Acknowledgment: "This material is based upon work supported by the Department of Energy under Award Number DE-NT0005638."

## Technology Status Assessment Report

### *Remote Sensing and Sea-truth Measurements of Methane Flux to the Atmosphere (HYFLUX)*

DE-NT0005638

Ian R. MacDonald, Texas A&M University - Corpus Christi

# Current Status of the Technology

## *Summary of Existing Methods for Gas Hydrate Detection*

Gas hydrates are ice-like solids that include molecules of methane or higher hydrocarbons in a lattice of water molecules(Kvenvolden 2000). They are abundant on the continental margins of the United States, but are most common as deeply buried and dispersed layers called bottom-simulating reflectors (Milkov 2004). The Gulf of Mexico is one of several world regions where gas hydrate occurs as dense deposits exposed or in shallow burial at the seafloor (MacDonald et al. 1994). The stability of gas hydrate is determined by the ambient temperature of the deposit and the hydrostatic pressure exerted by the overlying water and sediment mass (Sloan 1998). Because these variables may be affected by global climate change (Kennett and Cannariato 2000), there is interest in the locations of hydrates that would be most effected by such changes.

Current technology for localizing gas hydrate deposits relies heavily on 3-D seismic exploration (Dai et al. 2008; Frye 2008; Kleinberg and Brewer 2001; Trehu and Flueh 2001). However, this approach may not fully constrain sites where migration of gas into bottom waters is on-going because the geophysical signature of ancient deposits that are no longer active may resemble more active sites (Roberts and Carney 1997). Acoustic methods can also be used to image bubbles from mud volcanoes and gas hydrate deposits as they rise through the water column (Greinert et al. 2006; von Deimling et al. 2007), but this method requires detailed and localized searching. Satellite remote sensing offers the possibility to identify active oil seeps at a basin-wide scale (MacDonald et al. 1993).

Various satellite sensors have been used for detecting layers of oil floating in the sea; SAR (synthetic aperture radar) images are widely available and are not obscured by cloud cover (Brekke and Solberg 2005; Hu et al. 2009). Distinguishing accidental oil spills from natural seeps can be problematic, however detection of oil targets in repeated images over the same localized area is a robust indicator of a natural source on the seafloor (De Beukelaer et al. 2003). Modeling data and seafloor observations indicate that oil flows that reach the ocean surface do so in conjunction with copious discharge of gas (Leifer and MacDonald 2003; MacDonald et al. 2002). Methane release at depth is overwhelmingly coincident with shallow deposits of gas hydrate (Bohrmann et al. 2003; Dillon and Max 2000; Sassen et al. 1999). Satellite SAR images are therefore a proven technology for the census of active oil seeps and probably gas hydrate locations, however it may fail to detect methane release that do not include oil (De Beukelaer et al. 2003; Joye et al. 2005).

Fluxes of methane to the water column and atmosphere resulting from natural seeps have been estimated by in several papers (Judd 2004; Kvenvolden and Rogers 2005), generally on the basis of extrapolation from a very few well-constrained data points. Measurements of methane concentrations in the ocean have been published much more widely (Reeburgh 2007; Yvon-Lewis et al. 2004). Preliminary results from the Gulf of Mexico suggest that concentrations of methane in bubble plumes originating from natural oil seeps may be three to four orders of magnitude greater than ambient (Solomon et al. In Review). However, the cross-section of these plume is as yet poorly constrained. Technology required for the HYFLUX project include the following methodologies and equipment:

- Efficient methods for extracting natural oil layers from satellite data.
- Methods for obtaining real-time measurements of methane in surface waters and at the air-sea interface.
- Methods for measuring the concentration of $CH_4$ within the bubble plume in oceanic seeps.
- Methods for estimating the flux of gas in bubble streams at the seafloor.

## *Satellite Data Extraction*

The HYFLUX project team has developed a neural net method of feature recognition that reliably detects oil layers in SAR images from RADARSAT, ERS-1 and similar satellite sensors. The algorithm was "trained" based on a set of pixels extracted manually from SAR images covering the Gulf of Mexico. The SAR images used for the training set were collected under a range of wind and sea-state conditions and a variety of SAR sensor settings. Image data covered areas of the northern Gulf of Mexico known to contain abundant natural seeps and where environmental data from oceanographic buoys and other sources were available. This review demonstrates that SAR reliably detects natural oil slick, if they are present, under wind-speeds from 2 to 8 m/s. The algorithm performs a binary classification of oil-covered water versus open sea on a pixel-by-pixel basis. A comprehensive review of several hundred SAR images obtained from the Alaska Satellite Facility indicates that there is sufficient coverage to effectively inventory the locations of persistent natural oil seep and to examine their temporal variability.

