Natural Gas Hydrates in Permafrost and Marine Settings: Resources, Properties, and Environmental Issues

Interagency Agreement 89243320SFE000013

also known as "USGS Core Agreement"

Carolyn Ruppel

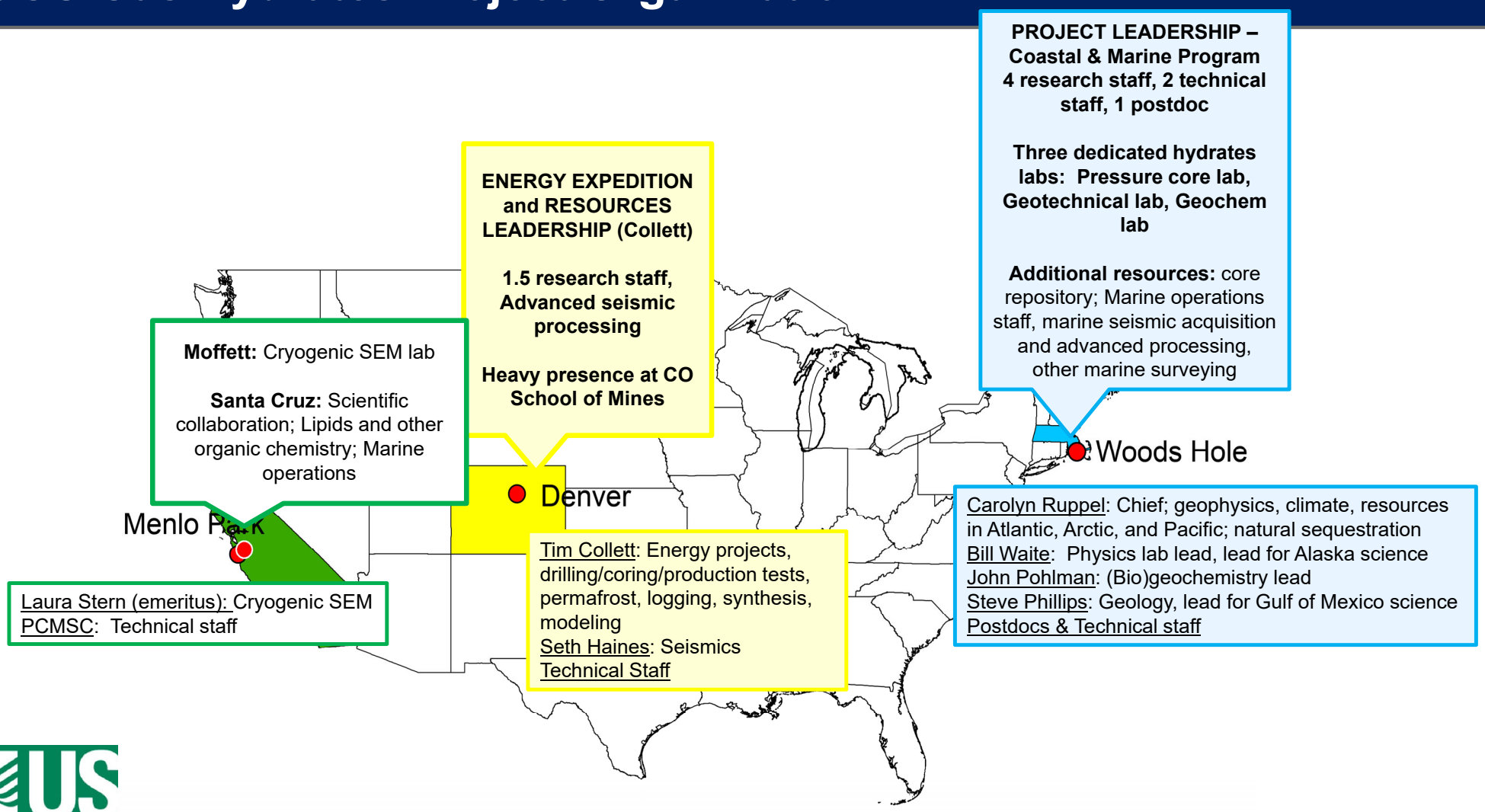
US Geological Survey

Woods Hole Coastal and Marine Science Center

U.S. Department of Energy
National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
April 2-4, 2024

U.S. Department of the Interior
U.S. Geological Survey

USGS Gas Hydrates Project Organization



USGS "Core Interagency" Agreement

Full Duration: Spring 2020 – Spring 2025 (*Year 4: Spring 2023 – Spring 2024)*

Funding

DOE provided funds:

Total through end of Year 4: ~$1.3 million

Year 4 alone: $285,757 (gross)

USGS funds all salaries:

~$2 million/yr for the USGS Gas Hydrates Project as a whole

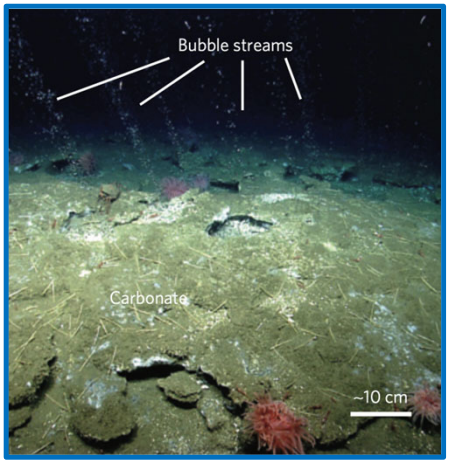
~$1 million/yr for USGS Gas Hydrates Project in Woods Hole from Coastal and Marine Program

Interagency Agreement provides science support only for USGS Gas Hydrates Project (Woods Hole component)

Carolyn Ruppel (Project Chief)
Bill Waite (Lead, Physical Properties & Alaska Hydrate Science)
John Pohlman (Lead, Biogeochemistry/Organic Chemistry)
Steve Phillips (Lead, Geology & Gulf of Mexico Science)
Postdoctoral Associates
Technical staff in Woods Hole and occasional operational staff shipboard
Plus collaborators at USGS Santa Cruz and USGS Earthquake Center (e.g., Laura Stern, Moffett Field)

