METHANE HYDRATE NEWS

FIRE IN THE ICE

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NATIONAL ENERGY TECHNOLOGY LABORATORY

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U.S. DEPARTMENT OF ENERGY

Understanding the Role of Hydrates in the Environment—A Retrospective of DOE-supported Work

Frances Toro

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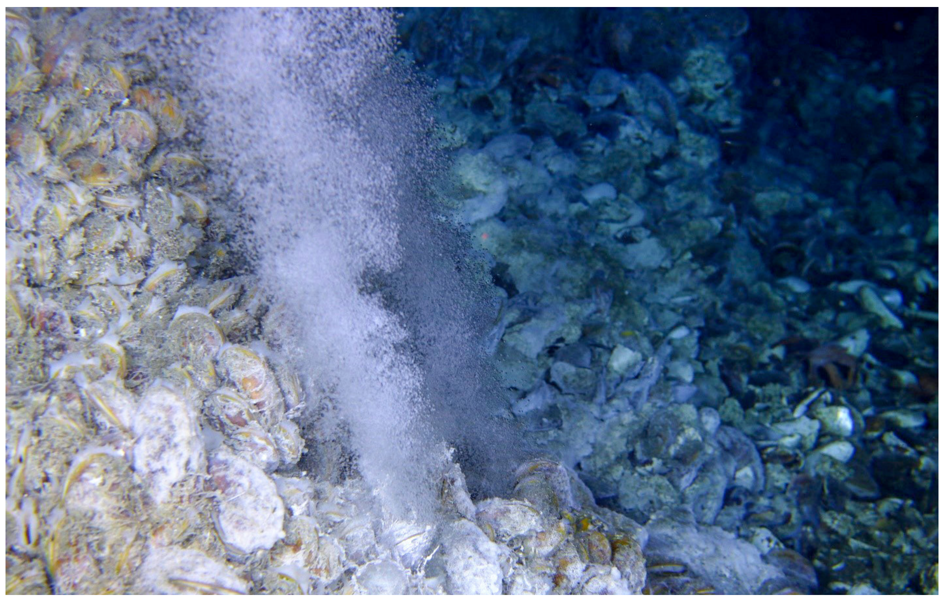

Figure 1. Methane bubbles emanating from gas seeps in chemosynthetic mussel beds off the coast of Virginia. Image acquired by Oceaneering, Inc. and provided courtesy of USGS.

Since the early 2000s, the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) Methane Hydrate Program has supported a number of research projects aimed at better understanding the role of naturally occurring gas hydrates in Earth's environmental processes and global climate change.

Gas hydrate deposits contain immense volumes of gas, predominantly methane (CH_4), stored in sedimentary strata in Arctic permafrost regions and along deepwater continental margins. Methane is a potent greenhouse gas, and its abundance and potential to influence and respond to climate change make it imperative that we understand the sources, stability, and fate of methane including that stored in hydrate deposits.

DOE-supported researchers have gathered high quality field and laboratory

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Fire in the Ice is published by the National Energy Technology Laboratory to promote the exchange of information among those involved in gas hydrates research and development.

This newsletter is available online at: https://www.netl.doe.gov/fire-in-the-ice

Interested in contributing an article to *Fire in the Ice*?

This methane hydrate newsletter now reaches 1170 individuals, representing 20 countries. If you would like to submit an article on research results likely to be of interest to the methane hydrate R&D community, please contact Fran Toro at frances.toro@netl.doe.gov or Karl Lang at karl.lang@keylogic.com. We look forward to hearing from you.

data, developed state-of-the-art numerical models, and scrutinized published scientific studies to evaluate how gas hydrate behaves, as both a methane source and a methane sink in the Earth's carbon cycle. Recent studies have focused on the fate of methane released from hydrate and other marine sources into sediment and marine water column sinks. What impact does the released gas have on sediment and ocean conditions? What processes are in play, and how much of the gas makes it to the atmosphere?

The purpose of this article is to review DOE Program contributions to a better understanding of the role of methane hydrate in a changing global environment; to arm current and future researchers with links to Program research accomplishments in this area; and, ultimately, to inform and improve future R&D related to hydrate-environment interactions.

ONGOING RESEARCH
U.S. GEOLOGICAL SURVEY (USGS)

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

DOE-sponsored research on hydrates in the natural environment has been advanced, to a large degree, through an ongoing interagency partnership with the USGS. This has led to a wealth of effective, collaborative, and interdisciplinary studies involving USGS scientists and researchers from academic institutions, U.S. National Labs, other government agencies, and international organizations. Over the last 12 years or so, USGS scientists have been engaged in a diverse range of research activities on hydrate-environment topics, including:

- Global Processes—quantifying hydrate-sourced methane (CH_4) escaping to the ocean-atmosphere system; assessing the role of oxidation and dissolution on marine hydrates; and evaluating the impact of erosion, ocean warming, and submarine slide processes on marine hydrates.
- U.S. Atlantic Margin—mapping and exploration of gas seeps and plumes on the seafloor; subseafloor imaging for hydrate distribution and seep fluid pathways; piston coring; gas source analysis; and sea-air CH_4 and CO_2 flux mapping.
- Western Arctic Ocean—conducting sea-air CH_4 and CO_2 flux surveys from Nome to Banks Island; analysis of subsea permafrost and relic hydrate distribution on Beaufort shelf; imaging shallow subseafloor CH_4 and hydrate distribution in the Beaufort Sea; and performing water column CH_4 analyses.
- Alaska North Slope—studying the Holocene CH_4 record and role of microbial populations in production and consumption of CH_4.

- Pacific Northwest Margin—surveying and exploration of gas seeps and plumes; bubble and authigenic carbonate analyses; and studying hydrate formation and fluid migration in Vancouver margin sediments and seafloor expulsion of ancient carbon.
- Northern Gulf of Mexico—determining the fate of gas seep bubbles in the water column; making seafloor hydrate observations and studying the environmental implications; and examining seep emission intensity.
- North Sea and Svalbard Margin—studying sea-air greenhouse gas exchange; conducting water-column profiling of CH_4 and CO_2; and conducting gas source analyses, including analysis of CH_4 production by aerobic methanogenesis.
- Greenland Margin/Ellesmere Island—evaluating sea-air CH_4 escape near retreating glaciers and in the shallow Lincoln Sea.
- Baltic Sea—measuring water column and sea surface CH_4 and stable carbon isotopes.
- Western Pacific—evaluating seafloor gas emission intensity from geochemical markers.
- Laboratory Studies—noble gas fingerprinting to assess if gas is sourced from hydrate; developing tools and techniques for collecting, analyzing, and measuring critical gas flux and methane/hydrocarbon production from microbial processes.

Based on these and other studies, researchers have found that active hydrate dissociation on Earth is not widespread, and that the bulk of CH_4 released from both permafrost and deep marine areas remains trapped in sediments or is converted to CO_2 rather than being transported to the atmosphere as CH_4. Two seminal articles on USGS hydrate-environment studies funded by DOE are Ruppel (2011) and Ruppel and Kessler (2016). MORE INFO. SELECTED PUBLICATIONS.

Figure 2. Equipment onboard the R/V Hugh R. Sharp, deployed on the U.S. Mid-Atlantic margin to sample and extract methane from seawater. Photos courtesy of USGS.

ONGOING RESEARCH
U.S. NATIONAL LABS

NETL Research and Innovation Center (RIC), West Virginia University (WVU), and USGS: Life Cycle Analysis of Gas Hydrate Systems in the Arctic

NETL RIC is collaborating with WVU to perform an environmental life cycle analysis of gas hydrate systems to understand potential climate impacts from possible future production of gas from hydrates. USGS researchers will provide geological expertise in support of this project. In addition, RIC researchers are planning an effort to identify research gaps related to the permafrost-gas hydrate systems in the Arctic. Past work by NETL RIC scientists resulted in development of a state-of-the-art laboratory for pore-scale measurements and high-resolution 3D imaging of pressurized hydrate specimens.

