Gas Hydrate Occurrences in the Black Sea – New Observations from the German SUGAR Project

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Methane seepage, mud volcanism, and gas hydrates are very common in the Black Sea (Figure 1). In this large anoxic sea, methane expelled at cold vents causes methane-enriched bottom waters (up to ~11 µM), while hydrogen sulfide produced by microbial sulfate reduction in the water column below ~150 m leads to elevated sulfide levels (up to ~300 µM). As a consequence, surface sediments show rapidly decreasing sulfate concentrations towards the zone of anaerobic oxidation of methane (AOM) at depths of 3-5 m below seafloor (mbsf), compared to background concentrations.

Extrapolating the corresponding diffusive CH_4 flux yields an estimated depth of 30-50 mbsf as the expected depth at which gas hydrates should occur on the slopes and deep basins of the Black Sea. At active seep sites,

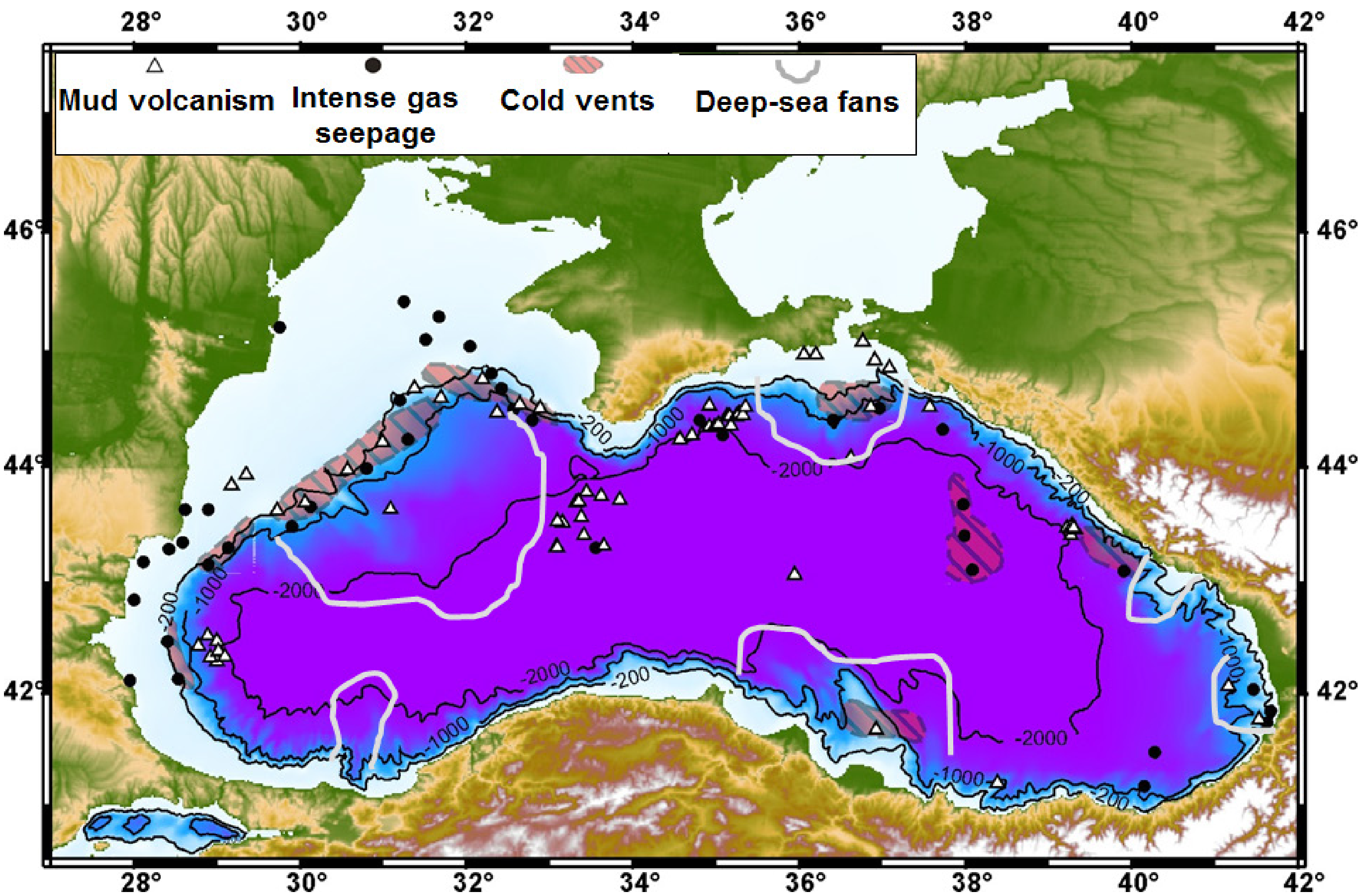


Figure 1. Map of the Black Sea indicating ubiquitous gas seepage, including cold vents and mud volcanoes. Major deep-sea fans are also shown (clockwise from upper left: Danube-Dnjepr, Sea of Azov, Bsipi, Rioni-Tschorochi, Kizilirmak-Yesilirmak, Sakarya). Modified from Schmale et al. (2011).

the AOM zone and the occurrence of gas hydrates are shifted further toward the seafloor.