## *In-situ bubble flux measurement*

The HYFLUX will develop instrument arrays to monitor bubble flow from gas hydrate deposits, which will be deployed at the Gulf of Mexico study sites during the research cruise. These instruments will requrire calibration and deployment tests. A suitable test bed is the Coal Oil Point seep field of southern California, which is located near the UCSB laboratory facilities of Dr. Ira Leifer. Two instruments will be are being considered for use: A 360° scanning sonar (Imagenex 881A digital multi-frequency sonar) would be used to quantify individual bubble streams within a ~150m diameter surveillance region within the seep. Sonar data should also document locations of individual vents and monitor their relative activity during water column and sea-surface sampling. Actual flow rates from individual vents will be quantified using ROV video and imaging capabilities to make visual bubble-measurements (Leifer and MacDonald 2003; Leifer and Patro 2002). Additionally, a bubble-flow meter will be deployed over a representative vent for direct measurement of bubble volume. The Imagenex sonar and the bubble flow meter have been developed by Dr. Vernon Asper at the University of Southern Mississippi for use at the Gulf of Mexico gas hydrate observatory.

## *Real-time Measurement of $CH_4$ Concentrations*

To determine the sea-to-air flux of methane, the saturation state of $CH_4$ and $C_2$-$C_4$ hydrocarbons in the surface ocean will be monitored continuously using a shipboard seawater pumping system, a Weiss-style Plexiglas equilibrator, and a fully automated GC/FID instrument (Fig. 1), which will draw samples from a Weiss-style Plexiglas equilibrator (Yvon-Lewis et al. 2004). The instrument will cycle continuously between ambient air, seawater-equilibrated air, and a gas standard. The system will have a 5-7 minute cycle time from the start of one sample to the start of the next. The saturation anomaly sequence is: calibration gas, air, equilibrator, air, equilibrator. This sequence is repeated continuously while the ship is underway.

