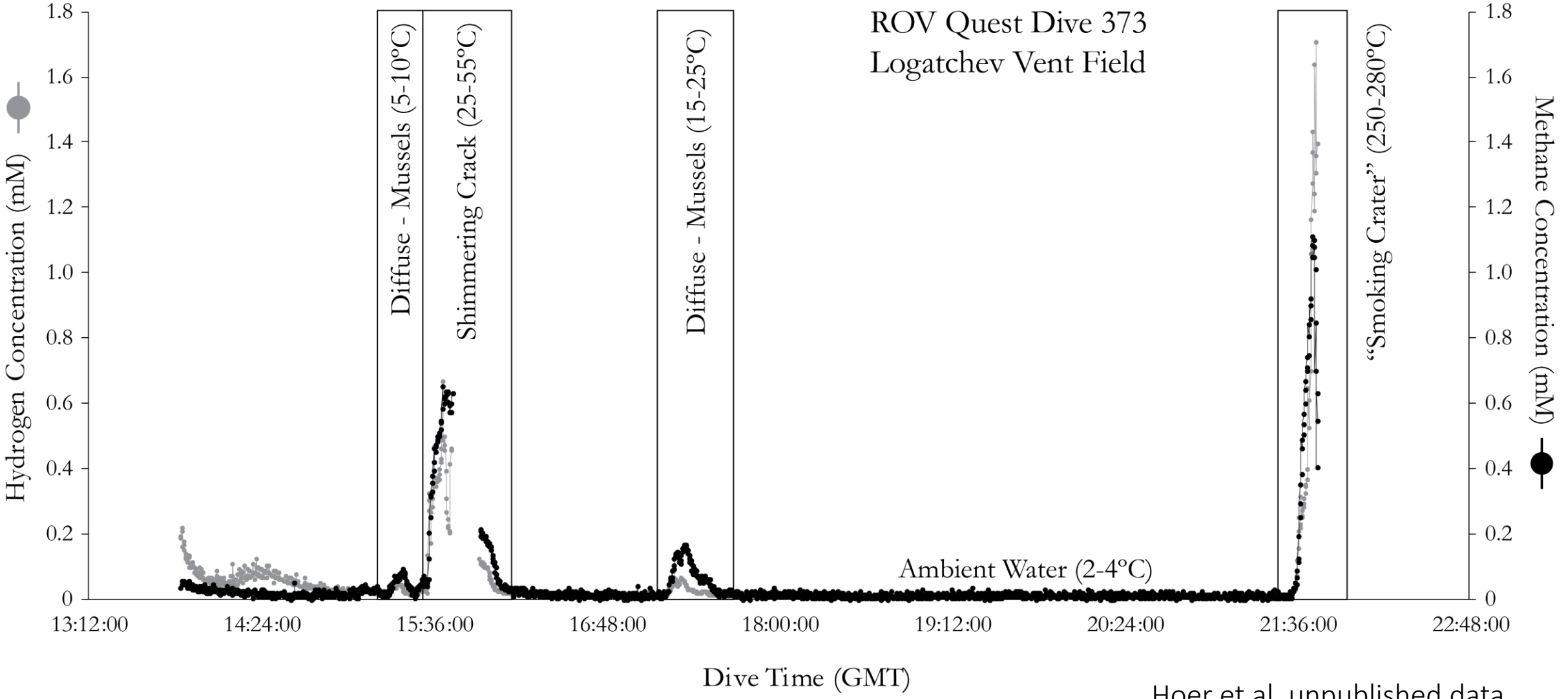
Hoer et al. unpublished data

Mid Atlantic Ridge Deployment 2016



Hoer et al. unpublished data

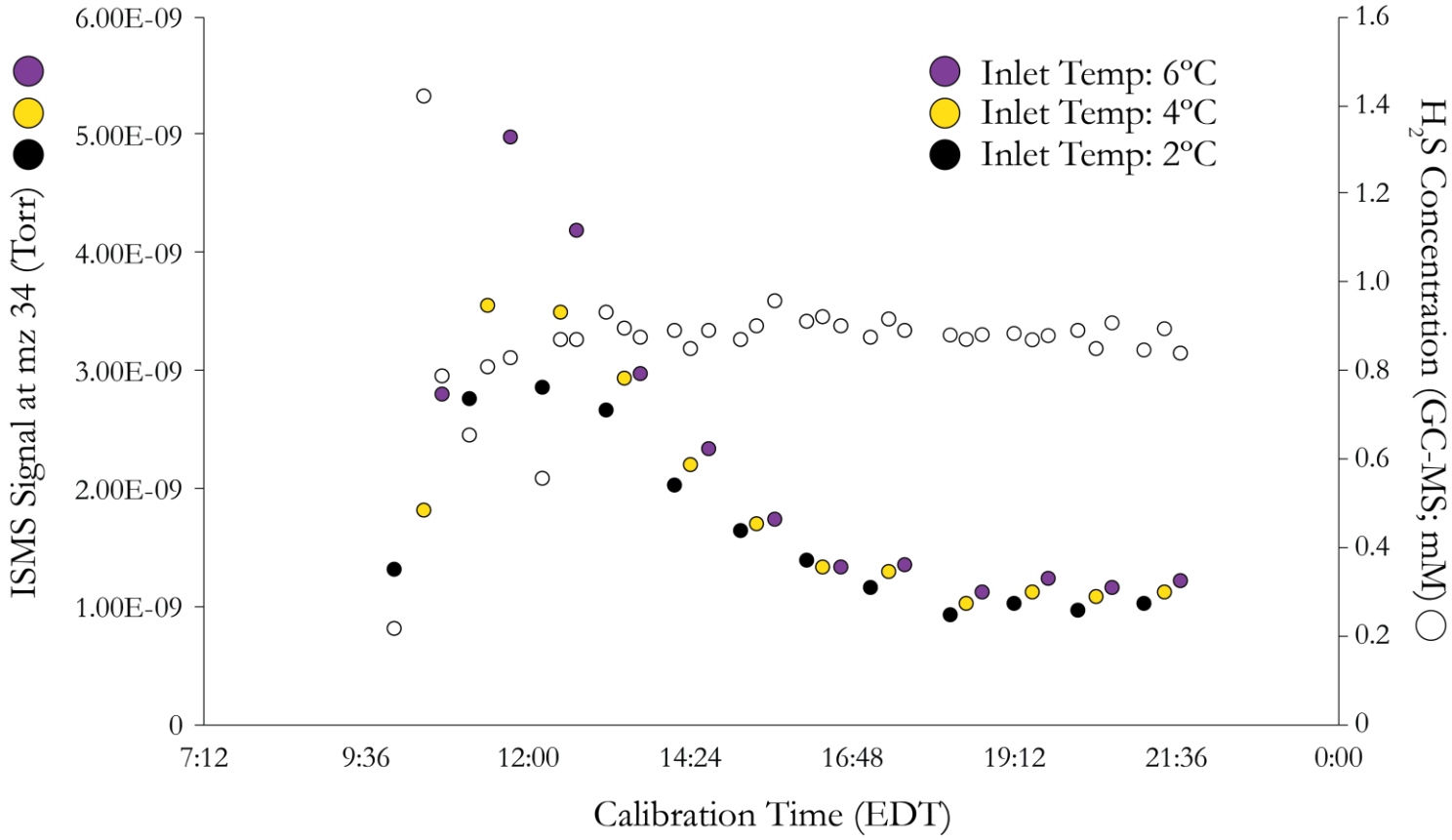
Mid Atlantic Ridge Deployment 2016