Lawrence Berkeley National Laboratory (LBNL): Numerical Studies of Gas Hydrates

LBNL researchers are using their TOUGH+HYDRATE modeling tools to evaluate the impact of ocean warming on subsea permafrost and associated sub-permafrost hydrate systems on continental shelves. Scientists will examine the potential for hydrate dissociation and release of methane into the water column and atmosphere, with a careful look at the potential release of CO_2 to the atmosphere after oxidation of the methane. This project relies on data and expertise to be provided by the USGS. Prior DOE-funded work has been focused on hydrate reservoir simulation and laboratory investigations of hydrate-bearing specimens; results have consistently shed light on the fundamental behavior of hydrates as a resource but also as a source and sink in Earth's global carbon cycle.

Pacific Northwest National Lab (PNNL): Coupled Hydrologic, Thermodynamic, and Geomechanical Processes in Studies of Gas Hydrates

PNNL is currently using its STOMP-HYDT-KE simulators to investigate strategies for creating stable CO_2 gas hydrate in subsurface geologic reservoirs. Results will be used to evaluate the viability of pursuing this approach for carbon storage on a commercial scale. Prior DOE-funded research assisted with development of the hydrate simulator and brought experts from all over the world together to optimize hydrate reservoir modeling tools. These tools provide insights into physical and chemical influences on hydrate formation and dissociation. From an environmental standpoint, the same processes drive hydrate stability vs instability.

ACADEMIC RESEARCH, 2018-2022

University of Rochester and USGS: Characterizing Ocean Acidification and Atmospheric Emission Caused by Methane Released from Gas Hydrate Systems along the US Atlantic Margin

Scientists from the USGS and University of Rochester teamed up to evaluate how CH_4 emitted from the seafloor is processed in the water column, for example, through dissolution and aerobic oxidation. The researchers also tracked whether CH_4 emitted at seafloor seeps could reach the ocean surface. This was achieved by measuring real-time sea-air CH_4 flux and documenting how much of the fossil carbon emitted at the seafloor reached shallow levels in the water column. MORE INFO. FINAL REPORT.

Texas A&M University: Dynamic Behavior of Natural Seep Vents—Analysis of Field and Laboratory Observations and Modeling

Texas A&M researchers led a study of bubble plumes emanating from seeps in the Gulf of Mexico to understand the dynamics and fate of methane released in this environment. The science team developed and tested a seep model to predict gas dissolution at seep sites. The model shows that over 99% (by mass) of released gases from these seeps is dissolved in the water column within the hydrate stability zone. A synthesis of this work is available in Wang and others (2020). MORE INFO. FINAL REPORT.

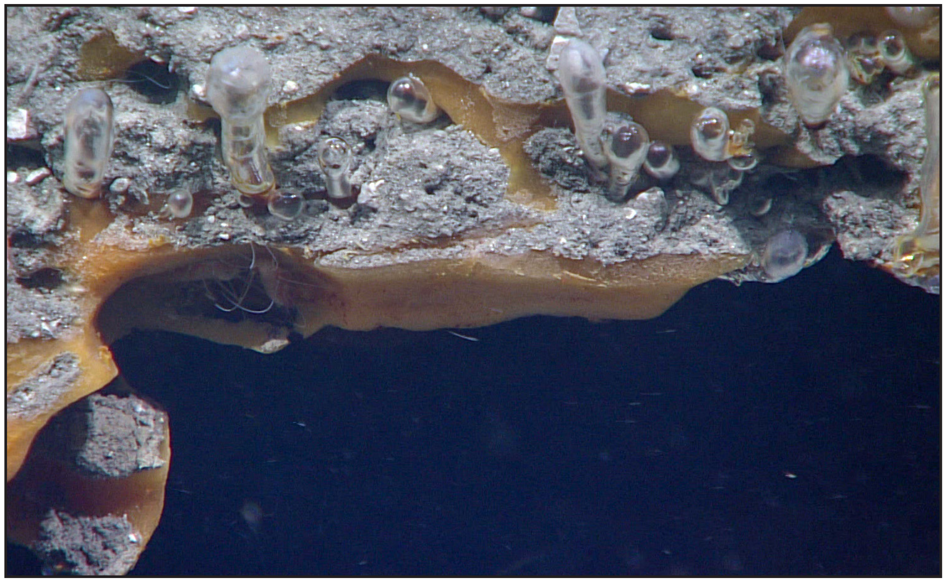


Figure 3. Gas hydrate (orange material) and gas bubbles near the seafloor in the northern Gulf of Mexico. Image acquired by NOAA and obtained for use courtesy of USGS.

ACADEMIC RESEARCH, 2014-2018

Oregon State University (OSU): Assessing the Response of Methane Hydrates to Environmental Change at the Svalbard Continental Margin

Researchers from OSU, USGS, and University of Rochester participated in European field programs along the Svalbard margin to examine whether gas seeps observed there were sourced from subsea hydrate deposits destabilized by warming seawater. They found that the seeps reflect a longer-term process and result in limited release of CH_4 to the atmosphere. Much remains in the water column or is subject to microbial oxidation. Some results are available in Mau and others (2017). MORE INFO.

Massachusetts Institute of Technology (MIT), USGS, and University New Hampshire: Fate of Methane Emitted from Dissociating Marine Hydrates—Modeling, Laboratory, and Field Constraints

This project focused on the fate of methane released from CH_4 seeps that could be tapping dissociating gas hydrate. Geophysical and geochemical data were collected and analyzed by scientists from MIT, USGS, and University New Hampshire to examine the source and fate of CH_4 emanating from seafloor gas seeps on the Mid-Atlantic margin. Researchers found that most CH_4 is dissolved in seawater, limiting the volume that makes it to the atmosphere. MORE INFO.

University of Washington: Characterizing the Response of the Cascadia Margin Gas Hydrate Reservoir to Bottom Water Warming Along the Upper Continental Slope

Scientists from the University of Washington studied CH_4 sources and sinks offshore Washington State and found that despite recent ocean warming there, hydrate dissociation is not widespread and is only a minor source of CH_4 seepage to the seafloor. MORE INFO. FINAL REPORT.

University of Oregon: Hydrate Evolution in Response to Ongoing Environmental Shifts

University of Oregon researchers led this effort to model slope failure in consolidated sediments, with the intention of understanding potential consequences for disrupting intact hydrate deposits. The study resulted in a model for slope stability that incorporates internal physical properties and elastic stress transmission in consolidated sediments. MORE INFO.

Southern Methodist University, Oregon State University, USGS, and University of California Scripps Institute of Oceanography: Gas Hydrate Dynamics on the Alaskan Beaufort Continental Slope—Modeling and Field Characterization

Project scientists focused on characterizing the thermal state of the Beaufort upper continental slope and the distribution and sources of CH_4 seeps on the U.S. Atlantic margin upper slope. Upper continental slopes are considered climate sensitive, because it is a setting where warming intermediate ocean waters impinge on the thinnest part of the gas hydrate stability zone at its landward edge. MORE INFO. FINAL REPORT.

University of California San Diego, Scripps Institute of Oceanography and USGS: Mapping Permafrost and Gas Hydrate Using Marine Controlled Source Electromagnetic Methods (CSEM)

In this project, SCRIPPS scientists designed, built, and tested a surface-towed CSEM system for shallow water use. The system was used to map subsea permafrost on the U.S. Beaufort shelf, and results were published in Sherman and others (2017). MORE INFO. FINAL REPORT.

ACADEMIC RESEARCH, 2012-2016

University of Texas at Austin (UTA): Controls on Methane Expulsion During Melting of Natural Gas Hydrate Systems

UTA led this project aimed at predicting conditions under which onshore and offshore hydrate accumulations are most likely to dissociate and release CH_4. The project resulted in a fully-coupled multiphase fluid flow and heat transport model to simulate hydrate formation and dissociation. The model was tested for its ability to forecast hydrate stability under conditions of ocean warming at continental margin sites and atmospheric warming in permafrost regions. MORE INFO. FINAL REPORT.

Oregon State University: Application of Crunch-flow Routines to Constrain Present and Past Carbon Fluxes at Gas Hydrate-bearing Sites

Oregon State University led an effort to develop a kinetic model to describe the biogeochemical cycling near the sulfate-methane-transition zone. The model was successfully developed and applied to pore water data collected from offshore sites in the Ulleung Basin (South Korea), Cascadia Margin (offshore Oregon), and Krishna-Godavari Basin (India). MORE INFO. FINAL REPORT.