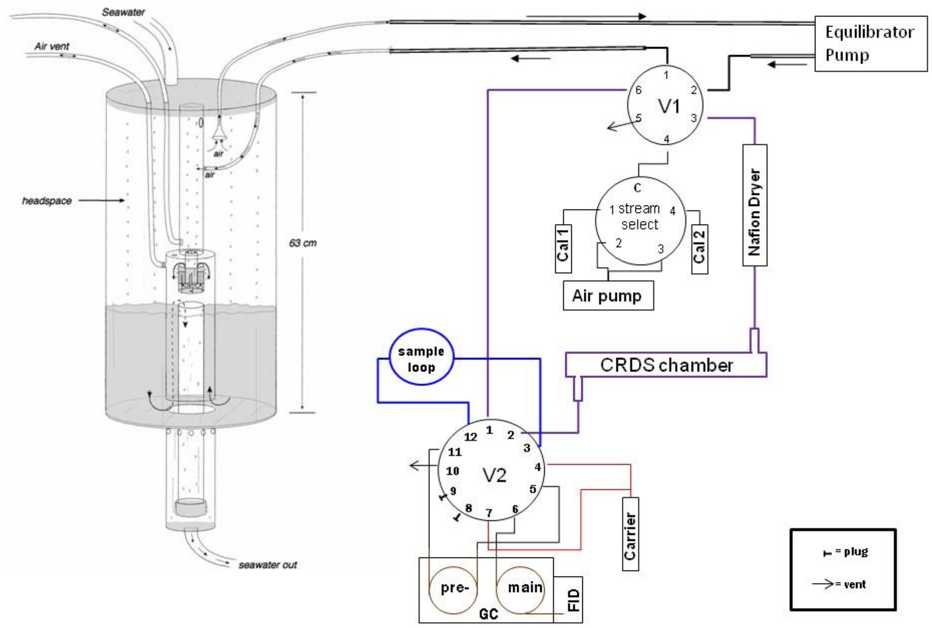


**Figure 1.** Schematic showing the connections between the CRDS, GC-FID, equilibrator and stream select valve.

## *Measuring $CH_4$ Concentrations in Bubble Plumes*

To sample the methane as it emerges from the sediment and travels through the water column, a CTD rosette will gather a total of 24 samples within each plume. The CTD will gather salinity and temperature profiles as well which will provide important physical parameters for equilibrium computations of methane concentrations as well as for flux calculations. In addition to the CTD sampling of the methane plumes, 3 hydrocasts consisting of CTD measurements and water column samples will be performed in a series that transects from the center of each plume to ~ a kilometer away to determine the extent of methane-saturated waters around the plume and to collect background waters. As with the methane plume waters, these water samples will be analyzed for C1-C4 hydrocarbon, DOC and DIC concentrations, as well as $\delta^{13}C-CH_4$, $\delta^{13}C$-DOC, $\delta^{13}C$-DIC and $^{14}C$-DOC isotopic analyses.

### *$C_1$-$C_4$ Hydrocarbon Concentrations and $\delta^{13}C-CH_4$*

Two sub-samples will be collected at each depth, one for ship-board analysis of hydrocarbon concentrations and one as back-up for analysis on-shore in case of equipment problems. Samples will be prepared for analysis by over-filling a 125ml serum bottle from the Niskin bottle. The bottle will be immediately capped with a gas-tight butyl stopper and crimp-sealed. All samples are poisoned with mercuric chloride to halt microbial metabolic activities such as methanogenesis and methane oxidation. Next, a headspace of 10cc of UHP $N_2$ is added by displacing an equal volume of water sample. After the headspace addition, a small additional volume of UHP $N_2$ is added as overpressure to insure that there is not a vacuum resulting when sampled for analysis. The samples are then shaken and allowed to equilibrate for at least 12 hours before being analyzed. Methane through butane analysis will be performed in triplicate on 3cc headspace aliquots, using a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector. C1-C4 compounds will be resolved on the GC-FID with $60^{o}C$ isothermal runs using UHP $N_2$ as carrier gas. Calibration curves will be constructed from certified hydrocarbon standards.

## *Literature Cited*


Bohrmann, G., M. Ivanov, J. P. Foucher, V. Spiess, J. Bialas, J. Greinert, W. Weinrebe, F. Abegg, G. Aloisi, Y. Artemov, V. Blinova, M. Drews, F. Heidersdorf, A. Krabbenhoft, I. Klaucke, S. Krastel, T. Leder, I. Polikarpov, M. Saburova, O. Schmale, R. Seifert, A. Volkonskaya and M. Zillmer, 2003. Mud volcanoes and gas hydrates in the Black Sea: new data from Dvurechenskii and Odessa mud volcanoes. Geo-Marine Letters 23(3-4): 239-249.

Brekke, C. and A. H. S. Solberg, 2005. Oil spill detection by satellite remote sensing. Remote Sensing of Environment 95(1): 1-13.

Dai, J., N. Banik, D. Gillespie and N. Dutta, 2008. Exploration for gas hydrates in the deepwater, northern Gulf of Mexico: Part II. Model validation by drilling. Marine and Petroleum Geology 25(9): 845-859.

De Beukelaer, S. M., I. R. MacDonald, N. L. Guinnasso and J. A. Murray, 2003. Distinct side-scan sonar, RADARSAT SAR, and acoustic profiler signatures of gas and oil seeps on the Gulf of Mexico slope. Geo-Marine Letters 23(3-4): 177-186.

Dillon, W. P. and M. D. Max, 2000. Oceanic gas hydrate. Natural Gas Hydrates in Oceanic and Permafrost Environments. M. D. Max. The Netherlands, Kluwer Academic Press. 5**:** 61-76.

Frye, M., 2008. Preliminary evaluation of in-place gas hydrate resources: Gulf of Mexico outer continental slope. U.S. Dept. Interior, Minerals Management Service OCS Report: MMS 2008-004.