Due to the warm bottom water temperatures (~9 °C) and low salinity (~22.3) in the Black Sea, gas hydrates become thermodynamically stable at water depths greater than ~720 m. Because the low salinity of 3 to 5 of the past limnic stages of the Black Sea still prevails in the sediments from 20 to 350 mbsf (see articles by Degens and Ross; and Soulet and others), the gas hydrate stability zone (GHSZ) may extend slightly upslope to a water depth of ~665 m (Figure 2). Depending on the local heat flow (27-35 °C/km) and the water depth, structure 1 CH_4 hydrates are generally stable down to 250-400 mbsf.

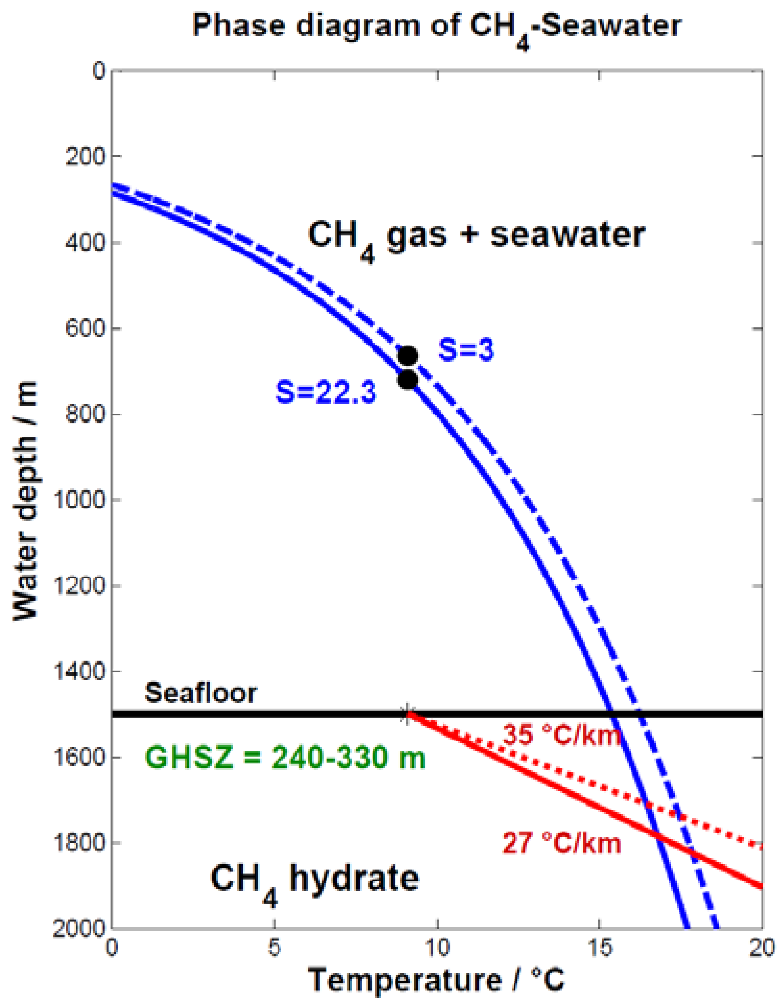
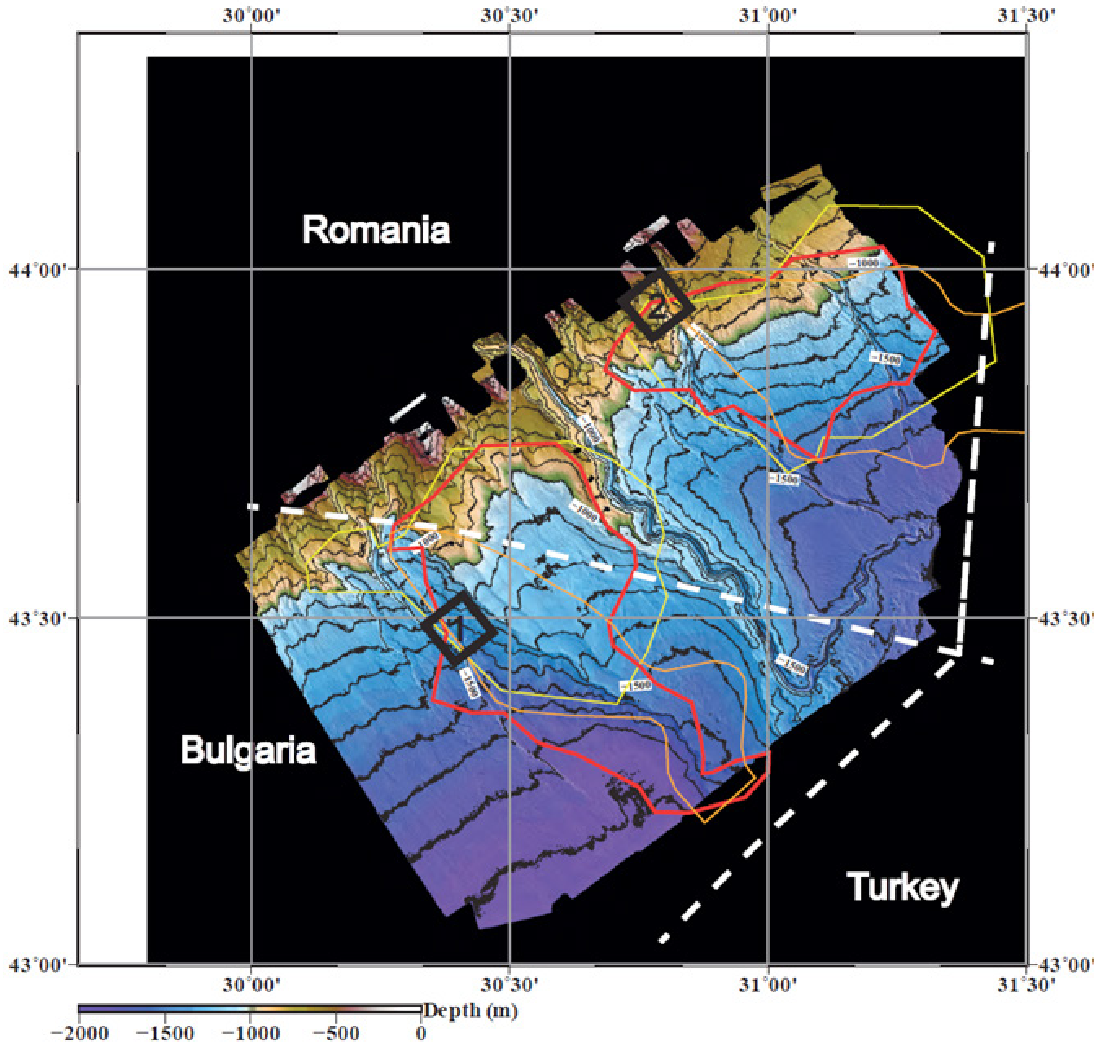