Figure 4. Gas hydrate (white material) in marine sediments collected off the coast of Oregon. Photo courtesy of USGS.

UNITED NATIONS ASSESSMENT PROJECT, 2010-2014

United Nations Environment Programme (UNEP): Global Assessment Project

This project was the result of a UNEP, Statoil, Schlumberger, and DOE partnership, and the work was performed by Stiftelsen GRID-Arendal. The goal was "to develop a global assessment of methane gas hydrates that will facilitate informed decision-making regarding the potential development of gas hydrate resources between the scientific community and other stakeholders/decision makers." The resulting assessment provides a wealth of scientific information on the role of gas hydrate in Earth's carbon cycle, its sensitivity to climate change, and potential environmental impacts of producing natural gas from hydrate reservoirs. Results are contained in 3 volumes: VOLUME 1, VOLUME 2, EXECUTIVE SUMMARY

ACADEMIC RESEARCH, 2008-2012

University of Alaska Fairbanks (UAF) and USGS: Source Characterization and Temporal Variation of Methane Seepage from Thermokarst Lakes on the Alaska North Slope in Response to Arctic Climate Change

UAF and USGS researchers studied CH_4 sources and sinks at thermokarst lakes on the Alaskan North Slope to evaluate potential links between methane seepage and permafrost degradation. The project spawned collaborative studies of permafrost carbon and CH_4 emissions under North Slope permafrost. Project results are summarized in Wooller and others (2009). MORE INFO.

Texas A&M University (TAMU): Remote Sensing and Sea-truth Measurements of Methane Flux to the Atmosphere

In this TAMU-led effort, satellite imagery was used to identify floating oil on the surface of the ocean in the Gulf of Mexico, and underwater acoustic profiling techniques were deployed to locate seafloor seeps that could be sourcing the oil. The project resulted in the identification of over 1000 seeps, with the highest density of seeps located in the Green Canyon area of the north-central Gulf slope. MORE INFO. FINAL REPORT.

University of Delaware: Characterization of Methane Degradation and Methane-degrading Microbes in Alaska Coastal Waters

University of Delaware scientists studied CH_4 degradation by microbial processes, by sampling and analyzing sediment cores collected on the Beaufort Shelf, north of Alaska, in a 12-day research cruise referred to as *Methane in the Arctic Shelf/Slope (MITAS)*. MORE INFO. CRUISE REPORT.

University of California Santa Barbara (UCSB): Assessing the Efficacy of the Aerobic Methanotrophic Biofilter in Methane Hydrate Environments

UCSB Researchers investigated water-column methane oxidation in hydrate environments to better define the role of aerobic methanotrophy in regulating how much CH_4 from marine hydrates reaches the atmosphere. MORE INFO. FINAL REPORT.

University of Chicago and University of California Berkeley: Integrating Natural Gas Hydrates in the Global Carbon Cycle

Scientists from the University of Chicago and UC Berkeley worked together to develop a two-dimensional, basin-scale model to examine the distribution and stability of seafloor hydrates in the context of the global warming. The model was developed to handle passive or active margin geologic settings.

MORE INFO. FINAL REPORT.

RESEARCH PRIOR TO 2008

Naval Research Laboratory: Gas Hydrate Research in Deep Sea Sediments—Chatham Rise, New Zealand

In 2006, the Naval Research Lab studied hydrate-water column interactions in deep sea sediments off the coast of New Zealand, along the Hikurangi Margin. The researchers collected core specimens, geochemical samples, and microbial samples to characterize CH_4 hydrate deposits on New Zealand's eastern, active continental margin.

MORE INFO. FINAL REPORT.

USGS and University of California Santa Cruz (UCSC): Gas Hydrate Instability in the Southeastern Bering Sea

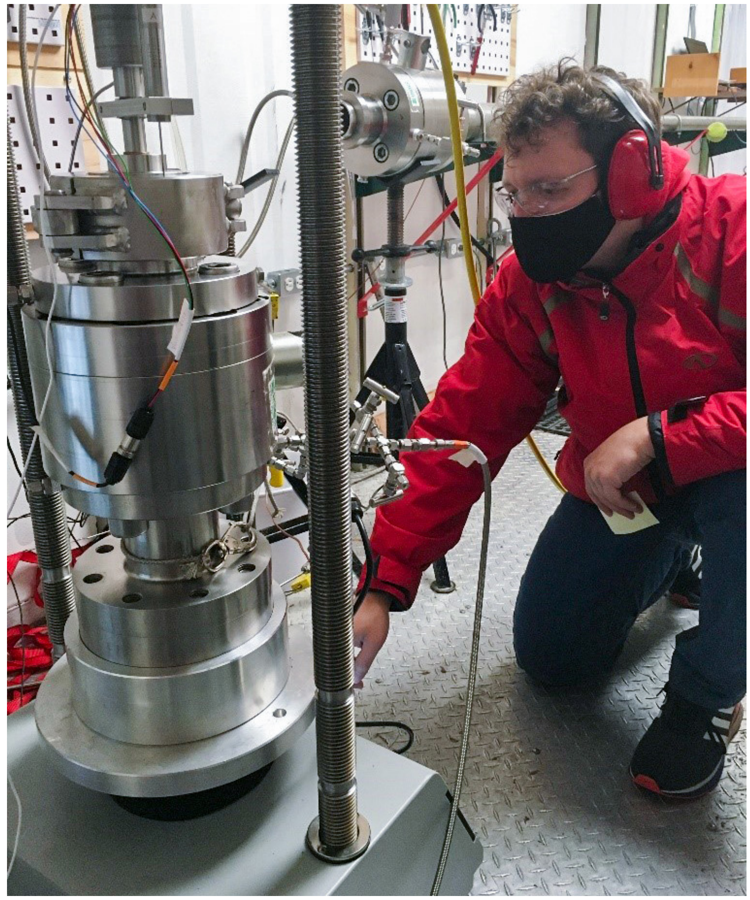
This project was carried out by USGS and UCSC scientists to investigate the stability of CH_4 hydrate formations during periods of rapid climate change. Results suggest that CH_4 in sediments contributed to Earth's greenhouse gases during times of rapid, natural climate warming in the past.

MORE INFO. FINAL REPORT.

FELLOWSHIP PROJECTS

Starting in 2007, NETL and the National Academy of Sciences (NAS) began supporting emerging gas hydrate researchers, under the banner of their Methane Hydrate Research Fellowship program, administered by NAS and funded by NETL (MORE INFO). Most of the fellowship recipients have engaged in research related to hydrate-environment issues. Hydrate-environment fellowship studies have included:

- 2021-2023 Vince Clementi, Rutgers University: Geochemical Constraints on the Effects of Warming and Tectonics on the Stability of Chile Margin Gas Hydrates
- 2020-2022 Adrian Garcia, USGS Woods Hole: Characterization of Effective Stress-Dependent Permeability in Hydrate-Bearing Pressure Core Sediments
- 2019-2020 Claire McKinley, University of Washington: Evaluating the Extent of Microbial Fe-reduction and its Role in the Global Methane Cycle
- 2016-2018 Benjamin Phrampus, Oregon State University: Analysis of Cascadia Margin Hydrate Destabilization in Response to Contemporary Ocean Temperature Warming
- 2014-2016 Jennifer Frederick, University of California Berkeley and Desert Research Institute: Pore Fluid and Gas Migration Patterns within Arctic Shelf Sediments Associated with Degrading Relict Gas Hydrate and Submarine Permafrost
- 2013-2015 Jeffrey Marlow, California Institute of Technology: Geobiological Controls on the Abundance and Stability of Methane Hydrates
- 2012-2014 Rachel Wilson, Florida State University: Factors Influencing Hydrate Dissociation Rates within the Hydrate Stability Zone—Interaction with Sand Substrates and Surface Armoring
- 2010-2012 Laura Brothers, USGS Woods Hole Sciences Center: Arctic Continental Shelf Response to Global Climate Change—A Geophysical Study of Permafrost Degradation and Potential Hydrate Dissociation in Nearshore Beaufort Sea
- 2010-2011 Ann Cook-Yockey, Columbia University-Lamont Doherty Earth Observatory: Investigating Gulf of Mexico Gas Hydrate Reservoirs Using LWD Images and Logs
- 2009-2010 Hugh Daigle, Rice University: Heterogeneous Hydrate Accumulations—Influence of Pore- and Fracture-Scale Processes
- 2008-2010 Laura Lapham, Florida State University: Controls on Hydrate Stability in Methane Depleted Sediments—Laboratory and Field Measurements
- 2008-2009 Evan Solomon, UC San Diego Scripps: Constraining Rates of Biogeochemical Reactions and Methane Generation Offshore India—Implications for Fluid and Gas Sources, Transport Processes, and Gas Hydrate Formation
- 2007-2010 Monica Heintz, UC Santa Barbara: Biological Control of the Flux of Methane from Marine Hydrates to the Atmosphere



Adrian Garcia with the effective stress cell in the USGS Hydrate Pressure Core Analysis Laboratory in Woods Hole Coastal and Marine Science Center. Photo courtesy of USGS.

