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Fate of Methane Emitted from Dissociating Marine Hydrates: Modeling, Laboratory, and Field Constraints

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1 Executive summary

Work during this period has focused on the following tasks:

- Subtask 2.1: Phase-field modeling of a static gas bubble
- Subtask 3.1: Laboratory experiments — flow-loop design, fabrication and construction
- Subtask 4.1: Quantitative analysis of newly-discovered US Atlantic margin methane plumes
- Subtask 2.2: Model of buoyant hydrate-coated gas bubble
- Subtask 4.2: Analysis of plume data acquired by NOAA OE
2 Accomplishments

2.1 Major goals and objectives of the project

The overall goals of this research are: (1) to determine the physical fate of single and multiple methane bubbles emitted to the water column by dissociating gas hydrates at seep sites deep within the hydrate stability zone or at the updip limit of gas hydrate stability, and (2) to quantitatively link theoretical and laboratory findings on methane transport to the analysis of real-world field-scale methane plume data placed within the context of the degrading methane hydrate province on the US Atlantic margin.

The project is arranged to advance on three interrelated fronts (numerical modeling, laboratory experiments, and analysis of field-based plume data) simultaneously. The fundamental objectives of each component are the following:

1. Numerical modeling: Constraining the conditions under which rising bubbles become armored with hydrate, the impact of hydrate armoring on the eventual fate of a bubbles methane, and the role of multiple bubble interactions in survival of methane plumes to very shallow depths in the water column.

2. Laboratory experiments: Exploring the parameter space (e.g., bubble size, gas saturation in the liquid phase, “proximity” to the stability boundary) for formation of a hydrate shell around a free bubble in water, the rise rate of such bubbles, and the bubbles acoustic characteristics using field-scale frequencies.

3. Field component: Extending the results of numerical modeling and laboratory experiments to the field-scale using brand new, existing, public-domain, state-of-the-art real world data on US Atlantic margin methane seeps, without acquiring new field data in the course of this particular project. This component will quantitatively analyze data on Atlantic margin methane plumes and place those new plumes and their corresponding seeps within the context of gas hydrate degradation processes on this margin.

2.2 Accomplishments in this reporting period

Work during this period focused on the following tasks:

- Subtask 2.1: Phase-field modeling of a static gas bubble
- Subtask 3.1: Laboratory experiments — flow-loop design, fabrication and construction
- Subtask 4.1: Quantitative analysis of newly-discovered US Atlantic margin methane plumes
- Subtask 2.2: Model of buoyant hydrate-coated gas bubble
- Subtask 4.2: Analysis of plume data acquired by NOAA OE

A detailed Milestones Status Report is included as Appendix 1.
Task 2.0: Theoretical and computational models of coupled bubble rise and hydrate formation and dissociation

Subtask 2.1: Phase-field modeling of a static gas bubble

Introduction. In previous reporting periods we described the phase-field formulation for a two-component ($\text{H}_2\text{O-CH}_4$), two-phase (liquid-gas) partially miscible system, including a discussion on the thermodynamics of the problem and the bulk and interfacial free energies of the system. We also presented simulation results in 1D and 2D related to the dynamics of bubble dissolution.

In this reporting period, we illustrate the performance of the model with simulation results in 3D, which conclude the objectives of this subtask.

Implementation and simulation results in 3D. Upon reaching milestone 3 (phase-field modeling of a static gas bubble in 2D, reported in the October 2014 quarterly report), we extended our static-bubble model to three dimensions, assuming periodic conditions in all three directions. Figure 1, illustrating a 3D simulation on a $128^3$ grid, shows that the model is successful in capturing a 3D gas bubble dissolution in undersaturated water. We also make sure that the bubble shrinkage stops once the ambient fluid is fully saturated (not shown here).

![Figure 1: A static 3D gas bubble shrinking in water due to dissolution. The color corresponds to gas concentration: (a) initial condition; (b) after 25 time steps and (c) after 67 time steps.](image)

Subtask 2.2: Phase-field modeling of a buoyant hydrated-coated gas bubble in 2D

Introduction. The static-bubble model developed for Subtask 2.1 has paved the way for the next stage of our modeling effort, which focuses on incorporating realistic momentum effects into the thermodynamic framework. Generally speaking, this means a bubble in the next-phase model will 1) rise naturally due to its buoyancy, 2) deform from its spherical shape due to viscosity contrast between gas and liquid, and lastly 3) dissolve into water. The last feature has already been captured by the thermodynamic model we established and...
the current mission is to build hydrodynamic features 1 and 2 into the model. For now we do not consider hydrate formation in the model—hydrate formation and dissociation will be incorporated at a later stage.