Hoer et al. unpublished data

Weaknesses of the Harvard ISMS

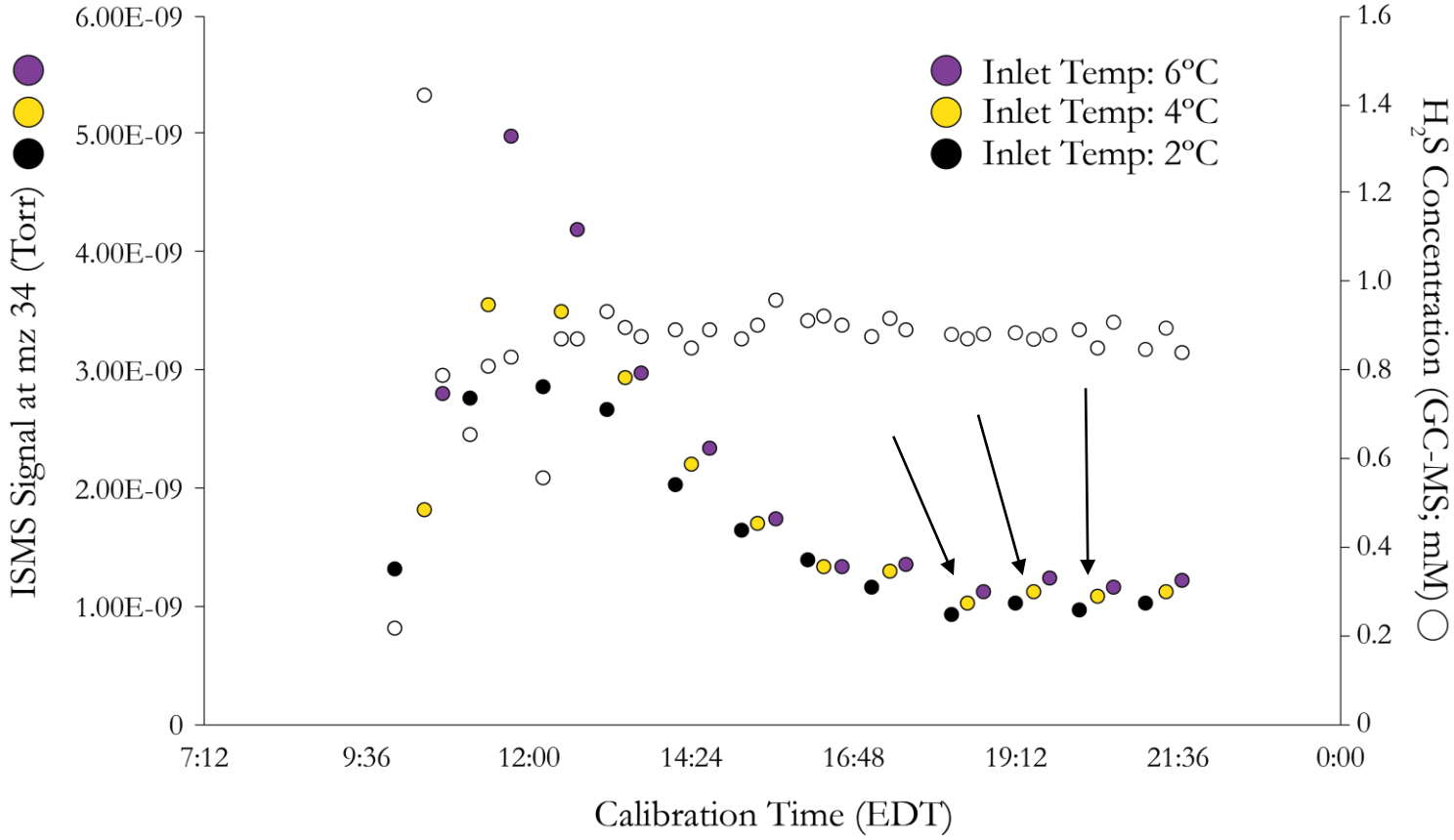
- Weaknesses of *in situ* MS
  - *Membrane variability*
  - *Response Time*
  - *Fluid flow rate*
  - *Power Consumption*