Figure 2. Thermodynamic stability of Structure 1 methane hydrates under typical environmental conditions prevailing in the Black Sea.

More than 15 years of seep research in the Black Sea conducted by the European marine science community makes it one of the best studied gas hydrate provinces in the world. Reservoir-quality gas hydrate accumulations are expected in permeable sandy-silty deposits, such as turbidites and channel-levee-systems of the large paleo-river systems around the Black Sea. The most prominent one is the paleo-Danube river system in the western Black Sea, located in the economic zones of Bulgaria and Romania (Figure 3).

Figure 3. *Map of the Paleo-Danube channel-levee system. The colored polygons outline the BSRs mapped by different studies (red: MSM34; orange: Popescu et al., 2007; yellow: Baristeas, 2006). Black rectangles mark Areas 1 and 2.*



From December 2013 to February 2014 scientists from the German SUGAR (Submarine Gas Hydrate Reservoirs) project, in collaboration with colleagues from IMST-Seislab in Turkey, IFREMER in France, and IOBAS in Bulgaria, began investigations of the gas hydrate accumulations in this area, deploying geophysical, geochemical, and geotechnical equipment from *R/V Maria S. Merian* (cruises MSM 34 and 35).

A continuous BSR is prominent in two areas, southwest and northeast of the central Viteaz canyon (Figure 3), as identified in the acquired high-resolution 2D seismic data. Additional 3D P-cable seismic cubes together with ocean bottom seismometer (OBS), and controlled-source electromagnetic (CSEM) data were collected in two selected working areas (rectangles indicate Areas 1 and 2 in Figure 3).