Core Interagency Tasks

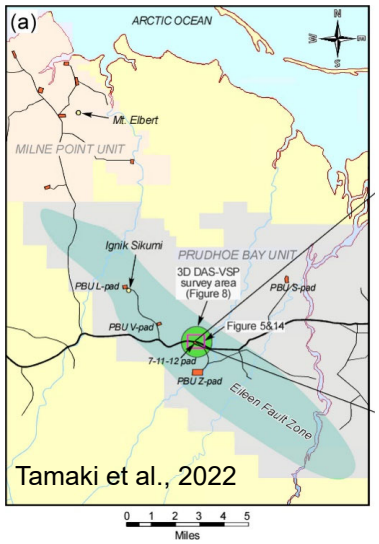
1. Permafrost-Associated Gas Hydrates in Alaska
2. Resource Grade Marine Gas Hydrates in the Deepwater Northern Gulf of Mexico (GOM)
3. U.S. Atlantic Margin Integrated Gas Hydrates Studies
4. Laboratory-Based Studies of Hydrate-Bearing Sediments and Hydrate-Related Processes
5. International Collaborations
6. Gas Hydrates and Environmental Issues



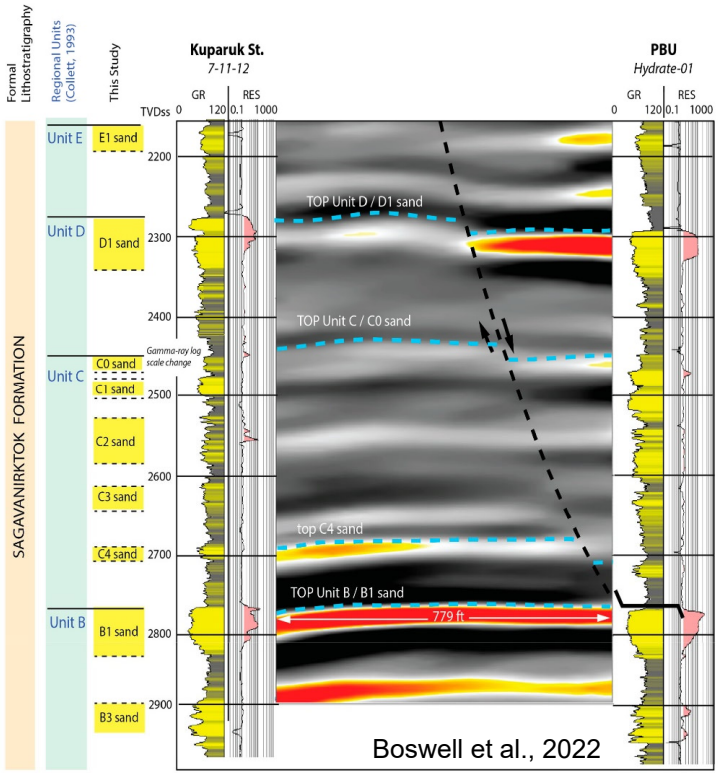
USGS

Task 1. Alaska Hydrate Well & Production Test

Pressure coring (late 2022: 5 personnel on site) and production test (starting mid-2023)



Tamaki et al., 2022



Boswell et al., 2022

Samples acquired

Gas, fluids, solid phases, microbiology

11 pressure cores

13 pressure cores

Iron sulfide bands in cores

Task 1. Alaska Hydrate Well: Pressure Core Analyses

ANS Pressure Core Recovery: Intact?

- Yes → Japan / DOE /**USGS**
- No → Degas on site → Sediment capture / Geotek → Gas chemistry on site / Geotek / **USGS Woods Hole**

Location:
ANS (blue)
USGS (green)
Georgia Tech (gold)

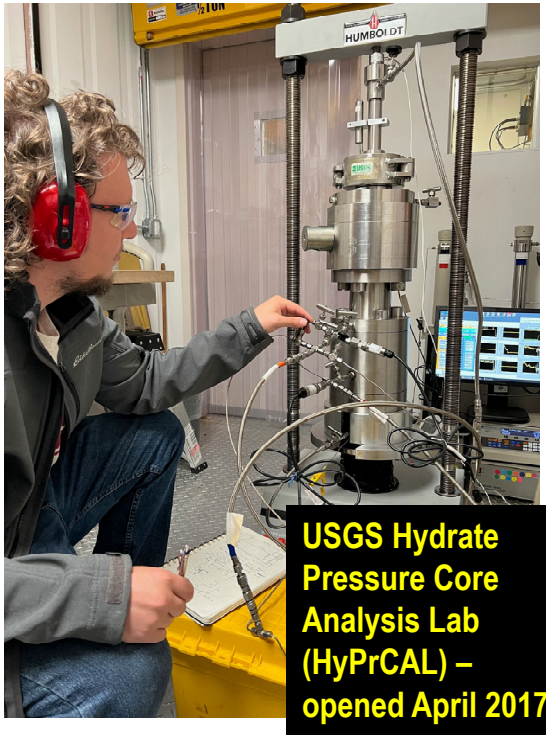
USGS Woods Hole (Pressure Core Characterization Tools, Effective Stresses 0 - ~15 MPa):

- Effective Stress Cell, ESC: Vertical permeability, relative permeability estimate, compressibility
- Direct Shear Cell, DSC: V_P, direct shear strength, compressibility
- *High-stress ESC (A. Garcia—DOE-NETL postdoc)*: ESC capabilities with maximum effective stress >15 MPa

USGS Woods Hole Dissociation: Gas chemistry on gas collected during dissociation

Index properties	Sediment Geomechanics	Georgia Tech (*S. Dai*)
Grain size Grain density Specific Surface Mineralogy Sedimentology SEM (L. *Stern, Menlo Park*)	Compressibility (oedometer) Permeability Fines Migration	Permeability: horizontal and vertical, with and without THF hydrate on intact specimens from PCCT dissociation with effective stress; Compressibility

USGS Woods Hole responsibilities shown in green shading



USGS Hydrate Pressure Core Analysis Lab (HyPrCAL) – opened April 2017

USGS

Task 1. Alaska Pressure Core Measurements (including post-degassing)

USGS responsibilities in yellow

Lithostratigraphy and Solid Phase Chemistry

- Bulk XRD
- Clay XRD
- Total N
- Total S
- Bulk $\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$
- Total C & TOC
- $CaCO_3$
- SEM
- SEM/EDS solid geochemistry
- Core Photos
- Thin Sections
- Core CT and X-ray scans
- MicroCT