Hoer et al. unpublished data

Weaknesses of the Harvard ISMS

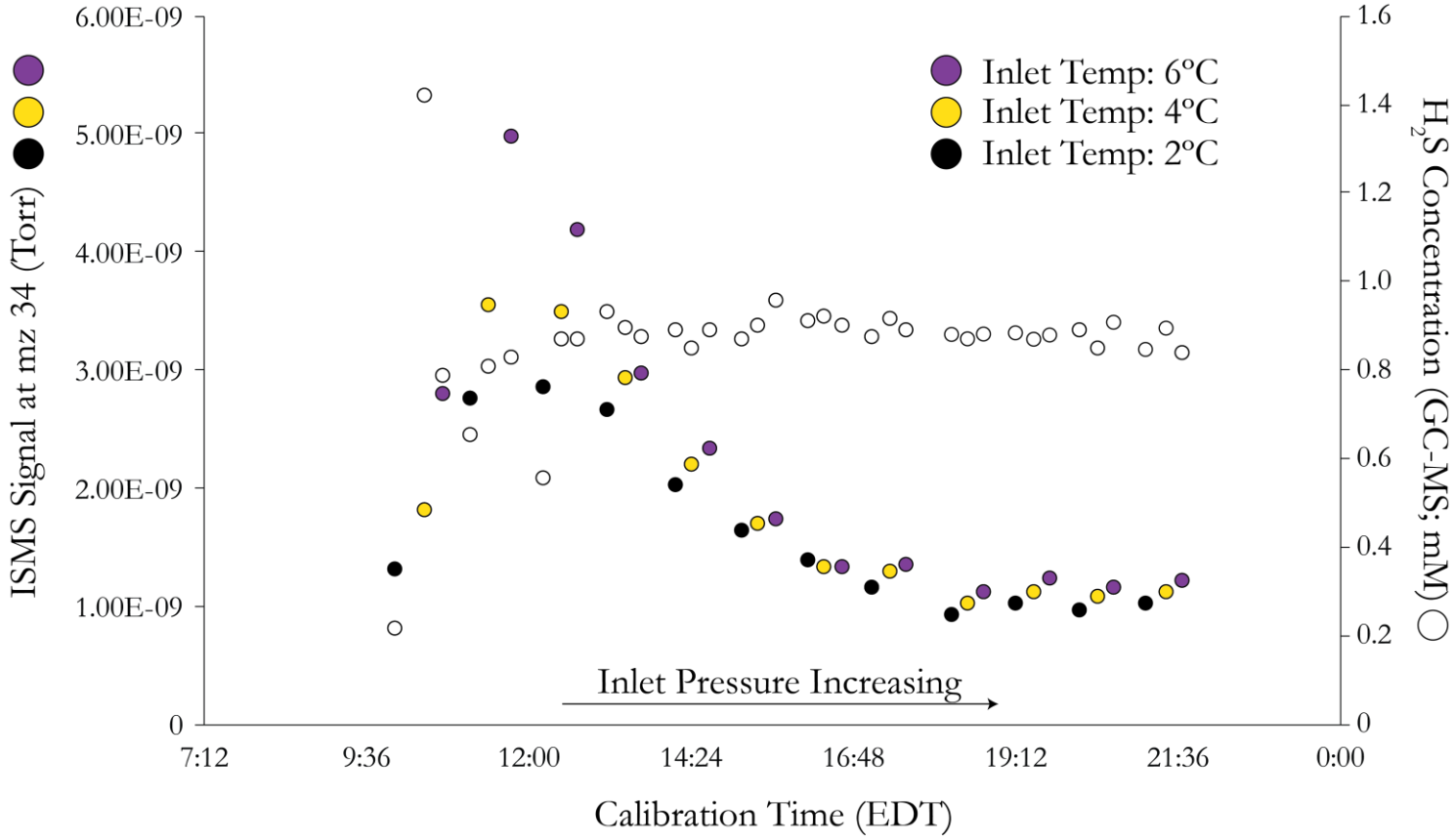
- Weaknesses of *in situ* MS
  - *Membrane variability*
  - *Response Time*
  - *Fluid flow rate*
  - *Power Consumption*