SUMMARY

NETL's Methane Hydrate Program has contributed to our understanding of gas hydrate processes in the context of Earth's environmental processes and a changing climate. We hope this retrospective of NETL's project portfolio of current, recent, and past projects on hydrate-environment topics will encourage the next generation of scientists to build on lessons learned. The embedded links are intended to provide access to more in-depth project information in the form of NETL project summaries and final reports, newsletter articles, and peer-reviewed publications.

USGS Tools Allow Precision Gas Source Analysis in the Field

John W. Pohlman, Michael Casso, Lee-Gray Boze, and Emile Bergeron

U.S. Geological Survey Woods Hole Coastal & Marine Science Center, Woods Hole, MA

Introduction

Field studies of gas hydrate systems rely on gas sampling and analysis tools to determine the origins of methane and other hydrocarbon gases. The conventional strategy for deciphering gas origins has been to collect samples in the field; pack, ship, and store them; and later analyze them in a laboratory. A critical drawback of the conventional strategy is that measurements and analyses made after completing the field program often reveal gaps where data should have been collected. Such data gaps increase the likelihood of missing small-scale, but significant, natural features.

In an effort to simplify gas analysis protocols and provide timely results in the field, researchers with the USGS Gas Hydrates Project have been developing devices that interface with portable laser absorption spectrometers, specifically cavity ring-down spectrometers (CRDSs). Originally designed for atmospheric monitoring, the CRDSs used by the Gas Hydrates Project are off-the-shelf products that measure methane and CO_2 concentrations as well as the stable carbon isotopes of these gases.

In the past, we and other gas hydrate researchers added components to CRDSs that allowed these parameters to be measured in near-surface ocean waters sampled continuously during marine surveys. In this article, we describe new instrumentation that extends the capabilities of CRDSs to analysis of discrete samples for gas concentration and stable carbon isotopic content at the field site in nearly real time. Doing so permits us to modify sampling and measurement plans while in the field, so that we may investigate anomalies, resolve small-scale features, and ensure a project's data coverage needs are met.

Background and Motivation

Methane and other hydrocarbon gases originate from organic matter that is either deeply buried and then heated (thermogenic) or degraded by microbes at relatively low temperature in shallow sediments (microbial). The most common approach to determining the origin of gases collected in the field combines: (1) measuring the composition of these gas mixtures; and (2) determining the isotopic characteristics of the different gases.

Researchers measure differences in the relative abundances of methane's chemically stable isotopic forms, $^{12}CH_4$ and $^{13}CH_4$, to distinguish thermogenic versus microbial gases. The difference between the two isotopes is expressed as $\delta^{13}C$. Methane in thermogenic mixtures usually has a greater proportion of the neutron-rich $^{13}CH_4$ variant (and thus a higher $\delta^{13}C$), while gas produced by microbes tends to have a lower proportion of the $^{13}CH_4$ variant (and thus a lower $\delta^{13}C$).

Measuring minute mass differences among gas isotopologues requires a highly sensitive instrument, such as an isotope ratio mass spectrometer (IRMS). IRMSs are large and expensive instruments, maintained and operated by specially trained individuals in sizeable laboratory facilities. They are not suitable for field applications. CRDSs are also able to measure these gases, but the measurement range of commercially available models is not suitable for concentrated samples.

Thermogenic gas mixtures often also include larger and more complex hydrocarbon gases like ethane, propane, and butane cleaved from source rocks during thermal decomposition. Their gas composition is most often measured with a gas chromatograph (GC), which separates gases along a meters-long column, based on differences in molecular mass and geometry, prior to quantification. Some GCs are field portable, but more sophisticated GCs often require permanent installation in a laboratory.

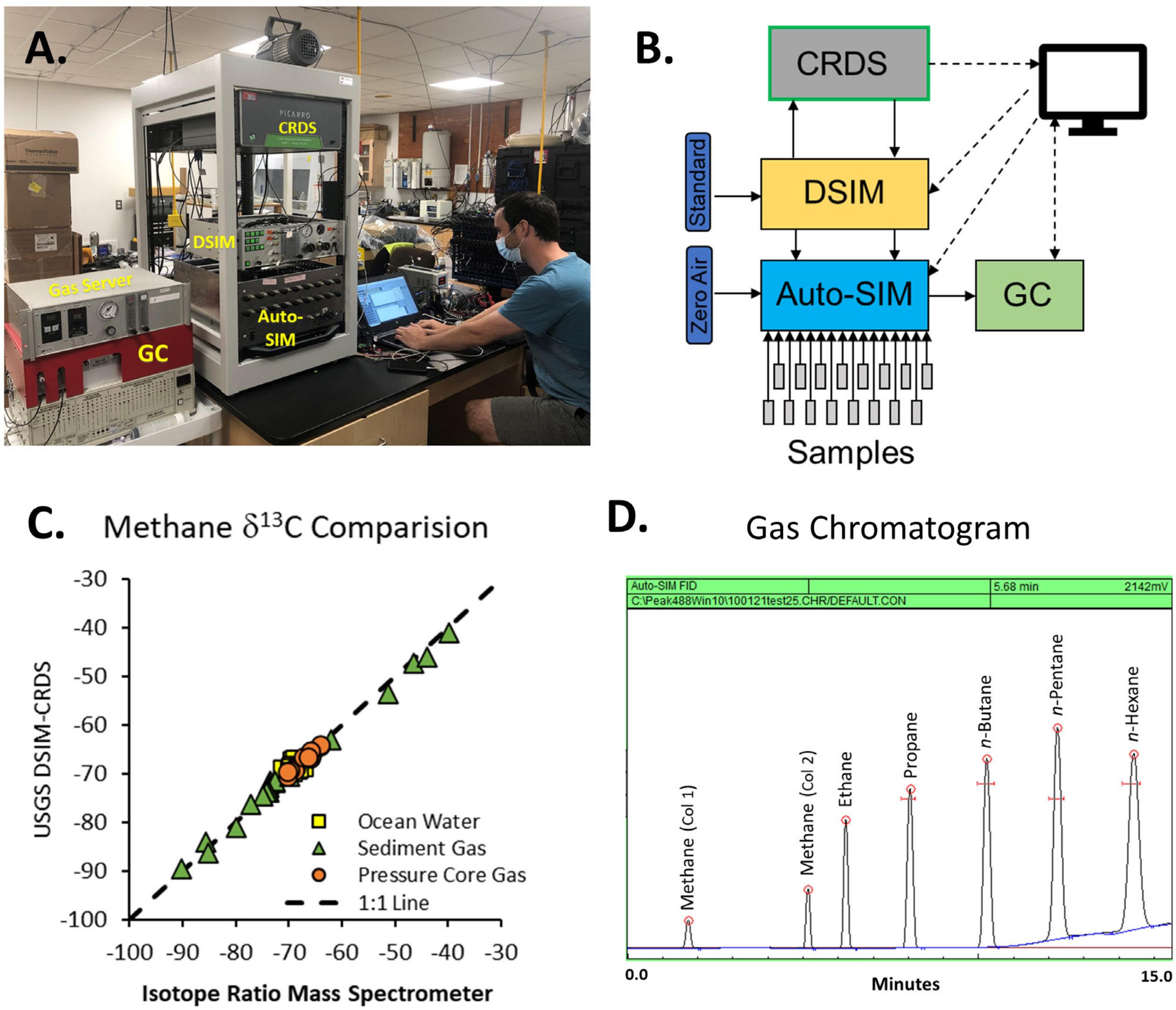


Figure 1. The USGS Automated Gas Analysis System (A and B) quantitatively introduces and dilutes (if desired) up to 16 discretely collected gas samples into a cavity ring-down spectrometer (CRDS) for stable carbon isotope analysis of methane (C) and compositional analysis by gas chromatography (D).