Physical/Geomechanical

- Porosity
- Hydrate saturation
- Hydrate grain size
- Grain Size
- Grain Specific Surface Area
- Grain Density
- Grain Shape
- Capillary Pressure
- NMR T2
  - Porosity
  - Pore size
  - NMR permeability
  - Bound/free water
- Permeability
  - Direct vertical permeability
  - Direct horizontal permeability
  - Relative Permeability
  - Intrinsic Permeability
- Shear Strength
- Stiffness
- Compressibility
- Poisson's Ratio
- Ko
- Vp
- Vs
- Thermal Properties
  - Thermal Conductivit
  - Heat Capacity
- Sand production
- Fines behavior
- Liquid Limit
- Electrical Sensitivity

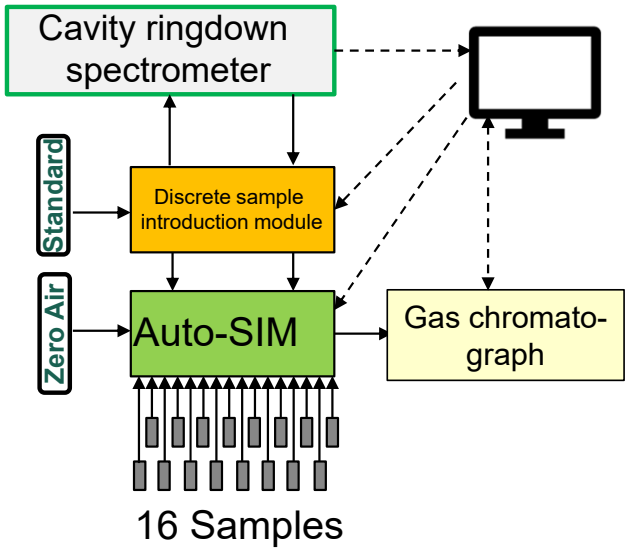
Task 1. Alaska Hydrate Well: Advanced Gas Analyses –Strat Well, Hydrate Well, Production Test--Facilitated by New Instrumentation Invented at USGS

Goal: Determine the origins of the hydrocarbons (primarily methane) within stratigraphic (hydrate and non-hydrate bearing) units to determine sources of gases produced from PTW1

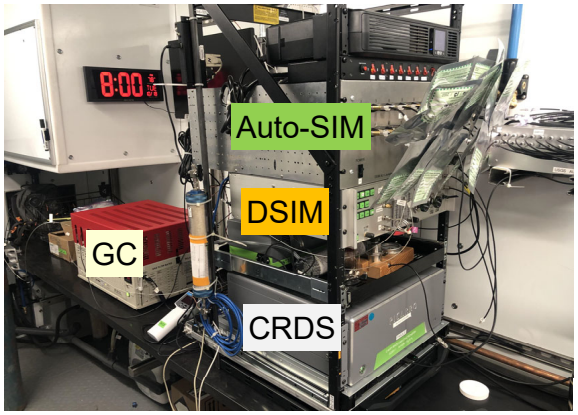
I. Analyze gases on-site in cuttings from the geologic data well (HY-02)

II. Analyze gases collected during pressure core degassing experiments to characterize hydrate-derived gases from stratigraphic units D and B and understand how gas chemistry changes during gas hydrate dissociation

III. Obtain a continuous (daily) record of gas chemistry from the PTW1 production stream



DSIM patent granted to USGS in June 2023



503 Total Samples Analyzed To Date:
168 Well Cuttings, 140 Pressure Core Degassing Samples, 85 Production Gases, and 110 Flowed Gas Samples

Task 1. Alaska Hydrate Well, Pressure Core, and Production Test Geochemistry

USGS responsibilities in yellow

Pore water chemistry

- Salinity
- Alkalinity & pH
- DIC & DOC
- Cations/Anions
  - Cl, Br, SO_4, NO_3, F,
  - Ca, Na, Mg, K, Sr, Li
- $\delta^{13}C$-DIC
- $\delta^{18}O$, δD
- $\delta^{7}Li$

Gas Analyses

- Hydration number
- $C_1 - C_6$
- N_2 O_2 CO_2
- $\delta^{13}C$-CH_4
- δD-CH_4
- $\delta^{13}C$-CO_2
- $\delta^{13}C$-C_2H_6

Microbiology

- DNA
- RNA
- Lipids
- Total cell counts
- Urease activity
- Drilling Fluids
- PCATS Fluids

Produced Water

- Cations/Anions
  - Cl, SO_4
  - Ca, Mg, K, Sr
- $\delta^{18}O$, δD
- C_{10}-C_{32} concentrations
- Conductivity/Salinity

Produced Gas

- $C_1 - C_6$
- N_2 O_2 CO_2
- δD-CH_4
- $\delta^{13}C$-CH_4
- $\delta^{13}C$-C_2H_6
- $\delta^{13}C$-C_3H_8
- $\delta^{13}C$-CO_2

USGS Woods Hole scientists producing nearly all fluid, gas, and solid phase chemistry for:

- Stratigraphic well (2018)
- Pressure cores
- Production tests

USGS facilitating microbiological measurements

- Collecting and appropriately packaging/shipping sensitive samples
- Collaborating with external partners
- Synthesizing geochemical and microbiological results

USGS

Task 1. Alaska Hydrate Well: Geologic Framework, Diagenesis, Search for Native Oil, and Microbial Analyses

Selected Goals:

Reconstruct depositional environment and diagenetic history of reservoir and bounding muds (focus on Units B and D)

Characterize iron sulfide mineralization for its impact on seal quality

Use lipid biomarkers to determine whether native oil is present in samples

Provide samples for microbial genomics and conduct ancillary measurements related to microbial methane dynamics in the reservoir

Additional outcomes: Origin and evolution of gas in reservoir, Paleogene paleoenvironment, record of past methane oxidation