Hoer et al. unpublished data

Weaknesses of the Harvard ISMS

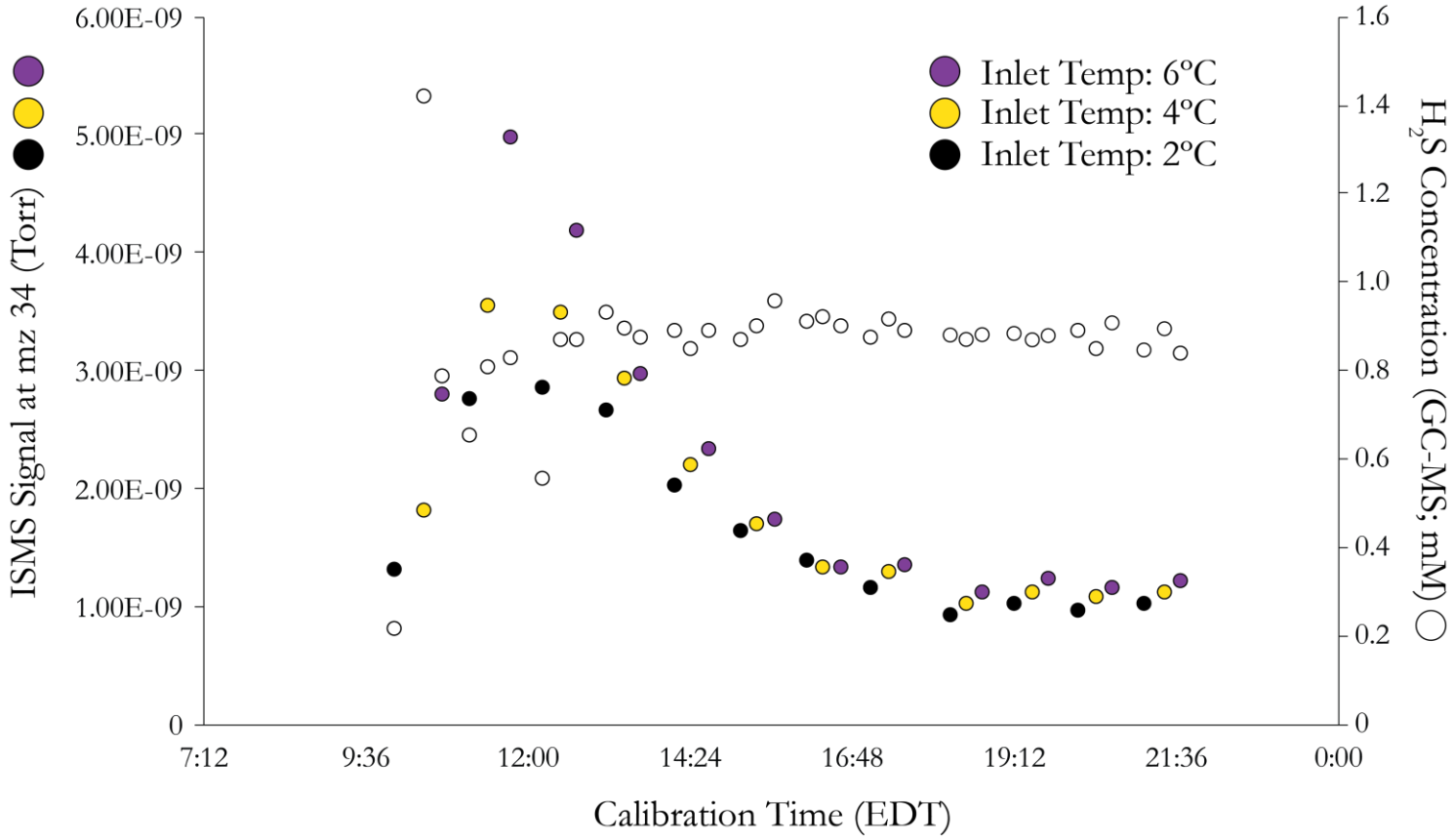
- Weaknesses of *in situ* MS
  - *Membrane variability*
  - *Response Time*
  - *Fluid flow rate*
  - *Power Consumption*



Hoer et al. unpublished data

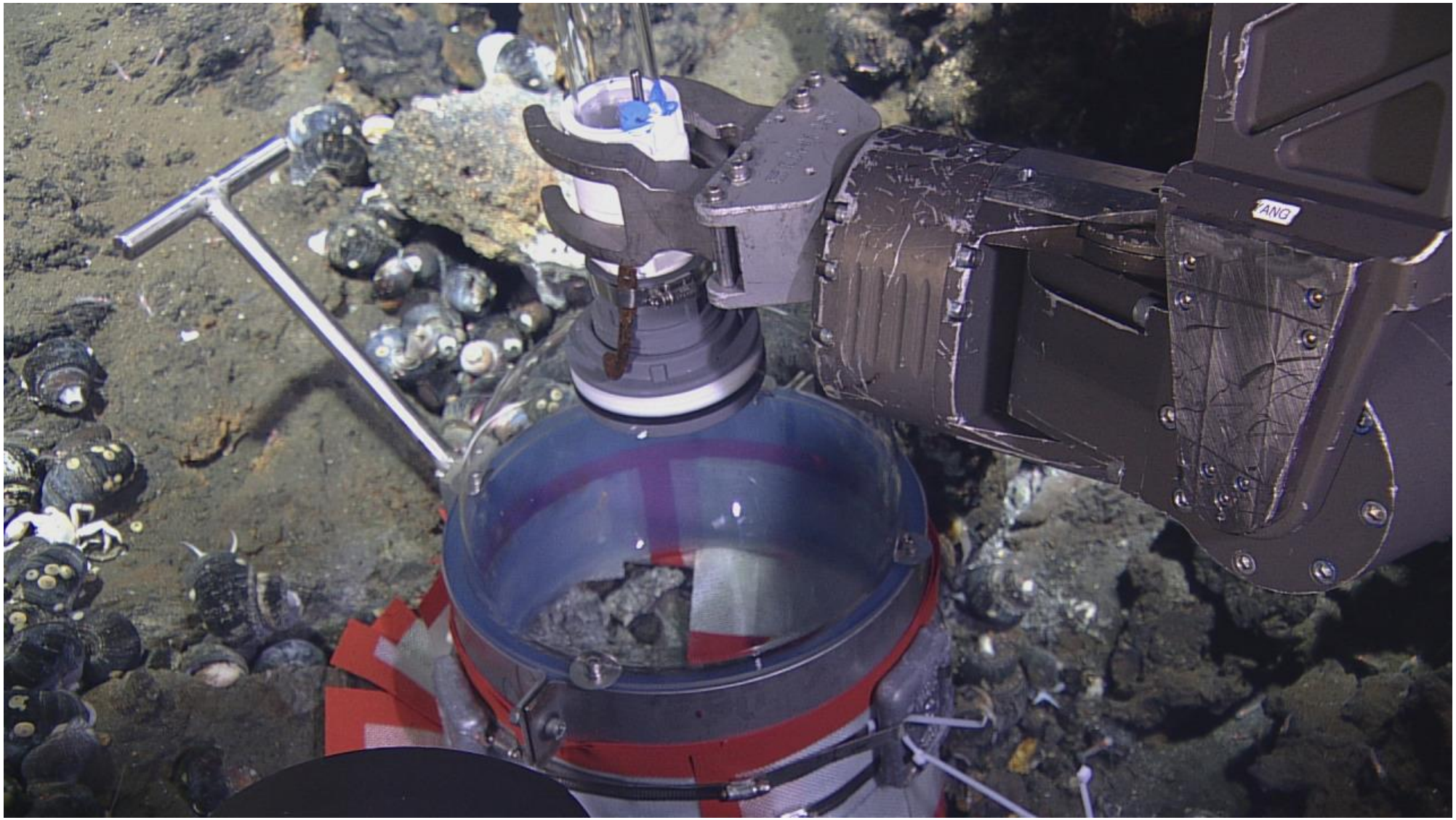
Weaknesses of the Harvard ISMS

- Weaknesses of *in situ* MS
  - *Membrane variability*
  - *Response Time*
  - *Fluid flow rate*
  - *Power Consumption*