USGS Discrete Sample Introduction Module (DSIM)

The analytical tool developed by the USGS Gas Hydrates Project uses a field-portable system to perform both compositional and gas isotopic analyses on discrete samples—vapor phase gas or dissolved gases in water—in nearly real time. The system uses a USGS-designed, patent-pending discrete sample introduction module (DSIM) interfaced with a CRDS. The DSIM renders the CRDS useful in settings where component concentrations range from trace atmospheric to 100%.

The USGS DSIM interfaces with a Picarro G2201-i CRDS (Figures 1A and 1B) that measures methane and CO_2 concentrations, as well as their stable carbon isotopes, after being calibrated with certified standards. Although the recommended upper limit for measurement of a sample's methane $\delta^{13}C$ and concentration is ~1000 ppm with this CRDS, the DSIM can quantitatively dilute samples using a system of dilution loops and expansion volumes. This process expands the dynamic concentration range by 6 orders of magnitude or more. As a result, samples with methane concentrations ranging from 100% analyte to the lower limit of detection by CRDS (~ 2ppm for $\delta^{13}C$ and < 40 ppb for methane concentration) can be measured with a precision of ~1% for concentration, and as low as 0.5‰ for $\delta^{13}C$. Without quantitative dilution by the DSIM, analysis of high concentration samples from gas hydrate systems and methane seeps is not possible with our Picarro G-2201*i* CRDS.

The DSIM system can analyze gas extracted from water samples (e.g., ocean water and sediment pore water) or from void space in recovered cores (Figures 1C and 2). Stable carbon isotopic values measured by DSIM-CRDS

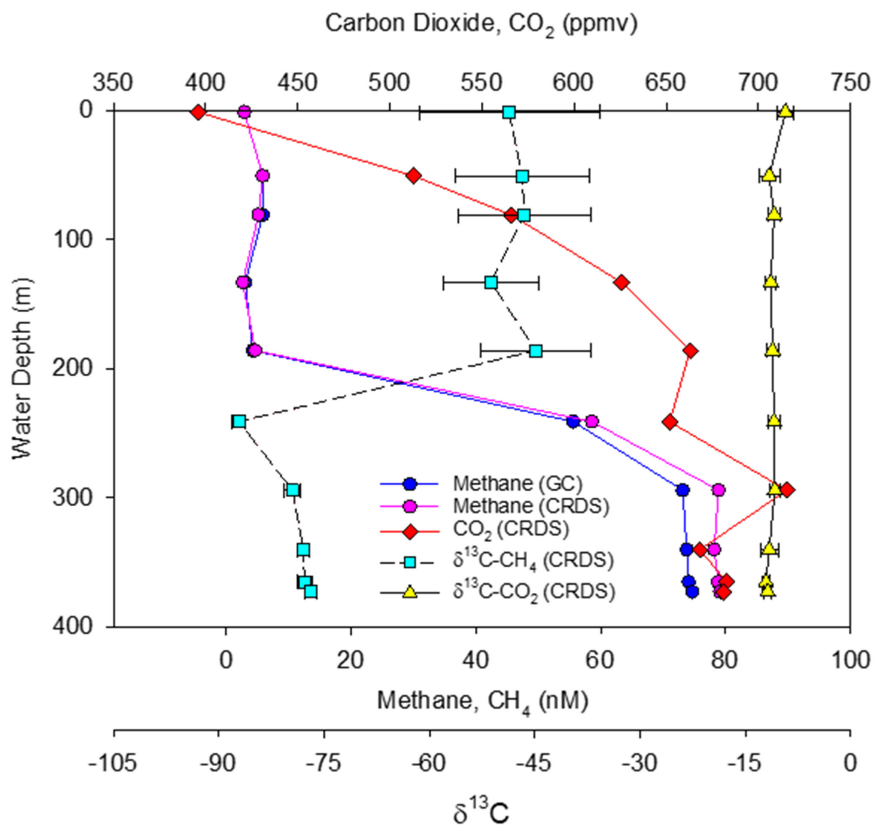


Figure 2. Oceanographic profile of DSIM-CRDS data obtained from the water column of the US Atlantic margin near a seafloor gas seep. Note comparison of gas analysis profiles obtained with gas chromatograph (GC in dark blue) and DSIM-CRDS (in pink).

for water column, sediment gas, and pressure-core methane samples are virtually indistinguishable from those measured by IRMS (Figure 1C). IRMS systems are the gold standard for isotopic ratio measurements of carbon, hydrogen, and other biologically active elements. Therefore, our ability to match the accuracy of the IRMS with a system that is deployable in the field represents a significant step forward for gas hydrate and other gas sampling expeditions.

In preparation for the upcoming DOE-JOGMEC-USGS gas hydrate production test on the Alaskan North Slope, the USGS Gas Hydrates Project has also designed an automated sample introduction module (Auto-SIM) that sequentially loads up to 16 gas samples from Cali-5-bond™ bags into the DSIM and an SRI MG#5 GC (Figures 1A and 1B). The SRI GC has flame ionization and thermal conductivity detectors that measure the concentrations of C_1 to C_7 hydrocarbons, CO_2, N_2, and O_2. The automated operation and data processing afforded by the Auto-SIM simplifies the process and minimizes time between sampling and analysis. Analytical results may therefore be available to guide project operations in nearly real time. While the Auto-SIM cannot provide unequivocal source attribution, rapid (~ 15 mins), automated, onsite analysis permits more comprehensive sampling programs that promise greater insight into the spatial and temporal changes that occur in the dynamic environments associated with gas hydrate.

Acknowledgments

The DSIM (U.S. Patent Appl. No 17/020,343) was designed, constructed, and tested with support from the USGS Coastal and Marine Hazards and Resources Program. Support for the development of the Auto-SIM was provided by the USGS and by DOE-USGS Interagency agreement 89243320SFE000013. Any use of trade, firm, or product name is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Suggested Reading

Pohlman, J.W., Casso, M., Magen, C., and Bergeron, E., 2021. Discrete sample introduction module for quantitative and isotopic analysis of methane and other gases by cavity ring-down spectroscopy. Environmental Science and Technology. https://pubs.acs.org/doi/10.1021/acs.est.1c01386

Pohlman, J.W., Bergeron, E.M., and Casso, M.A., 2021. Discrete sample introduction module (DSIM) for gas analysis by laser absorption spectroscopy. U.S. Patent Appl. No 17/020,525. https://pdfaiw.uspto.gov/.aiw?Docid=20210310936&idkey=NONE

Pohlman, J.W., Greinert, J., Ruppel, C., Silyakova, A., Vielstadte, L., Casso, M., Mienert, J., and Bunz, S., 2017. Enhanced CO_2 uptake at a shallow Arctic Ocean seep field overwhelms the positive warming potential of methane. Proceedings of the National Academy of Sciences. https://www.pnas.org/content/114/21/5355

Recent Natural Gas Discoveries in the Hydrate-Rich Area of the Black Sea, Turkey

Şükrü Merey

Department of Petroleum and Natural Gas Engineering, Batman University, Turkey

Introduction

Gas hydrates are widely distributed all over the world in both permafrost and marine regions. Over the last two decades, many countries have implemented gas hydrate exploration programs. Most of these countries, including Japan, China, and India, are looking to utilize gas hydrate resources to help meet their growing energy demands. Turkey also seeks additional energy resources to keep pace with its ever-increasing energy demands. In recent years, studies of conventional gas provinces and gas hydrate-rich areas in the Black Sea were undertaken as part of a national effort to boost Turkey's domestic energy supply and decrease its dependence on imported natural gas.

Turkey's annual natural gas consumption is approximately 50 billion cubic meters (bcm) or 1.77 trillion cubic feet (tcf). Production from conventional natural gas reservoirs in the Thrace Basin and near the shore of Akcakoca in the Black Sea satisfies less than 1% of this consumption. As a result, Turkey relies heavily on natural gas imports from Russia, Iran, Azerbaijan, and other countries to meet its energy needs.