USGS

Bagged sediment from whole round core sampling

Vibrating sample magnetometer

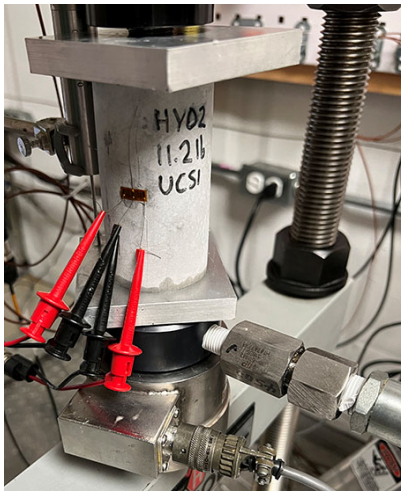
Task 1. Alaska Production Test Preparation

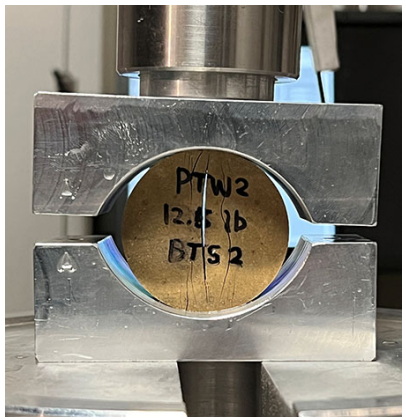
Fiber optic cable measurements that describe the reservoir are based on strain in the cable.

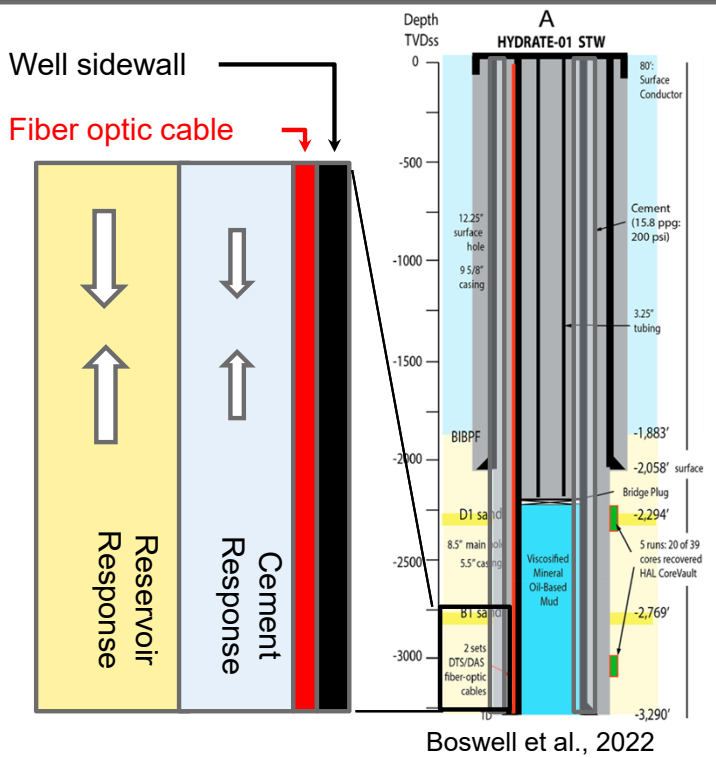
Stress-strain relationships for the cement must be measured to calibrate cable measurements and extract the response of the reservoir to production.

USGS had the flexibility, expertise, and instrumentation to conduct required measurements on the properties of the cement prior to the production test.

Finding: Strength and elastic properties stabilized within 4 months, well before the production phase began.





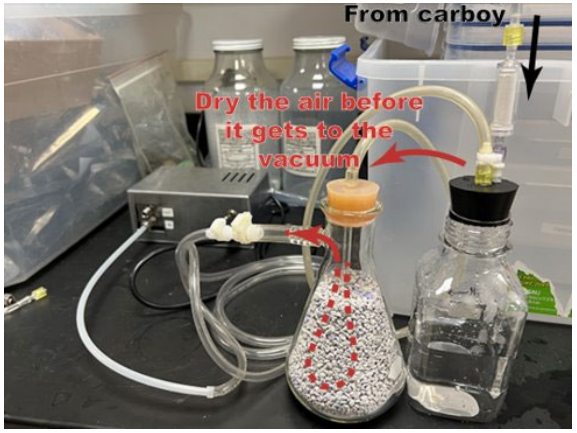


Boswell et al., 2022

- *Compressive strength*
- *Tensile strength*
- *Young's Modulus*
- *Poisson's Ratio*

Task 1. Alaska Production Test Sampling and Analyses

- USGS designed, tested, vetted with on-site contractor, and shipped production test kits and ancillary devices (e.g., dry ice maker, pump, filtering materials)
- Explicit sampling protocol allows Arctic Fox contractors to conduct high-quality sampling during production test without USGS scientists on-site
- Daily water sample: Compare composition of produced waters to samples obtained from reservoir and bounding units during hydrate well phase
- Daily gas sample: Track evolution of gases during production phase
- Specialized sample suite (less often): 40 liters of water subsampled for microbial, fluid, and solid chemistry and frozen for direct shipment to Boston



Protocols provided to Arctic Fox

USGS sampling kit in cold shipper

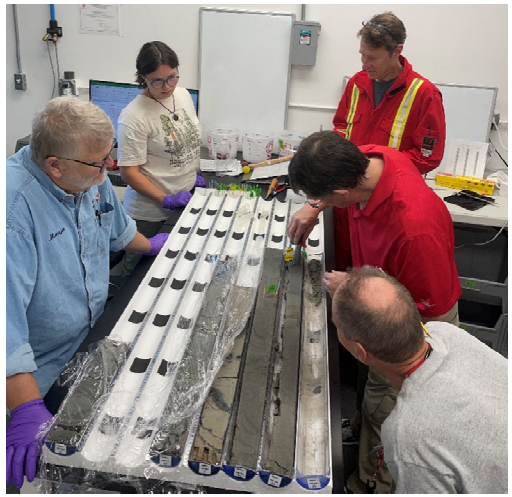
Dry ice maker

Task 2: Gulf of Mexico UT GOM2-2 Offshore/Shorebased Participation

Offshore Program

- Participated in offshore operations at WR 313 from July 30 to September 1, 2023 (Phillips and Collett)
- USGS provided leadership for coring and core processing
- Generated pressure core cut plans for PCATS
- Performed quantitative degassing of pressure core sections
- Led gas sampling and conventional core sampling
- Completed hazmat shipments of gas and microbiological samples from offshore program