Hoer et al. unpublished data

Overcoming Weaknesses

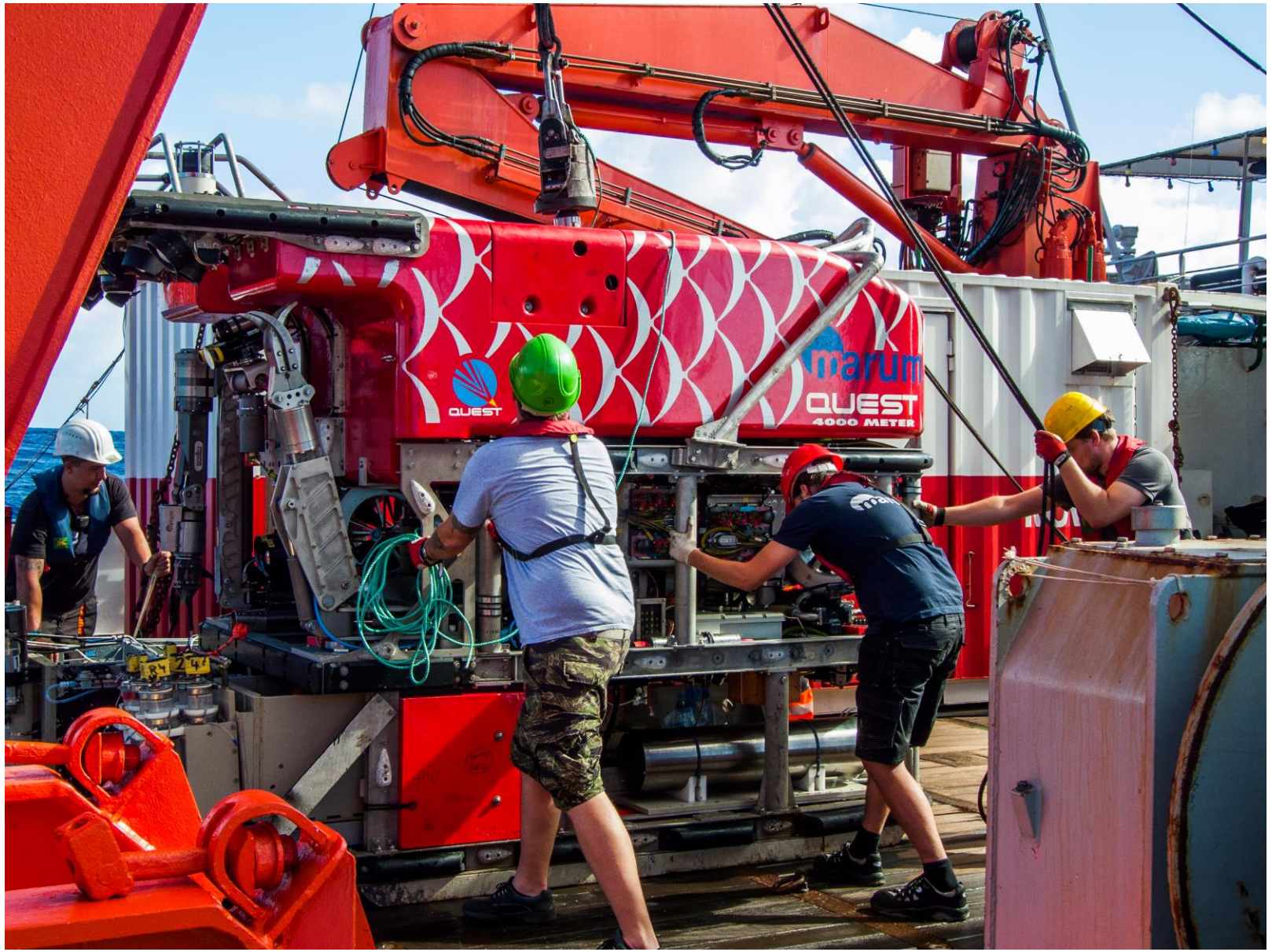


“Flux Integrator” in Lau Basin; Photo: ROV ROPOS

Overcoming Weaknesses

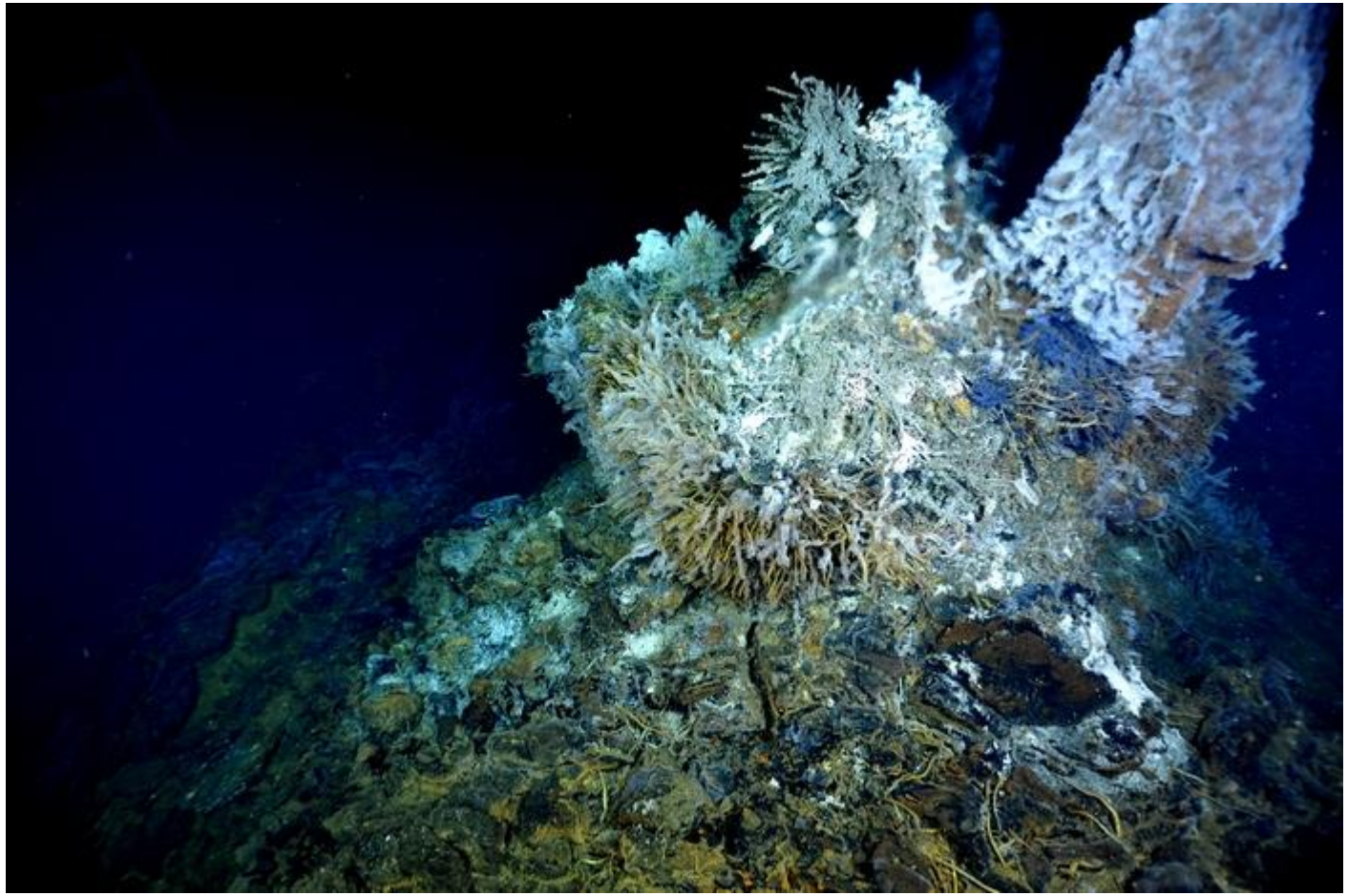
Monitor Instruments TETHYS MS; Photo: C. Martens