In an effort to address this imbalance, Turkey began in 2017 to acquire drillships to facilitate hydrocarbon exploration in the offshore regions along its borders, in both the Mediterranean Sea and the Black Sea. Four drillships were purchased and are being used to stage exploratory drilling, primarily in Turkey's Exclusive Economic Zone (EEZ) in the western Black Sea.

Recent Free Gas Discoveries in the Black Sea

After a detailed seismic survey, the Tuna-1 exploratory well was drilled and logged in August, 2020 (Figure 1, red diamond) at a location where the water depth is 2117 m. The well encountered more than 100 m net thickness of conventional natural gas-bearing reservoir in Pliocene and Miocene sands. This free gas discovery occurs in turbidite sands of the Danube Delta, at a depth of 3125–3615 m below sea level (mbsl). In October 2020, drilling operations at the Tuna-1 well were finalized at a total depth of 4775 mbsl. The lower part of the Tuna-1 well encountered an additional 30 m-thick natural gas-bearing sand zone. The combined reserve potential for these two gas-bearing zones is estimated to be 405 bcm or 14.3 tcf, and the discovery is now known as the Sakarya Gas Field.

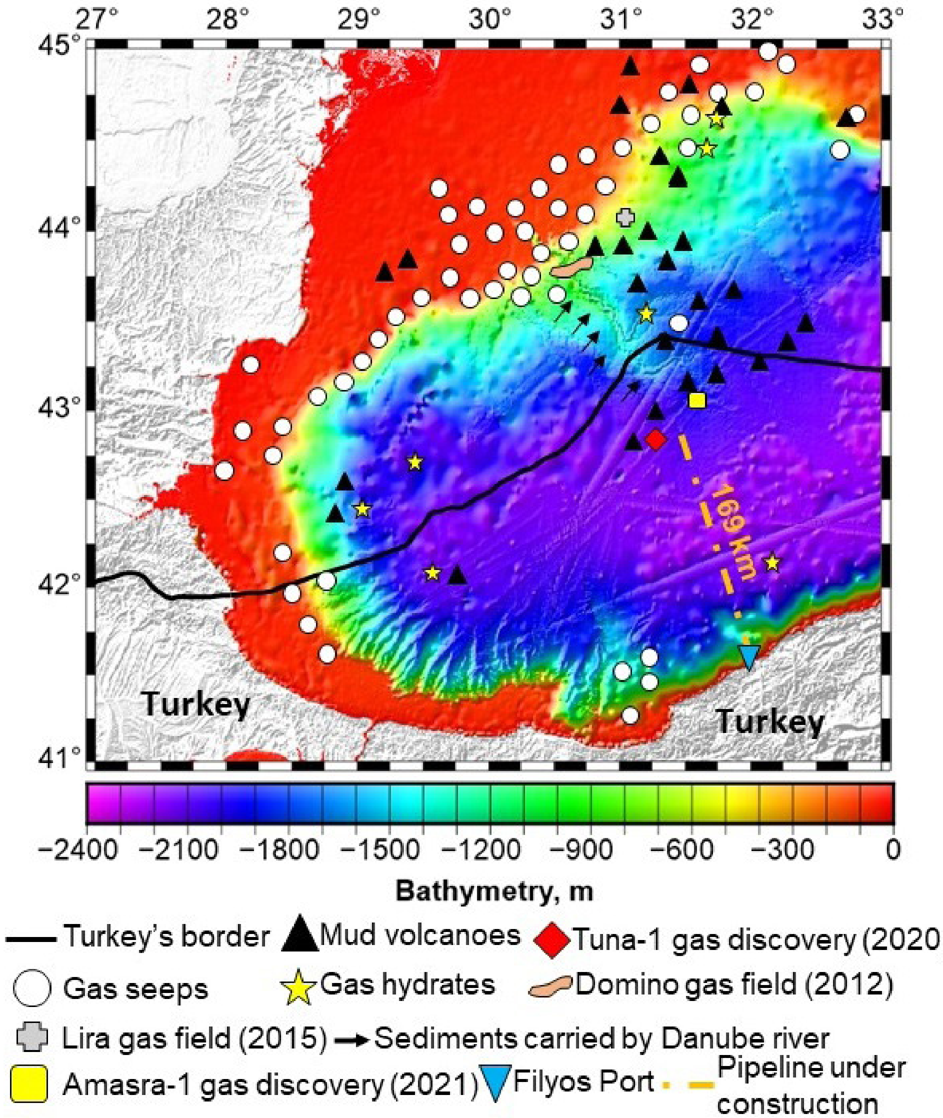
Another field, known as the Northern Sakarya Gas Field, was also discovered to the northeast of Tuna-1, with the drilling of the Amasra-1 well (Figure 1, yellow square). The Amasra-1 well was drilled in water depths of 1938 m to a total well depth of 3850 mbsl. Based on the Amasra-1 discovery, the reserve potential of the Northern Sakarya Gas Field is estimated as 135 bcm, or 4.8 tcf.

By 2023, Turkish Petroleum Corporation, the national oil and gas company, plans to have completed the infrastructure needed to produce gas from the Sakarya and Northern Sakarya Fields and deliver it to market. They are constructing a subsea production facility in the Black Sea EEZ, onshore gas processing facilities at Filyos Port on Turkey's Black Sea coast, and a 169-km natural gas pipeline to transport the produced gas to the processing plant (Figure 1). Gas produced from these fields is forecasted to contribute significantly to Turkey's natural gas supply and will likely provide 20% or so of its total annual consumption.

From Free Gas to Gas Hydrates

The technically recoverable gas hydrate potential of the Black Sea has been addressed in many international studies. There are many gas hydrate indicators in the Black Sea (Figures 1 and 2), including gas seeps, mud volcanoes, bottom simulating reflections (BSRs), and direct samples of gas hydrate on or near the seafloor.

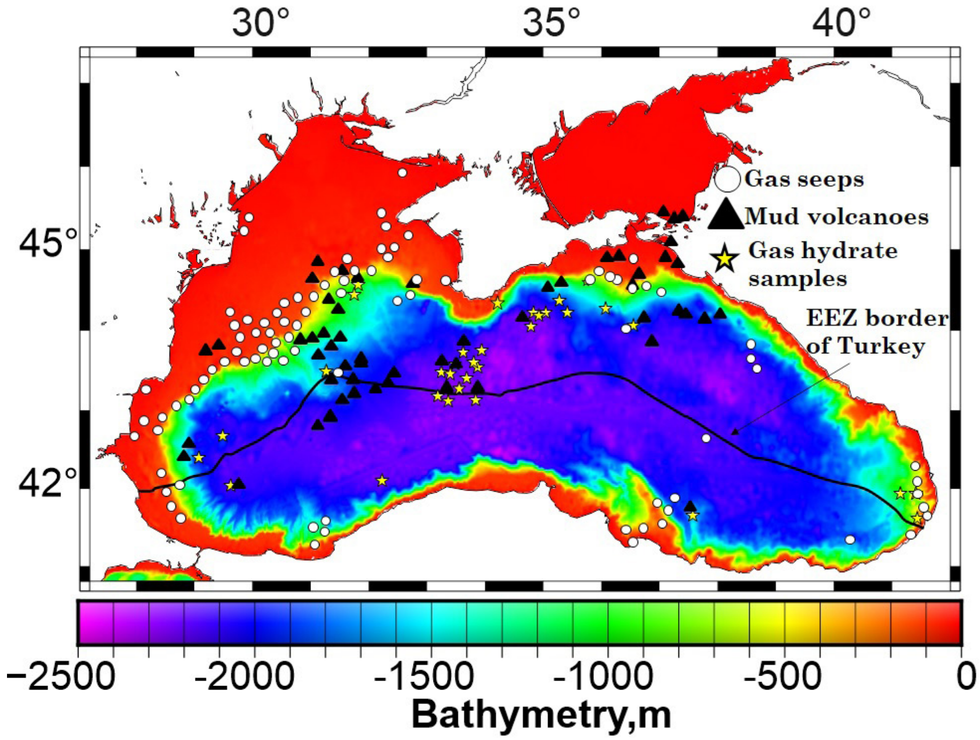
Figure 1: Gas hydrate indicators in the Western Black Sea. The black line represents Turkey's offshore border-- the marine region to the south of the border lies within Turkey's Exclusive Economic Zone or EEZ.