Helix Q4000



Shorebased Science Party

- Three USGS scientists participated in shorebased operations in Salt Lake City, UT (Waite, Phillips, and Collett)
- Split core sediment sampling
- Additional quantitative degassing of pressure core sections (for estimation of hydrate saturation)
- Collection of pressure core gas and hydrate/hydrate-bearing sediment gas (gas shipped to Woods Hole)
- USGS has continued work on creating a compressed depth scale (to deal with overlap from expansion), compiling core scan data, and report writing

NATIONAL ENERGY TECHNOLOGY LABORATORY

USGS

TEXAS Geosciences
The University of Texas at Austin
Jackson School of Geosciences

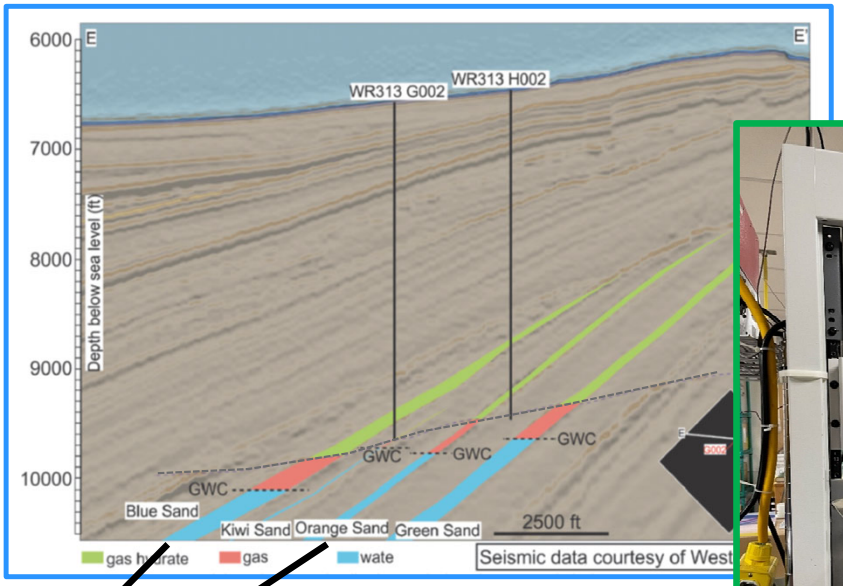
Task 2: Gulf of Mexico Project– Hydrate Characterization and Methane Dynamics

- Calculated dissolved methane content or hydrate saturation based on total methane released from core sections during quantitative degassing
- Dissolved methane profile in upper 150 mbsf provides unprecedented look at microbial methane generation with depth
- Characterized low saturation hydrate in background sediments and in bounding muds
- Ongoing studies of sedimentation rates from radiocarbon/oxygen isotope stratigraphy with goal of understanding the evolution of the hydrate system over glacial-interglacial time scales

Geotek degassing container with 4 degassing stations

Task 2: Gulf of Mexico Project– Gas Analyses

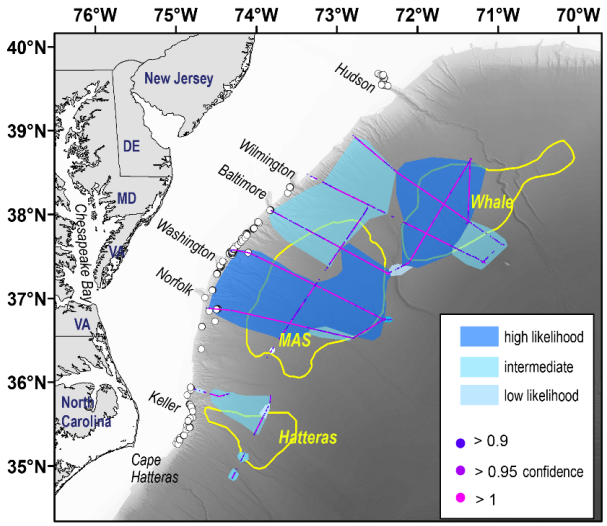
- 60 samples in gas bags analyzed at the USGS Woods Hole for $\delta^{13}C$-CH_4 and C1-C5 hydrocarbons using USGS Auto-SIM system – Provides insight into relative microbial and thermogenic contributions
- ~10 samples will be analyzed at MIT for clumped CH_4 isotopologues (collaborative with USGS Mendenhall postdoc) - Provide information about temperature of methane generation (depth interpretation)
- Remaining samples to Ohio State for additional stable isotopic analysis
- Additional samples generated from future degassing of Orange and Blue sand intervals at UT-Austin will be analyzed at USGS Woods Hole



USGS Auto-SIM with in-line gas chromatograph analyzing GOM2-2 gas samples

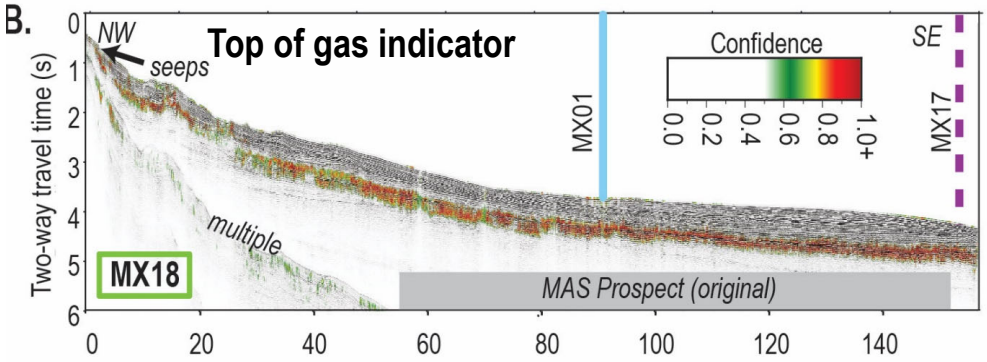
Task 3: U.S. Atlantic Margin Resources (not a Year 4 funding focus)