Future Directions



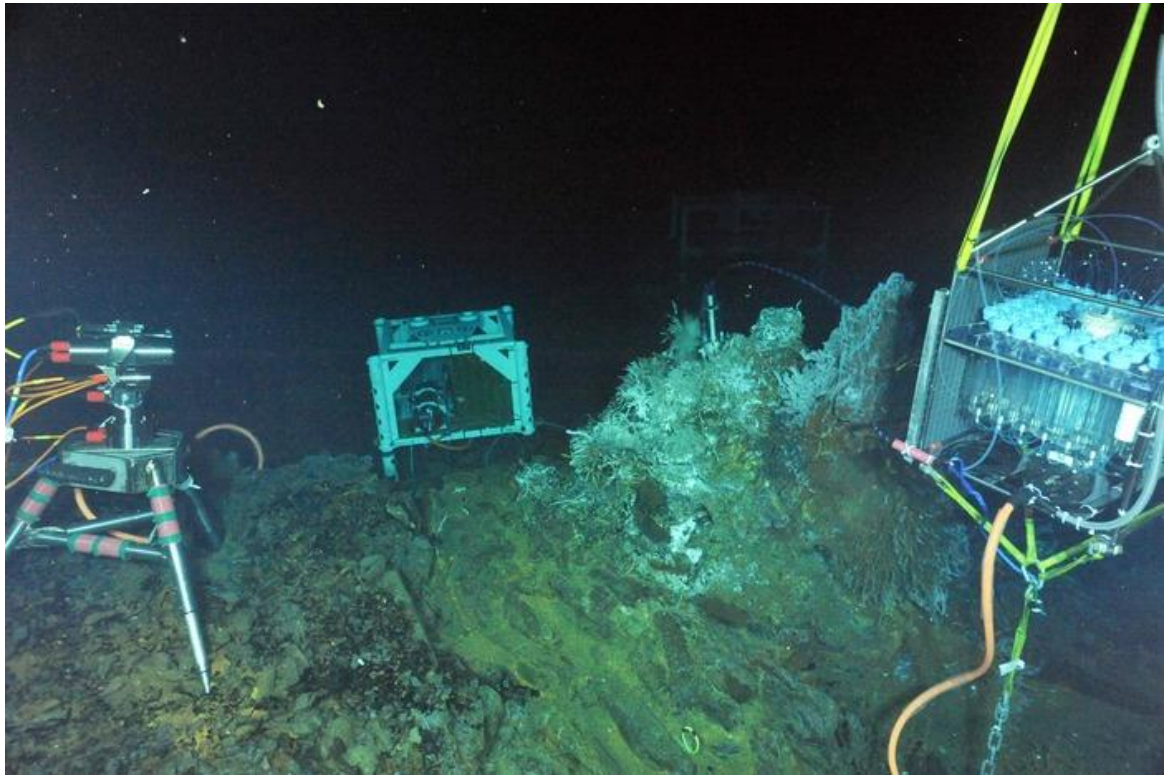
Long Term Deployments

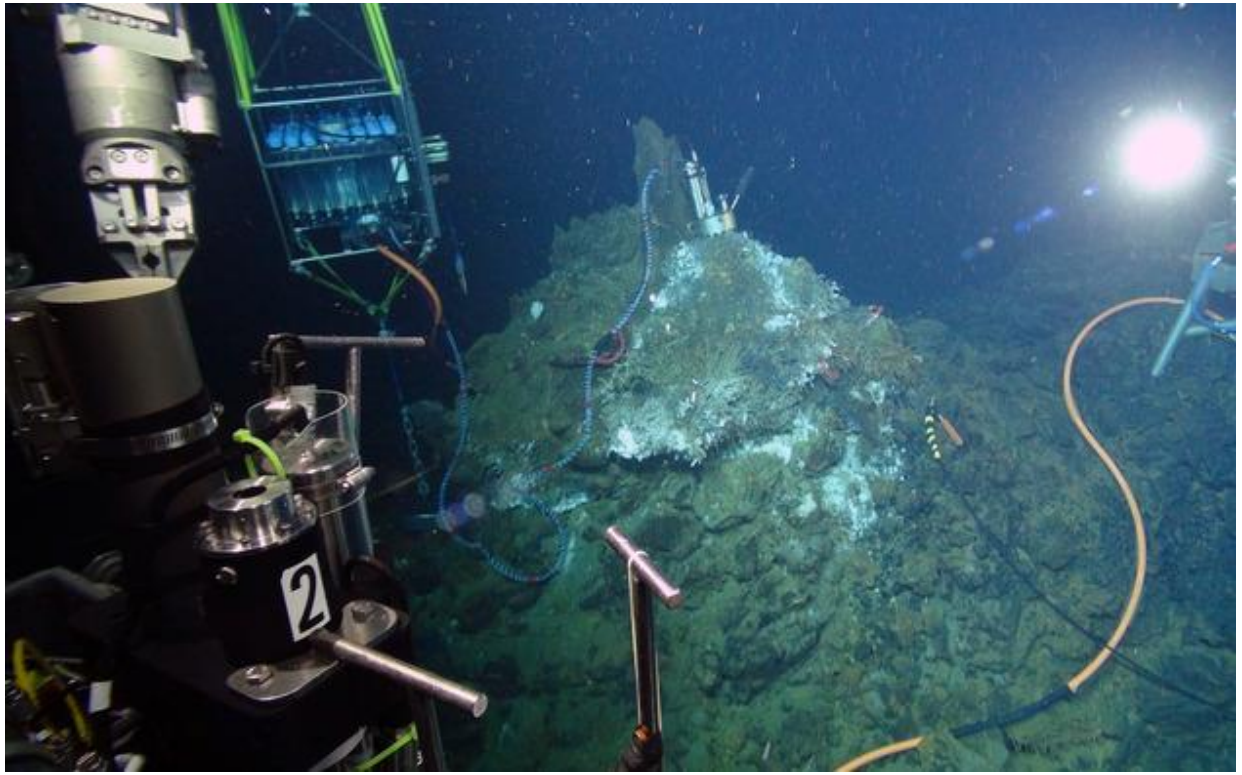
- Power and Communications
  - *Cabled Observatories*
- Redundant Systems
- *in situ* Calibration
  - *Calibration Solutions*