In the Danube Delta of the Western Black Sea, gas hydrate studies have been conducted over the years, and the gas hydrate potential of this region is considered to be promising. Indeed, one of the first gas hydrate samples in the world was obtained in the Danube Delta near the seafloor at a water depth of 1950 m in the 1970s. More recently, between 2014-2018, Turkey conducted a gas hydrate exploration project in the Western Black Sea, which included geophysical surveys and seafloor sampling.

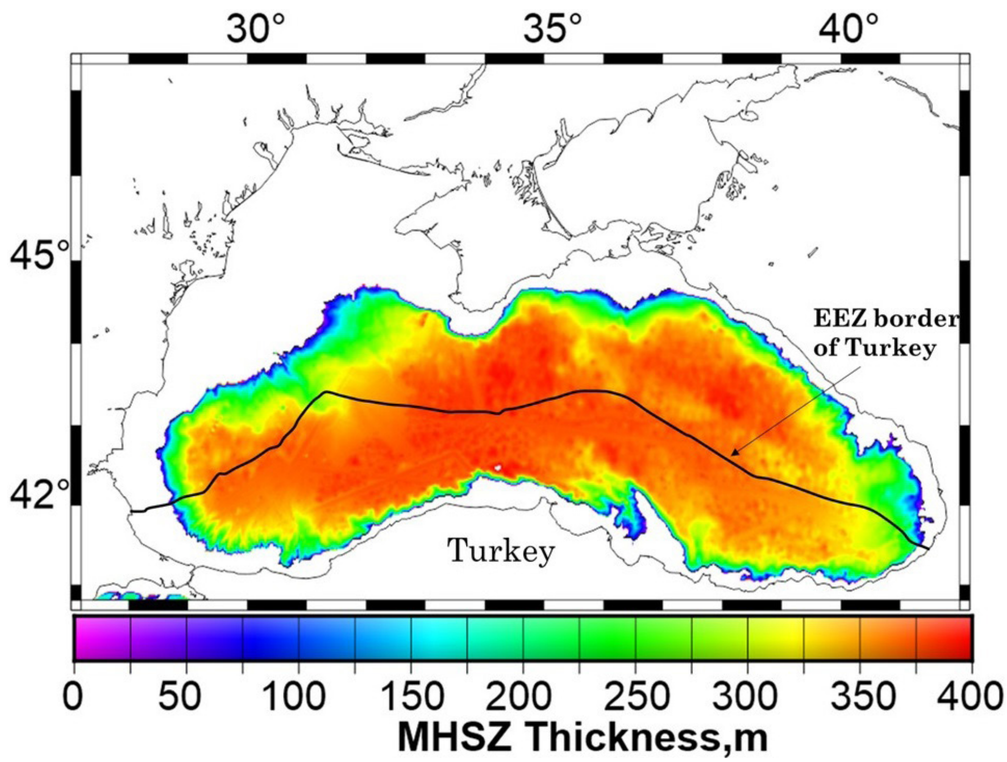
Based on these data, the Turkish EEZ portion of the Black Sea has been estimated to contain 4.63 tcm or 163.5 tcf of technically recoverable methane stored in hydrates. This represents an average derived from multiple independent estimates. Such estimates are highly generalized and should be considered statistical approximations dependent on the quality and quantity of available geophysical data, geothermal gradients, pressure gradients, salinity, reservoir thickness estimates, and direct observations from wells.

Figure 2: Gas hydrate indicators in the Black Sea include gas seeps (white circles), mud volcanoes (black triangles), and direct samples (yellow stars). The black line is the northern limit of Turkey's EEZ.



The gas hydrate potential in the vicinity of the Tuna-1 well (Sakarya Gas Field) and Amasra-1 well (Northern Sakarya Gas Field) in Figure 1, is estimated at nearly 393 bcm or 13.9 tcf of methane stored in hydrate-bearing sediments. Figure 3 shows the estimated thickness of the methane hydrate stability zone (MHSZ) beneath the seafloor in the Black Sea. The estimated maximum thickness exceeds 350 m in much of the basin.

Figure 3: Estimated thickness of methane hydrate stability zone (MHSZ) below the seafloor in the Black Sea, based on measured geothermal gradients, observed/estimated pressure gradients and salinity. Black line is, again, the northern limit of Turkey's Exclusive Economic Zone.



Conclusion

Some might argue that conventional natural gas discoveries in the Sakarya and Northern Sakarya Gas Fields could diminish the importance of gas hydrates in Turkey's Black Sea EEZ. On the contrary, these discoveries have led to construction of new natural gas infrastructure and an overall technical readiness for offshore gas production. These factors make production of gas from hydrates more feasible and achievable for Turkey in the future.

With the addition of subsea production facilities, onshore processing facilities in Filyos Port, and a gas pipeline connecting the two, we can imagine this same infrastructure being used for potential future production of gas from proximal hydrate reservoirs in Turkey's Black Sea EEZ. Moreover, appraisal wells and production wells in the basin are likely to yield valuable information about the much shallower hydrate reservoir zone, which extends from the seafloor to about 500 m below the seafloor. New data, including gas shows, lithology, rate of penetration, and other mud logging measurements are likely to contribute to refined estimates of the gas hydrate potential of the region.

Suggested Reading

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Merey, S. (2021). Technically recoverable methane hydrate potential of the marine regions in the exclusive economic zones of Turkey. E3S Web of Conf., 230 (2021) 01001, https://doi.org/10.1051/e3sconf/202123001001

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Zander, T., Haeckel, M., Berndt, C., Chi, W.C., Klaucke, I., Bialas, J., Klaeschen, D., Koch, S., Atgin, O. (2017). On the origin of multiple BSRs in the Danube deep-sea fan, Black Sea. Earth and Planetary Science Letters, 462 (March 2017), 15-25, https://doi.org/10.1016/j.epsl.2017.01.006

George Moridis Receives SPE's Highest Honor for Outstanding Scientific Achievements

Dr. George J. Moridis, Senior Scientist at Lawrence Berkeley National Laboratory (LBNL) and professor and holder of the Robert L. Whiting Chair in the Petroleum Engineering Department of Texas A&M University, was recently awarded the Society of Petroleum Engineers (SPE) Honorary Membership Award. The award, which represents the highest SPE International accolade, was given on behalf of SPE's Board of Directors and worldwide membership in recognition of Moridis' outstanding scientific achievements in advancing knowledge and understanding of unconventional reservoirs. Much of George's research has been focused on numerical simulation of gas hydrate reservoir behavior through development of the TOUGH+HYDRATE modeling platform.

George's TOUGH+HYDRATE code broke new ground in the modeling world by addressing the most pressing and fundamental scientific questions related to naturally occurring gas hydrates. Seeing a need for a reliable code, George focused on advancing a reservoir simulator that would be able to handle all phases of hydrate reservoir behavior. This resulted in a rigorous and internationally-known numerical modeling tool that has been employed across the globe in a wide range of gas hydrate field programs. The model is capable of forecasting hydrate formation and dissociation behavior under varying pressure and temperature conditions, in virtually any geologic setting. Moridis notes that concurrent and complementary laboratory work at LBNL opened the door to 3D imaging of hydrate-bearing samples during phase changes and has provided important ground truth to constrain the numerical modeling.

George is grateful for opportunities to collaborate with others in the gas hydrate R&D community. He says, "I began working on hydrates with NETL's support in 1999. Up to now, the TOUGH+HYDRATE code, in its various versions, has been used by over 70 organizations in 20 countries." He is also thankful for research support provided by DOE/NETL. He says, "DOE support has been very important to my career, and a substantial fraction of my 16,000+ citations are related to NETL-funded hydrate work."

SPE President Tom Blasingame presented the award to Moridis during the Society's Annual Technical Conference and Exhibition in September, 2021.