Area 1 is marked by a stack of up to 5 BSRs below the levees, and inverted reflection events with increased amplitudes in buried channels that are interpreted as indications for gas migration and hydrate formation within the GHSZ. Gas migration is believed to move laterally along the buried permeable channel fills and levees, because no vertical pathways, such as fractures, seismic pipes, or chimneys, are present. In addition, no active seep sites were detected in hydro-acoustic surveys in the entire southwestern BSR area, and geochemical analyses did not reveal enhanced methane fluxes towards the seafloor in this area. Together, these observations suggest a sealed gas hydrate deposit beneath this area. First analysis of the CSEM data reveal very high electrical resistivities (> 10 Ωm), which are partly explained by low porewater salinity but may also indicate high gas hydrate saturations within the upper 300 mbsf.

In contrast, active gas expulsion from several spots on the seafloor was observed in Area 2. The gas flares are associated with a slump feature

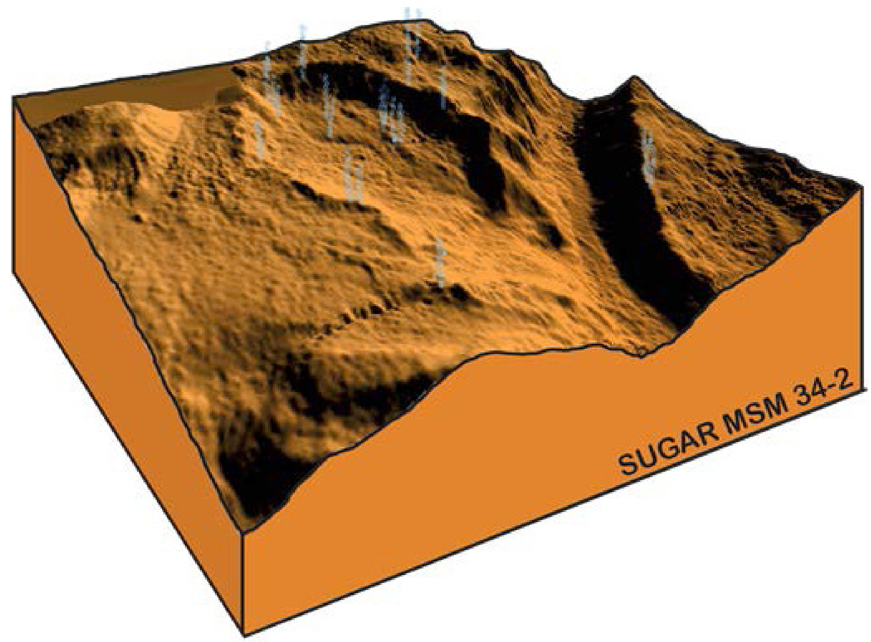


Figure 4. 3D view of the bathymetric map of the slope failure in Area 2. Gas seeps are imaged in water depths of 580-750 m by their hydro-acoustic reflections ("gas flares" shown in light blue) in the multibeam data.

(Figure 4), which is underlain by a BSR event with an unexpected strong upward bending shape. Geochemical analyses indicate the emission of biogenic gas with up to ten-fold increased AOM rates in the area of the slope failure.

Follow-up work in both areas is taking place currently, in Phase III of the SUGAR project. This phase includes characterizing the identified gas hydrate reservoir, addressing relevant environmental challenges, and developing appropriate production scenarios and monitoring strategies. A drilling campaign with the mobile rig MeBo200 is anticipated to take place in 2017. Further joint European gas hydrate activities will be organized within the framework of the recently launched COST Action MIGRATE.

Acknowledgments

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SUGGESTED READING

Baristeas N. (2006) Seismische Fazies, Tektonik und Gashydratvorkommen im nordwestlichen Schwarzen Meer, Diploma thesis, University of Hamburg, 110 pp.

Degens E. and Ross D. A. (1974) The Black Sea – Geology, Chemistry, and Biology. American Association of Petroleum Geologists Memoirs 20.

Popescu I., Lericolais G., Panin N., De Batist M., Gillet H. (2007) Seismic expression of gas and gas hydrates across the western Black Sea, Geo-Marine Letters 27(2), 173-183.

Soulet G., Delaygue G., Vallet-Coulomb C., Böttcher M. E., Sonzogni C., Lericolais G., Bard E. (2010) Glacial hydrologic conditions in the Black Sea reconstructed using geochemical pore water profiles. Earth and Planetary Science Letters 296, 57-66.

Schmale O., Haeckel M., McGinnis D. F. (2011) Response of the Black Sea methane budget to massive short-term submarine inputs of methane. Biogeosciences 8, 911-918.