- Recommendation for “sweet spot” for U.S. Atlantic hydrates drilling target based on USGS data (including 2018 MATRIX seismic program) and advanced analyses
- Published machine learning analysis of MATRIX data for “top of gas” indicator (2022), greatly expanding area of potential hydrates on U.S. Atlantic margin
- Further studies (hydrate saturation determinations, extension of MATRIX analyses, modeling climate forcing of hydrate reservoir based on seismic evidence) in progress now
- Gas sourcing study wrapping up
- Overlap of USGS shallow gas/marine hydrates seismic characterization studies with goals of below-seabed carbon sequestration studies—Potential for USGS Woods Hole to collect modern multichannel seismic data to serve both shallow gas/hydrates and below-seabed CO_2 sequestration goals simultaneously



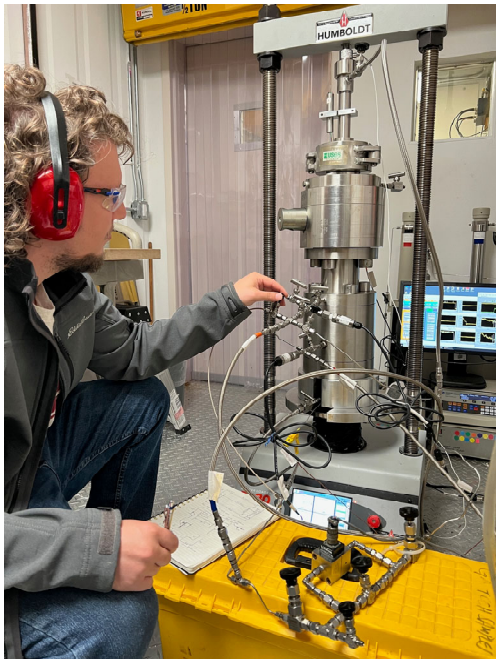
Majumdar et al., 2022

During MATRIX (2018), the USGS collected 2000 km of state-of-the-art multichannel seismic data on the US Atlantic margin with DOE and BOEM sponsorship



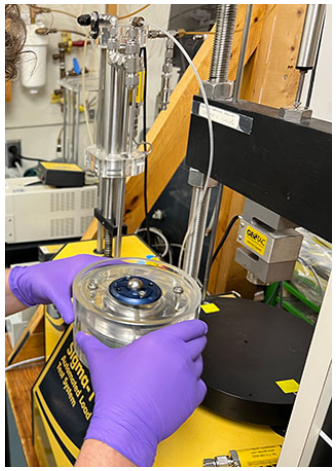
Task 4: Laboratory Developments for Geotechnical Properties (not a Year 4 focus)

High Stress Permeameter



Modified (for Alaska) Direct Shear Cell

Innovative Use of Oedometer Measurements



USGS Pressure Coring and Geotechnical Lab

- Built new high stress permeameter for pressure cores
- Modified direct shear cell for Alaska pressure cores
- Working oedometers in USGS geotechnical lab, producing results in excellent agreement with high stress permeameter
- Pressure core parameters from these devices: consolidation coefficients, direct permeability, shear strength, Vp
- In addition, USGS facilitated design of, build, and obtained DOT permits for pressure core shipping and storage chambers for US hydrates community

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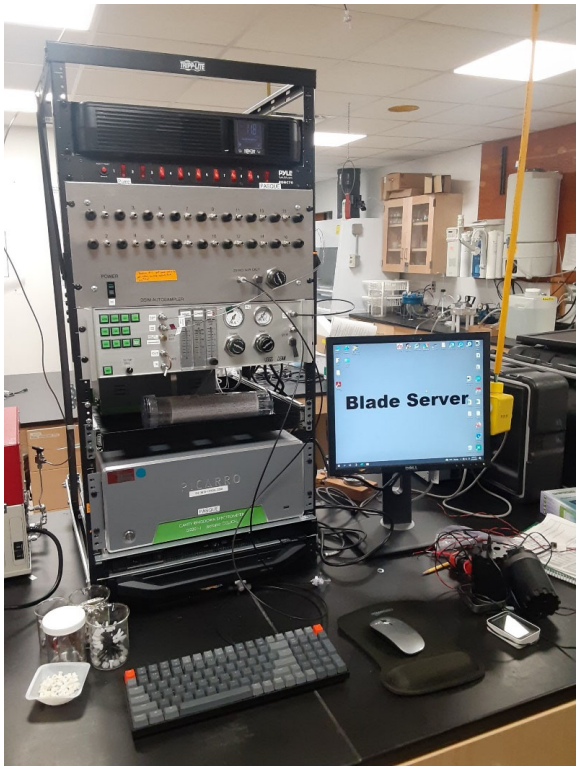
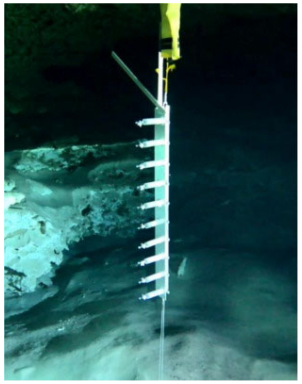
Task 4: Laboratory Developments for Geochemistry (not a Year 4 focus)



USGS Gas Analysis System

- Gas composition (hydrocarbon and CO_2)
- Gas concentrations
- $\delta^{13}C$ CH_4 and CO_2 (gas sourcing in real-time) at very high precision—USGS patented device
- 16 discrete samples at once, with auto-injection
- Highly portable (successfully used on ships, on-site at Alaska Hydrate Well)
- Widespread applications for wetlands, lakes, open ocean, estuary, and terrestrial studies
- Now miniaturizing key component to make instrumentation more widely accessible to research community

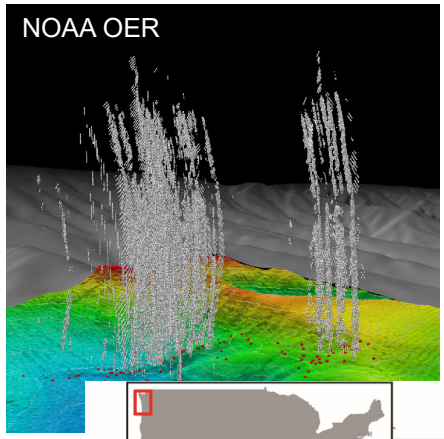


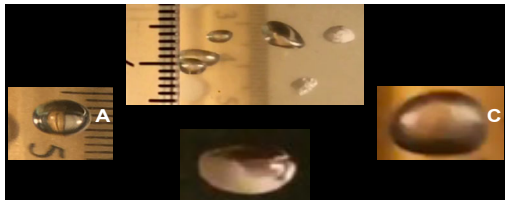
OctoPiPi
Bottom sampler to obtain high-resolution profiles of concentrations and $\delta^{13}C$ of DOC, DIC and methane, plus ions