  - *Metal Carbides*



‘El Gordo’; Photo: ROV ROPOS

Long Term Deployments: Cabled Observatory





Long-Term Deployment ISMS at the ‘El Gordo’ OOI RSN; Photos: ROV Jason

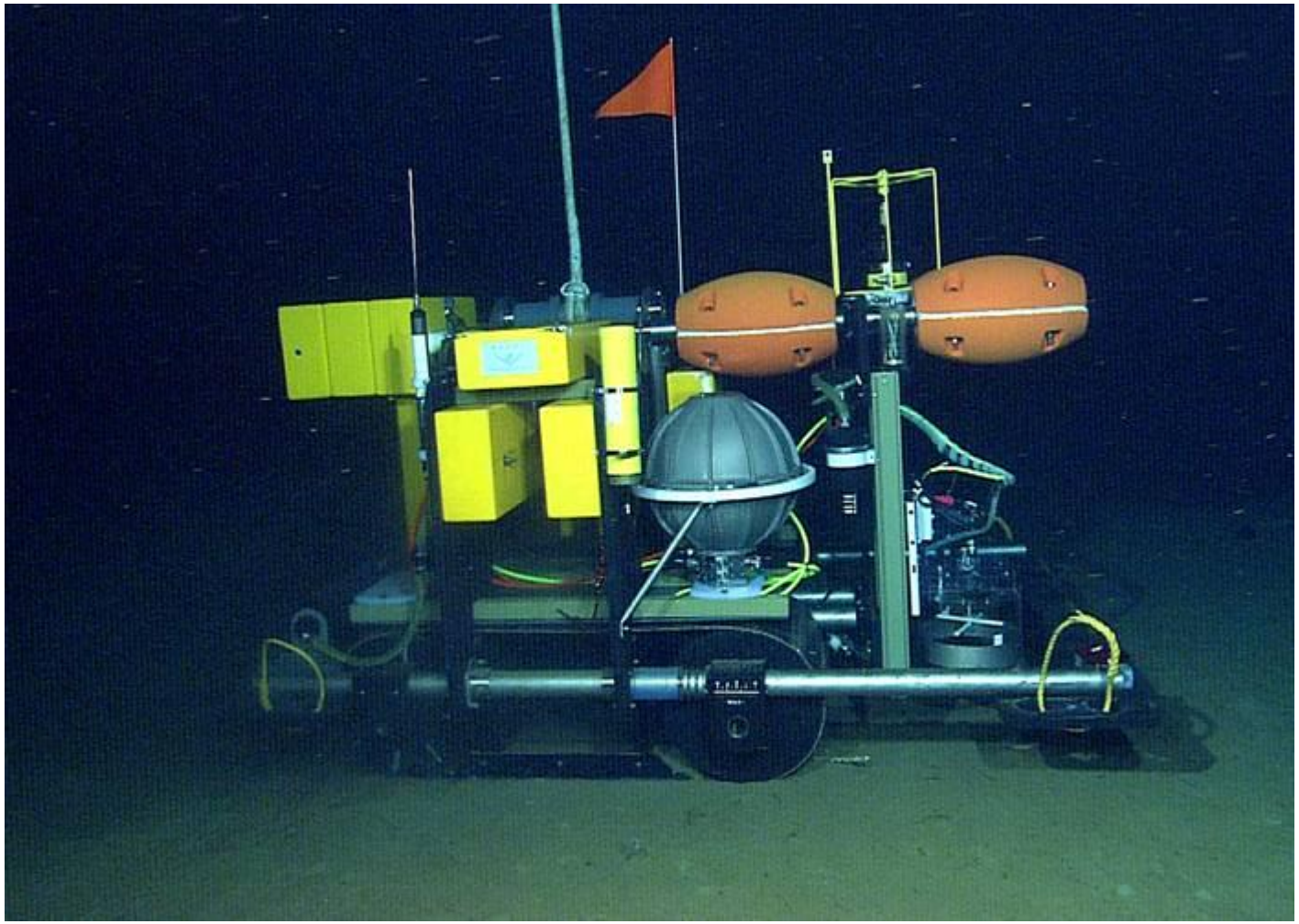
Autonomous Underwater Vehicle Deployments