Methane Hydrate Dynamics on the Northern US Atlantic Margin

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Most gas hydrate studies on the US Atlantic margin (USAM) have focused on the southern sector, which includes the Blake Ridge and Cape Fear areas. However, recent assessments by the Bureau of Ocean Energy Management (BOEM; FITI, Vol. 13, Iss. 1) imply that the greatest resource potential for USAM methane hydrates is in deep water (>1500 m) sediments farther north. In recent years, more than 570 methane seeps have been discovered on the USAM upper continental slope (<1500 m below sea level or mbsl) and outer shelf between Cape Hatteras and Georges Bank (Figure 1), partially overlapping the area with the highest gas hydrate resource potential. On both the energy and climate fronts, this region is primed for more in-depth investigation as a gas hydrate province.

Seafloor Methane Seeps and Gas Hydrates

Scientists have identified methane seeps on the northern USAM using water-column backscatter data collected with multibeam sonar on the National Oceanic and Atmospheric Administration (NOAA)'s ship Okeanos

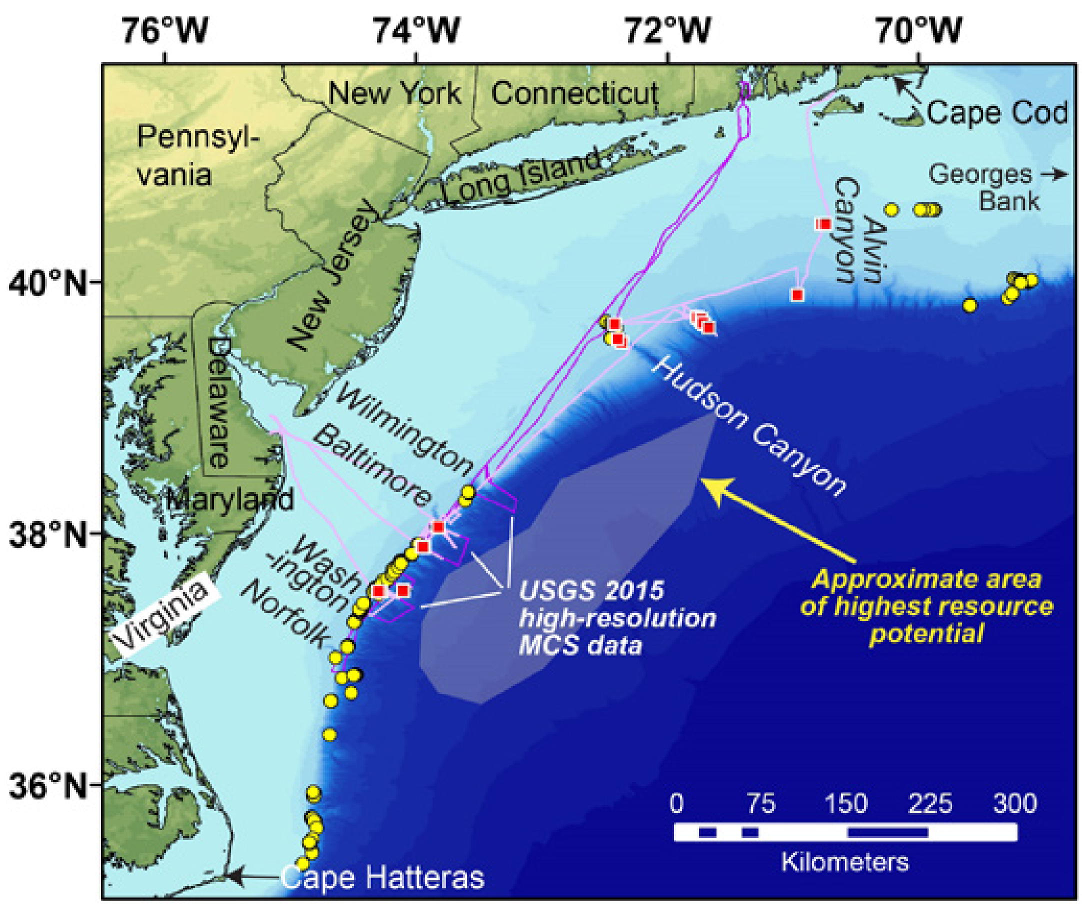

Figure 1. The northern US Atlantic margin with the ~570 seeps described by Skarke et al. (2014) shown as yellow circles. The purple and pink paths are the shiptracks for the April 2015 R/V Endeavor *and the September 2015* R/V Sharp *cruises, respectively. Red symbols denote piston or multicore samples, and italicized names refer to key shelf-breaking canyons. Most of the new MCS lines lie in the area between Wilmington Canyon and Norfolk Canyon, a sector that hosts more than 240 upper slope methane seeps.*

Explorer between 2011 and 2013. The results and a seep database were reported in 2014 in Nature Geoscience (see Skarke and others article, listed under Further Reading). Backscatter data reveal water-column gas plumes that can be traced downward into seafloor seeps, as verified during dives by NOAA's remotely operated vehicles.