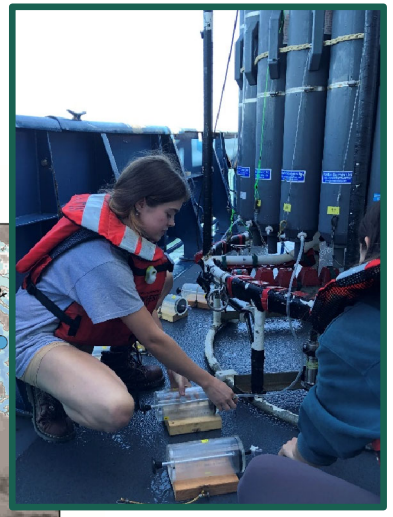
Monitoring Gas – Microbial Processes
Massively parallel microbial incubations and real-time measurements of evolving gases over days to weeks

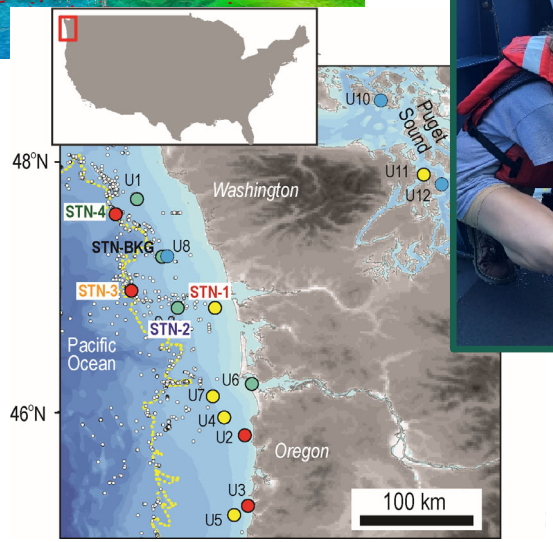
Task 6: Environmental Issues (not a Year 4 funding focus)

- Continue international leadership on hydrate interactions with the global climate system, including ocean chemistry (acidification, enhanced CH_4/DOC export to oceans) and effects of intermediate ocean warming
- Only US contributor to 2023 Arctic Report Card invited chapter on subsea permafrost and other international and across-USGS interactions on permafrost-hydrate (includes T. Collett)
- Major U.S. Atlantic margin methane seeps study close to publication with new, greatly expanded seeps database
- Continued studies of water column methane sinks (MOx), DOC export from hydrate-related gas seeps, age of methane emissions on U.S. Atlantic margin from methane-derived authigenic carbonates, and fate of methane (bubbles) in water column
- New discoveries of gas seeps from hydrate areas on Aleutian margin (with NOAA OER)









Joung et al., 2022

Outreach and Workforce Development

DOE-NETL NASEM Postdoc Fellow: Dr. Adrian Garcia (2020 – 2022)

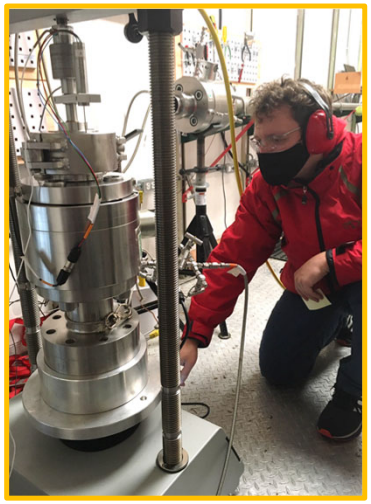
- Subsequently hired at USGS as term Research Civil Engineer (2022-2023)
- Now employed by Golder Associates in Atlanta and recently conducted a job for Golder on the Alaska North Slope, chosen due to his experiences at USGS

USGS-WHOI Postdoctoral Scholar: Dr. Alexandra Padilla (2022-2023)

- Ocean engineer with PhD from UNH (Tom Weber advisor)
- Continued work on gas hydrate-bubble dynamics for “fate of methane” studies
- Now employed by CU-Boulder as a program manager

USGS Mendenhall Postdoctoral Fellow: Dr. Ellen Lalk (2023-2025)

- Geochemist (clumped isotope expert) with PhD from MIT (Shuhei Ono advisor)
- Working on samples from Alaska and GOM2-2 energy resource expeditions
- Core research related to marine carbon cycling and methane dynamics



Previous USGS-WHOI postdoctoral scholar Dr. Urmi Majumdar (2019-2021; PhD. from Ohio State) led machine learning analysis of MATRIX data

Outreach and Workforce Development

Providing Growth Opportunities for USGS Technical Staff (with USGS salary funds)

- USGS Woods Hole geologist with master's in paleoceanography assisting with foram analyses for Gulf of Mexico sample processing
- USGS Woods Hole sediment Ph.D.-level lab staff with background in rock magnetics assisting with iron oxidation studies
- USGS Santa Cruz Ph.D.-level organic chemist conducting lipid biomarker analyses to search for native oil in Alaska North Slope samples

Providing Opportunities for Undergraduate Students (with USGS funds)

- Analyzing gas and fluid samples
- Advancing development of new instrumentation
- Assisting with sediment processing

Supporting USGS Workforce Development

- Two USGS Woods Hole Gas Hydrates Project scientists are named coauthors on the USGS *Unlearning Racism in Geoscience* (URGE) report

USGS

Outreach Activities (Examples)

- Science talks at Tennessee State University (HBCU) in 2023 and 2024 by gas hydrates postdocs
- High school outreach in 2023 and 2024 in Boston area
- Extensive background interviews to support 2024 episode of "This American Life" and "Flammable Ice" chapter of 2023 book entitled *Ice: Mixed Drinks to Skating Rinks,* by Amy Brady
- "Forward to Professorship" panel highlighting government science employment for New England postdocs (annually, hosted by Northeastern University)
- PhD and MS thesis committee service
- Media interviews