Vince Clementi Receives 2021 NETL-NAS Methane Hydrate Fellowship for Work on Chilean Margin Hydrates

Vince Clementi received the 2021 NETL-NAS Methane Hydrate Research Fellowship award for his research on “Geochemical Constraints on the Effects of Warming and Tectonics on the Stability of Chile Margin Gas Hydrates.” Vince is conducting this research as a PhD candidate at Rutgers University, in the Department of Marine and Coastal Sciences, under the direction of Dr. Yair Rosenthal.

Vince’s research centers on naturally occurring hydrate deposits off Chile’s tectonically active coast. The objective is to understand gas hydrate stability on the Chile Margin by studying pore water geochemistry parameters of samples collected at four offshore sites. Geochemical profiles will be developed to provide a first-order estimate of hydrate dissociation, and complementary modeling will be used to untangle possible triggering mechanisms. Vince states, “Unlike other hydrate systems that have been heavily studied, the Chile Margin is rapidly warming and tectonically active, making it an ideal region to study these two forces in conjunction.”

Congratulations to Vince for being selected as the newest recipient of the NETL-NAS Methane Hydrate Fellowship!

The Spring 2022 application window for the NETL-NAS fellowship opens June 1st and will remain open through August 1st. Please see the announcement on the facing page for additional information.

NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL-NAS Methane Hydrate Fellowship Summer Application Period Approaches June 1 – August 1, 2022

The National Energy Technology Laboratory-National Academy of Sciences, Engineering, and Medicine (NETL-NAS) Research Fellowship Program is designed to support the development of methane hydrate science and technology and enable highly qualified graduate and post-graduate students to pursue advanced degrees and training in hydrate research.

Applications for this NETL-NAS fellowship are accepted and reviewed during two open periods: 1) December 1 – February 1; and 2) June 1 – August 1.

M.S., Ph.D., and Postdoctoral applicants, who are U.S. citizens and are affiliated with a federal laboratory or accredited university in the U.S., are eligible for these fellowships and encouraged to apply. The fellowships are two to three years in duration and include stipends ranging from $30,000 – $60,000 per year, with adjustments for experience. There are also supplements for research equipment and travel.

The 2022 summer application period is approaching, and potential fellows are encouraged to apply, through the NAS website, at: NETL Methane Hydrate Fellowship Program (nationalacademies.org)

The National Academies of SCIENCES ENGINEERING MEDICINE

Ancient Methane in Sediment Cores Reveals Clues about Methane Hydrate Dissociation Across the Oligocene-Miocene Boundary

Graduate student Bumsoo Kim and Assistant Professor Dr. Yi Ge Zhang of Texas A&M University published an article in the February 14th, 2022 issue of *Nature Geoscience* titled "Methane hydrate dissociation across the Oligocene–Miocene boundary." The paper reports the presence of diagnostic lipid biomarkers with depleted carbon isotopes in sediment cores from three sites in the Antarctic Southern Ocean. The biomarkers are linked to methane release and subsequent oxidation across the Oligocene–Miocene boundary, 23 million years ago. The biomarker evidence indicates that hydrate destabilization in the Antarctic Southern Ocean was initiated during the peak of the Oligocene–Miocene boundary glaciation, during a sea-level low stand. This finding is consistent with model results that suggest a decrease in hydrostatic pressure, resulting from the fall in sea level, eroded the base of the methane hydrate stability zone. Subsequent aerobic oxidation of the released methane in seawater may have facilitated the rapid termination of glaciation in the early Miocene. MORE INFO.

University of Washington Researchers Identify 349 Methane Gas Plumes in Puget Sound

According to a study published in the January 19th, 2022 issue of *Geochemistry, Geophysics, Geosystems,* 349 methane plumes have been documented at seafloor sites in Puget Sound. Many of the plumes were detected with sonar data collected during recent research expeditions, but the first indication of their presence dates back to a surprise discovery, also gleaned from sonar images, back in 2011. Dr. Paul Johnson, University of Washington professor of oceanography, and co-authors Tor Bjorklund, Chenyu (Fiona) Wang, Susan Hautala, and Susan Merle of the National Oceanic and Atmospheric Administration, describe two persistent bubble plumes that emanate from crisp, discrete holes in the seafloor and follow two geologic faults—one is a branch of the Seattle Fault, and the other is the South Whidbey Fault. The methane bubbling upwards seems to be of microbial origin, and it appears to provide sustenance to methane-eating bacterial mats in surrounding seawater. The research was funded by the National Science Foundation. MORE INFO.

Spotlight on Research

LAURA STERN

U.S. Geological Survey (USGS)

Laura is an emeritus Research Geophysicist at the USGS's Earthquake Science Center in Menlo Park, California and has contributed to gas hydrate science for 30 years. She has been a vital contributor to the USGS Gas Hydrates Project and in 2019 received the U.S. Department of Interior's Meritorious Service award.

Growing up in Lexington, Massachusetts, Laura Stern acquired an early love of science and the outdoors. Family hiking trips in the White Mountains of New Hampshire inspired subsequent summer employment with the Appalachian Mountain Club. A ninth grade field trip to Yosemite, the Grand Canyon, and other parts of the western U.S. kindled an affinity for the west, and Laura left New England after high school to attend Stanford University. At Stanford, she completed a B.S. and M.S. in Geology, the latter focused on crystal chemistry and mineralogy.

Laura joined the USGS in 1985 to work with geophysicist Steve Kirby, as well as Bill Durham of Lawrence Livermore National Laboratory (LLNL), on studies of extraterrestrial ices and gas hydrates. The USGS Menlo Park Gas Hydrates Laboratory was established in 1993 as an outcome of their efforts. It began as a low-tech outfit equipped with discount kitchenware and matured into a proper lab with custom-built instrumentation and superb technical support provided by John Pinkston. Laura took over as the laboratory chief in 2011.

Initially, work in the hydrate lab focused on synthesizing pure methane hydrate with reproducible grain characteristics for physical property measurements. Laura led the development of the "seed ice" synthesis method, which became a 1996 cover story in Science. A quarter century later, that cover photo of a flame sustained by methane hydrate is the most frequently reproduced USGS hydrate image. The team later showed that, surprisingly, methane hydrate is vastly stronger than water ice.

Starting in the late 1990s, the lab hosted postdoctoral researchers Sue Circone and Bill Waite and graduate students Mike Helgerud and Brian deMartin; and yielded some of the first measurements of acoustic wave speeds and thermal properties of pure methane hydrate. Studies in the lab also led to discovery of "anomalous preservation," a thermal window in which rapidly depressurized methane hydrate can be sustained for weeks, in some cases months, at temperatures well outside its stability field. This finding is Laura's most highly cited contribution to gas hydrate science.

Laura says collaborating with other researchers has been a rewarding—and fun—aspect of her work. She worked with Peter Brewer and colleagues from the Monterey Bay Aquarium Research Institute to measure hydrate dissolution rates and partnered with Steve Constable (Scripps Institution of Oceanography) and Wyatt Du Frane, Jeff Roberts, and Ryan Lu (LLNL), to measure gas hydrate electrical conductivity. With USGS colleagues, she investigated noble gas uptake by gas hydrates and characterized gas hydrate reservoir sediments. She also helped pioneer cryogenic scanning electron microscopy (cryo-SEM) to image natural and lab-synthesized gas hydrates, research she looks forward to continuing as an emeritus scientist.

When not in the lab, Laura enjoys hiking, skiing, and cycling—especially bicycle touring in beautiful places like the Alps, Pyrenees, and Dolomites. She raced in cross-country ski competitions and long-distance cycling events for decades, but these days she relishes the simple joy of being outside and active. During a bike ride in 2015, Laura and four others had a near-fatal encounter with an out-of-control vehicle and its inebriated driver. After a long and challenging recovery, she returned to her previous pursuits with newfound gratitude and resolve. She reflects, "I have no memory of being airlifted from the scene, but I do remember waking up in the hospital feeling profoundly thankful and lucky to be alive! My steel bike, on the other hand, was utterly destroyed." In 2021, she finally revisited the Grand Canyon to check off a goal formulated during that ninth grade trip—hiking from one rim of the canyon to the other and back. Laura beams, "It exceeded all expectations!"

If you or someone you know would like to be the subject of the newsletter's next "Spotlight on Research," please contact Karl Lang (karl.lang@keylogic.com) or Fran Toro (frances.toro@netl.doe.gov). Thank you!