As part of the seeps study, 240 upper slope seeps were identified from Washington to Wilmington Canyon, at depths between 180 (nominal shelf-break) and 600 mbsl. This depth range brackets the updip limit of gas hydrate stability (505 to 550 mbsl). Warming of intermediate ocean waters over several decades may be driving dissociation that feeds contemporary seepage at some of these sites. There is also evidence for ephemeral seeps that are active at timescales of days to months and may recur at the same location for thousands of years.

Approximately 40 seeps identified in the 2014 database occur at >1000 mbsl, well within the gas hydrate stability zone. In contrast to southern USAM deepwater seeps (e.g., Blake Ridge), which are fed by gas hydrate dissociation in sediments overlying salt diapirs, the deepwater seeps in the northern USAM leak methane from underlying fractured rock.

Recent Cruises

In April 2015, the USGS acquired approximately 500 km of high-resolution multichannel seismic (MCS) data (Figure 2) and coincident sea-air methane flux measurements over upper slope sites from just south of Norfolk Canyon to Wilmington Canyon aboard the *R/V Endeavor*. The surveys included dip lines between the shelf-break and ~2000 m water depth and strike lines collected parallel to the margin. The seismic source was a sparker that produced up to ~400 m sub-seafloor penetration at a nominal vertical resolution of ~2.6 m. In high-resolution sparker data, the base of gas hydrate stability typically does not manifest as a strong, negative-polarity bottom-simulating reflector (BSR), rendering sparker data more difficult to interpret than airgun data.

USGS researchers, led by J. Kluesner, are using seismic attribute analyses to better identify the gas hydrate-free gas transition and fluid-migration pathways in the high-resolution sparker data. In 2014, the USGS applied this approach to high-resolution MCS dip lines that were collected north of Hudson Canyon and across the New Jersey margin. In the attribute analyses, shallow, coarse-grained strata characterized by high reflectivity and high frequencies were interpreted as hosting gas hydrate. The continuation of one of these layers to depths shallower than the current updip limit of gas hydrate stability implies ongoing dissociation at this location, possibly in response to decadal warming of ocean temperatures. For the 2015 MCS data, frequency-based attribute analysis has produced good agreement between the inferred top of gas and the theoretical depth to the base of gas hydrate stability.

In September 2015, USGS researchers Ruppel and Pohlman, co-principal investigator Colwell, and collaborator Krause, representing Treude, conducted a 13-day sampling program on the *R/V Sharp* to study upper slope gas hydrate dynamics along some of the MCS lines (Figure 3).

The USGS piston coring system recovered nearly 100 m of sediment in 19 cores between Norfolk and Alvin Canyons. Thermistors attached to the corer measured sediment thermal gradients, expanding the region's limited heat flow database. A mini-multicorer equipped with a real-time video system was deployed to acquire undisturbed, 30-cm-long sediment