Greinert, J., Y. Artemov, V. Egorov, M. De Batist and D. McGinnis, 2006. 1300-m-high rising bubbles from mud volcanoes at 2080m in the Black Sea: Hydroacoustic

characteristics and temporal variability. Earth and Planetary Science Letters 244(1-2): 1-15.
Hu, C. M., X. F. Li, W. G. Pichel and F. E. Muller-Karger, 2009. Detection of natural oil slicks in the NW Gulf of Mexico using MODIS imagery. Geophysical Research Letters 36.
Joye, S. B., I. R. MacDonald, J. P. Montoya and M. B. Peccini, 2005. Geophysical and geochemical signatures of Gulf of Mexico seafloor brines. Biogeosciences 2: 1-15.
Judd, A. G., 2004. Natural seabed gas seeps as sources of atmospheric methane. Environmental Geology 46(8): 988-996.
Kennett, J. P. and K. G. Cannariato, Hendy, Ingrid L., Behl, Richard J. (2000). Carbon isotopic evidence for methane hydrate instability during quaternary interstadials. Science. **288:** 128-133.
Kleinberg, R. L. and P. G. Brewer, 2001. Probing gas hydrate deposits. American Scientist 89(3): 244-251.
Kvenvolden, K. A., 2000. Gas hydrate and humans. Gas Hydrates: Challenges For the Future. 912**:** 17-22.
Kvenvolden, K. A. and B. W. Rogers, 2005. Gaia's breath - global methane exhalations. Marine and Petroleum Geology 22(4): 579-590.
Leifer, I. and I. R. MacDonald, 2003. Dynamics of the gas flux from shallow gas hydrate deposits: interaction between oily hydrate bubbles and the oceanic environment. Earth and Planetary Science Letters 21(3-4): 411-421.
MacDonald, I. R., N. L. Guinasso, Jr., S. G. Ackleson, J. F. Amos, R. Duckworth, R. Sassen and J. M. Brooks, 1993. Natural oil slicks in the Gulf of Mexico visible from space. Journal of Geophysical Research 98 C9: 16351-16364.
MacDonald, I. R., N. L. Guinasso, Jr., R. Sassen, J. M. Brooks, L. Lee and K. T. Scott, 1994. Gas hydrate that breaches the sea floor on the continental slope of the Gulf of Mexico. Geology 22: 699-702.
MacDonald, I. R., I. Leifer, R. Sassen, P. Stine, R. Mitchell and N. Guinasso, 2002. Transfer of hydrocarbons from natural seeps to the water column and atmosphere. Geofluids 2(2): 95-107.
Milkov, A. V., 2004. Global estimates of hydrate-bound gas in marine sediments: how much is really out there? Earth-Science Reviews 66(3-4): 183-197.
Reeburgh, W. S., 2007. Oceanic methane biogeochemistry. Chemical Reviews 107(2): 486-513.
Roberts, H. H. and R. S. Carney, 1997. Evidence of episodic fluid, gas, and sediment venting on the northern Gulf of Mexico continental slope. Economic Geology and the Bulletin of the Society of Economic Geologists 92(7-8): 863-879.
Sassen, R., S. Joye, S. T. Sweet, D. A. DeFreitas, A. V. Milkov and I. R. MacDonald, 1999. Thermogenic gas hydrates and hydrocarbon gases in complex chemosynthetic communities, Gulf of Mexico continental slope. Organic Geochemistry 30(7): 485-497.
Sloan, E. D. (1998). Clathrate Hydrates of Natural Gases. New York, NY, Marcel Dekker, Inc.
Solomon, E., M. Kastner and I. MacDonald, In Review. Methane flux to the atmosphere from perennial hydrocarbon plumes in the Gulf of Mexico. Nature Geosciences.

Trehu, A. M. and E. R. Flueh, 2001. Estimating the thickness of the free gas zone beneath Hydrate Ridge, Oregon continental margin, from seismic velocities and attenuation. Journal of Geophysical Research-Solid Earth 106(B2): 2035-2045.

von Deimling, J. S., J. Brockhoff and J. Greinert, 2007. Flare imaging with multibeam systems: Data processing for bubble detection at seeps. Geochemistry Geophysics Geosystems 8.

Yvon-Lewis, S. A., D. B. King, R. Tokarczyk, K. D. Goodwin, E. S. Saltzman and J. H. Butler, 2004. Methyl bromide and methyl chloride in the Southern Ocean. Journal of Geophysical Research-Oceans 109(C2): 6.