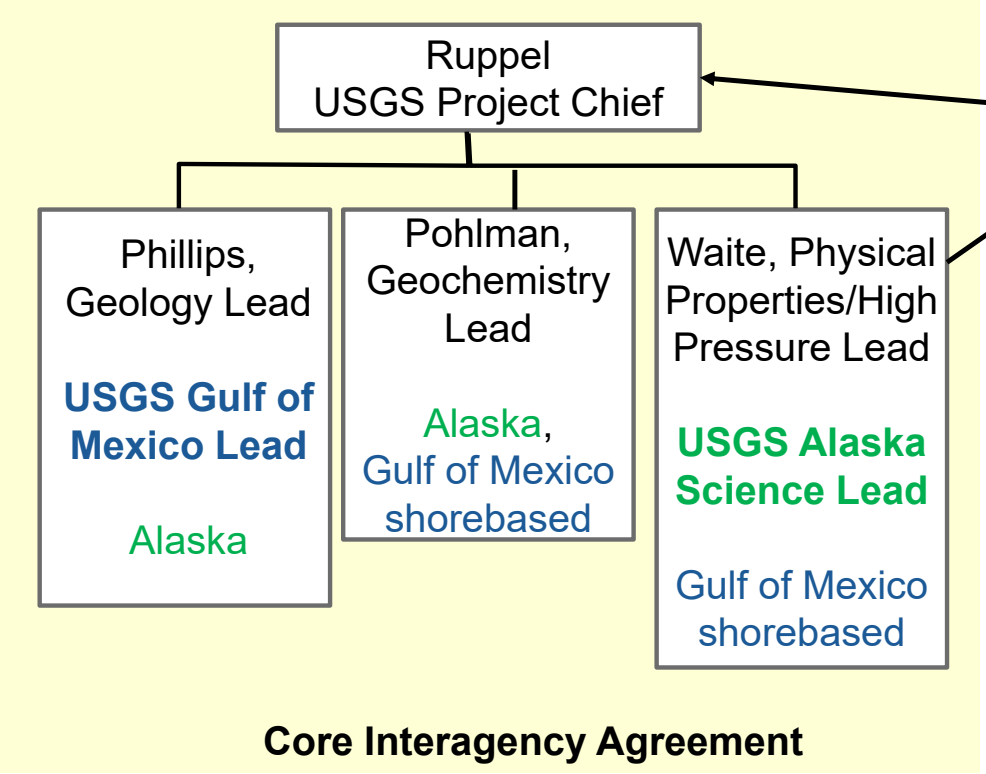
Summary

- Activities in Years 3 through 5 are heavily focused on:
  - Alaska Gas Hydrate Testing and Geologic System Analysis
  - Gulf of Mexico GOM2-2 Science
- Providing comprehensive data sets on the chemistry of solids, fluids, and gases for energy resource projects
- Producing comprehensive geotechnical and physical properties data sets to support hydrate reservoir characterization
- Using these state-of-the-art data sets to address critical questions about the evolution of hydrate reservoirs, paleoclimate, and paleo-depositional environments
- Exploring lessons of marine gas hydrate science, especially seismic data acquisition and analysis, for below-seabed carbon sequestration
- Continuing leadership in climate-hydrates interactions and characterization of marine gas hydrate provinces and methane dynamics in U.S. Atlantic, Pacific, and Arctic Oceans
- Aspirational: Expanding portfolio to include more focus on deepwater seafloor stability and connections to gas hydrates and shallow gas

Appendix

– These slides will not be discussed during the presentation but are mandatory.

Organizational Chart (Funded Tasks 1&2)



Collett
USGS Energy Lead

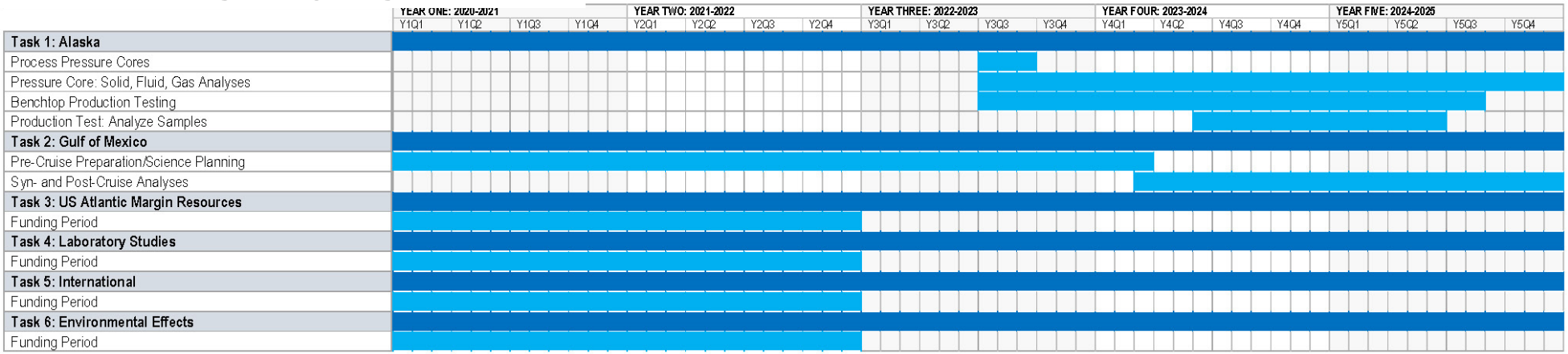
Leader, Alaska Hydrate Well and Production Test

Gulf of Mexico

Key U.S. Partners for Tasks 1 and 2:
DOE-NETL
JOGMEC & AIST
ASRC/AES
Colorado School of Mines
Georgia Tech
UNH
U South Alabama
UT-Austin
Oregon State University
MIT

Required Gantt Chart

Core Interagency Agreement



Tasks 3-6 have been unfunded for past two performance years. Significant work has continued to advance Tasks 3, 4, and 6 and to maintain USGS activities and contributions related especially to hydrate-environment interactions and U.S. Atlantic Margin and U.S. Arctic Ocean margin hydrates research without additional Core Interagency funding for Years 3 and 4.

Anticipated plan for Alaska North Slope project: Complete all analyses for which USGS Woods Hole is responsible in 12/2026; Publications timeline has not been established by project owners, but publications are expected to occupy the 2027 – 2029 timeframe.