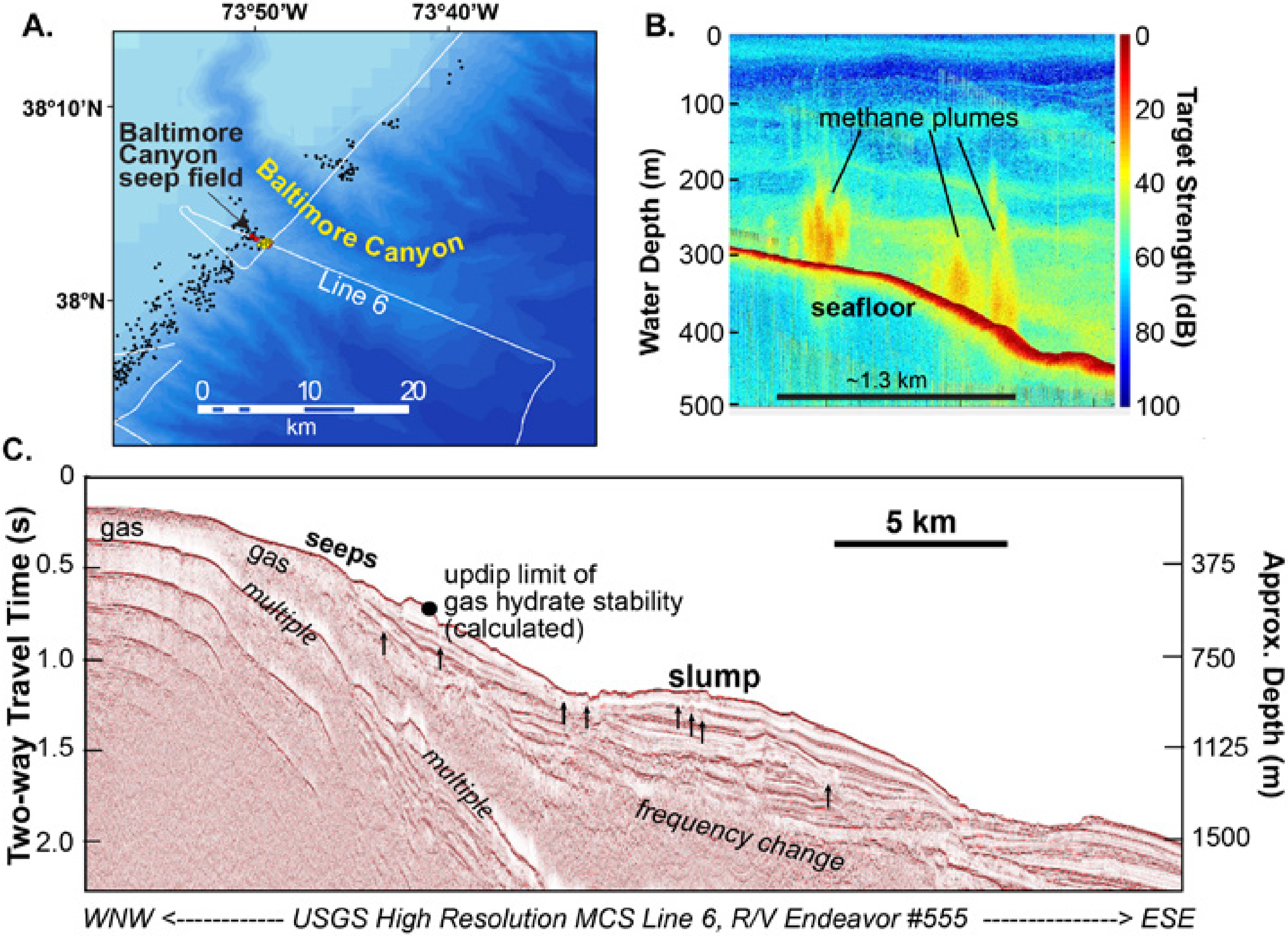

Figure 2. The Baltimore Canyon seep field lies on a promontory south of the canyon's axis and hosts extensive chemosynthetic communities explored by BOEM, NOAA, NSF, and USGS cruises from 2012-2015.

(A) The 14 seeps shown as yellow circles were found in multibeam backscatter analyses (Skarke et al., 2014). The yellow circles denote seeps found using the USGS EK60 in April 2015, and at least 7 of these were previously-unrecognized sites. Black dots mark pockmarks mapped by the USGS in Brothers et al. (2014).

(B) Target strength calculated using M. Veloso's Flarehunter scripts based on EK60 data collected across the Baltimore Canyon seep field on the upslope portion of MCS Line 6.

(C) Migrated MCS data on Line 6, with key features marked. Arrows show some of the locations where gas migration is detected. The frequency change is one of the features being exploited to track the distribution of gas and gas hydrate in these MCS data.

samples for microbiological, biogeochemical, and oxidation rate studies, especially near seafloor chemosynthetic communities at seep sites.

Fourteen Conductivity-Temperature-Depth (CTD) deployments retrieved water samples for dissolved methane measurements and for microbiological studies. Unlike some CTDs compiled in global databases, the CTDs on this cruise were run to full ocean depth, yielding a true bottom water temperature reading to constrain gas hydrate stability calculations.

The USGS also used a modified cavity ringdown spectrometer to measure stable carbon isotopic compositions of methane and CO_2 in the water column and in pore water samples retrieved aboard the ship. During nighttime operations, the USGS deployed a towed Chirp seismic instrument to acquire high-resolution images of the shallow sedimentary

SUGGESTED READING

BOEM, 2012, Assessment of the in-place gas hydrate resources of the lower 48 United States Outer Continental Shelf, Fact Sheet 2012-01, online only: http://www.boem.gov/uploadedFiles/BOEM/Oil_and_Gas_Energy_Program/Resource_Evaluation/Gas_Hydrates/BOEM-FactSheetRED_2012-01.pdf

Brothers, D.S., Ruppel, C., Kluesner, J.W., ten Brink, U.S., Chaytor, J.D., Hill, J.C., Andrews, B.D. and Flores, C., 2014, Seabed fluid expulsion along the upper slope and outer shelf of the U.S. Atlantic continental margin, Geophys. Res. Lett., doi: 10.1002/2013GL058048