- Payload Size
- Power Requirements
- Response Time

AUV Sentry; Photo: Ryan Siebert

Other Deployment Platforms

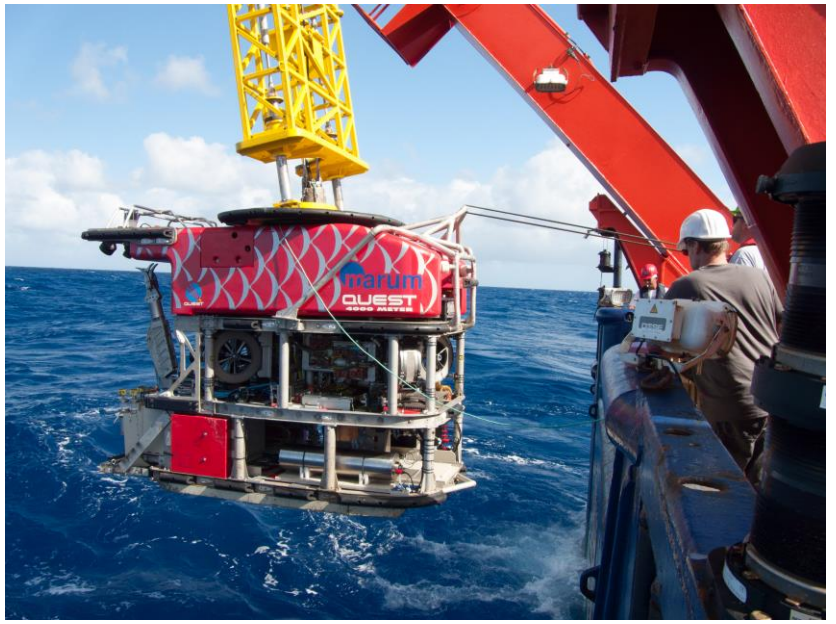
- Reactive Sampling Mooring
- Benthic Rovers
- Cast CTD Rosette from Ships

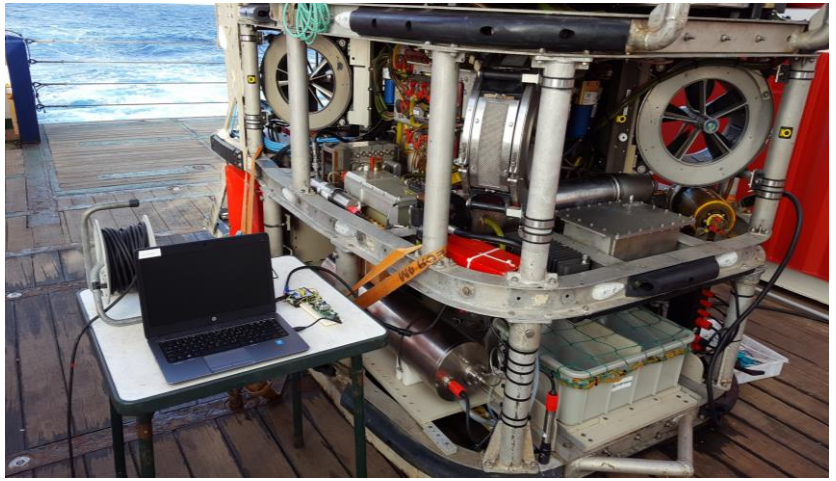


MBARI Benthic Rover; Photo: MBARI

Underwater Mass Spectrometry and Marine Biogeochemistry

- Strengths, Weaknesses, and Field Experiences
- Overcoming Weaknesses: Technological Future Directions
  - Careful Calibrations
  - Technological Updates and Adjustments
- Future scientific applications
  - (More) Long Term Deployments
  - (More) AUV Deployments
  - Different Vehicles
  - Reactive Sampling Platforms






St Peter's
LONELY HEARTS
Club Lab
MiCROBES

Questions?