Ruppel, C., 2011, Methane Hydrates and Contemporary Climate Change, Nature Education Knowledge, 3(10):29. (online only)

Ruppel, C., Kluesner, J., and Danforth, W., 2015, Imaging methane seeps and plumes on the US Atlantic margin, Sound Waves, March-June 2015. Online: http://soundwaves.usgs.gov/2015/06/fieldwork3.html (online only)

Skarke, A., C. Ruppel, M. Kodis, D. Brothers, and E. Lobecker, 2014, Widespread methane leakage from the seafloor on the northern US Atlantic margin, Nature Geoscience, doi:10.1038/ngeo2232.

section to guide the choice of coring sites. The September 2015 data are still being processed, but key observations include low concentrations of methane in the recovered cores and dramatic warming of bottom water temperatures in a seep field located just at the updip limit of gas hydrate stability.

During both the April and September cruises, the USGS acquired continuous water column imagery using a Simrad EK60 transceiver and a 38 kHz split-beam transducer. The EK60/EK80 system is a fishery instrument that geoscientists use for bubble plume studies. While the wide cone of ensonification produced by multibeam sonars can readily detect gas plumes, fisheries echosounders provide quantitative information about bubble size and concentration in a narrower cone.

The USGS used the EK60 to discover new upper slope and deepwater seeps and to survey previously-identified upper slope seep fields that were in some cases found to be no longer emitting methane. Plumes associated with deepwater seeps were more persistent in time and could be traced hundreds of meters above the seafloor, ending near the top of the methane hydrate stability zone in the water column.

Future Work

Future work on the northern USAM will focus on acquiring data to establish whether gas hydrate dissociation is supplying methane to upper slope seeps; and determining the timing of methane emissions relative to major climate events over the past 20,000 years. The rate at which the upper edge of gas hydrate stability adjusts to ocean warming remains unknown and could be constrained by a combination of data acquisition and numerical modeling. Currently, the distribution of gas hydrate on the continental slope of the USAM is unknown, and mapping this distribution should be a priority for both climate and energy studies.

Acknowledgments

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Figure 3. Sampling activities carried out in September 2015 aboard the R/V Sharp. *(Left) USGS operational personnel preparing to put the piston corer over the side. (Center) Deploying the mini-multicorer, which was equipped with USGS-built real-time video system. (Right) F. Colwell and S. Krause sampling the CTD.*

Gas Hydrate, Carbonate Crusts, and Chemosynthetic Organisms on a Vestnesa Ridge Pockmark—Preliminary Findings

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During the CAGE15-2 cruise in May, 2015, we deployed a towed system equipped with a high-resolution, digital still camera and multi-core capabilities to study the Vestnesa Ridge, offshore West Svalbard, at approximately 79° N latitude. We observed a pervasive, thin hydrate pavement, carbonate crusts, and bacterial mats on surface sediments of two Vestnesa Ridge pockmarks. Our discovery of these hydrate-associated features informs our understanding of gas hydrate dynamics and methane release in the Arctic Ocean, and how these processes may impact carbon budgets and cycles, ocean acidification, and benthic community survival

Vestnesa Gas Hydrate Ridge

Vestnesa Ridge is a NW-SE trending elongate feature, approximately 100 km long and 100 m high, comprised largely of drifted sediment. It is located in the Fram Strait, north of the Molloy Transform Fault, in water depths of ~1200 m (Figure 1). It is characterized by intensive seabed faulting and rifting, and by prominent 400 to 600 m-wide pockmarks that lie above acoustic blanking zones. The acoustic blanking zones are thought to correspond to regions of active gas migration.

The two features described here are active gas release systems, based on repeat mapping of hydro-acoustic flares that extend upward and nearly reach the sea surface (Figure 1b). Gas analyses indicate both biogenic and thermogenic hydrocarbon sources, with migration pathways likely controlled by reactivated fracture networks.

Methods

The towed system is based on the Woods Hole Oceanographic Institution (WHOI) MISO (Multidisciplinary Instrumentation in Support of Oceanography) TowCam deep-sea imaging system, which is equipped with a deep-sea digital camera and a real-time Conductivity, Temperature, Depth (CTD) instrument that provides both altimetry and depth data (http://www.whoi.edu/main/instruments/miso). The system has the ability to transmit images from the camera and CTD in real time so that operational and sampling decisions can be made onboard the ship.

The UiT multicorer system (integrated TowCam and Multicorer; TC-MC) allowed for collection of six 60 cm-long, visually-guided cores. Selection of areas where the instrument was deployed along the six survey lines shown in Figure 1a was determined using multibeam bathymetry and hydro-acoustic data.