**Model equations** We describe the rising of methane gas in a water-filled Hele-Shaw cell (mimicking 2D flow) with the following system of equations:

\[
\begin{align*}
\mathbf{u} &= -\frac{k(\phi)}{\mu(\phi)}(\nabla P - \rho(\phi)g\hat{z}); \\
\nabla \cdot \mathbf{u} &= 0; \\
\frac{\partial \phi}{\partial t} + \nabla \cdot (\mathbf{u}\phi) + \lambda^\phi \frac{\delta F}{\delta \phi} &= 0; \\
\frac{\partial c}{\partial t} + \nabla \cdot (\mathbf{u}c) - \nabla \cdot (\lambda^c \nabla (\frac{\delta F}{\delta c})) &= 0,
\end{align*}
\]

where \( \mathbf{u} \) is the Darcy velocity, \( P \) is pressure, \( \rho \) is the density of gas-liquid mixture, \( g \) is the gravitational acceleration, \( \hat{z} \) is the unit vector pointing in the direction opposite to gravity. Symbol \( \phi \) is the phase variable, defined here as the gas volume fraction; \( \mu(\phi) \) is the phase mobility; \( c \) is the concentration of methane (mass fraction), and \( \lambda^c \) is the mass mobility. The permeability \( (k) \), viscosity \( (\mu) \), mobilities \( (\lambda^\phi \text{ and } \lambda^c) \) and mixture density \( (\rho) \) are defined as:

\[
\begin{align*}
k(\phi) &= 0.1 + 0.9\phi; \\
\mu(\phi) &= \mu_g e^{M(1-\phi)}, \\
\lambda^\phi &= \frac{\lambda^c}{b^2} = \frac{D\nu}{RT}(0.01 + c(1-c)(0.5 + 0.5\phi)); \\
\rho(\phi) &= \rho_l + \Delta \rho \phi; \quad \Delta \rho = \rho_g - \rho_l,
\end{align*}
\]

where \( \mu_g \) is the gas viscosity and \( M = \log(\mu_l/\mu_g) \) is the liquid–gas viscosity contrast. In the definition of mobility, \( D \) is the diffusion coefficient, \( \nu \) is the kinematic viscosity, \( R \) is the ideal gas constant and \( T \) is temperature. \( \Delta \rho \) is the density difference between gas and liquid (a negative value). We adopt the same definition of free energy from the static bubble and compute the potentials accordingly:

\[
\begin{align*}
F &= \frac{1}{2}\epsilon_c^2 T(\nabla c)^2 + \frac{1}{2}\epsilon_{\phi}^2 T(\nabla \phi)^2 + \omega T W(\phi) + \omega_{\text{mix}} T \left[ f_l(c)(1 - g(\phi)) + f_g(c)g(\phi) \right]; \\
\frac{\delta F}{\delta \phi} &= -\epsilon_{\phi}^2 T \nabla^2 \phi + \omega T W'(\phi) + \omega_{\text{mix}} T \left[ f_g(c) - f_l(c) \right] g'(\phi); \\
\frac{\delta F}{\delta c} &= -\epsilon_c^2 T \nabla^2 c + \omega_{\text{mix}} T \left[ f_l'(c)(1 - g(\phi)) + f_g'(c)g(\phi) \right].
\end{align*}
\]

The coefficients \( \epsilon_c^2 T \) and \( \epsilon_{\phi}^2 T \) describe the interfacial energy on the compositional interface \( c \) and the phase boundary \( \phi \), respectively. The constants \( \omega T \) and \( \omega_{\text{mix}} T \) set the magnitudes for system bulk free energy and mixing energy respectively.
Scaling analysis  We choose the following characteristic quantities to scale the system:

- **Energy:** \( \varepsilon_\phi^2 T / b^2 \) has unit of \([ J / \text{cm}^3 ]\)  
- **Length:** \( b \) (gap thickness of hele-shaw cell)  
- **Pressure:** \( p_c \Delta \rho g b \) \( (14) \)  
- **Velocity:** \( u_c = \frac{k_c p_c}{\mu_g b} \) \( (15) \)  
- **Time:** \( t_c = \frac{b}{u_c} \) \( (16) \)  
- **Mobility (for potentials):** \( \lambda_c \) has unit of \([ D / [\text{cm}^3 J] ]\) \( (17) \)

Adopting the above scales, the model takes the following dimensionless form:

\[
\begin{align*}
\mathbf{u} &= -\frac{k(\phi)}{\mu(\phi)} \nabla P - \phi \hat{z}; \\
\nabla \cdot \mathbf{u} &= 0; \\
\frac{\partial \phi}{\partial t} + \nabla \cdot (\mathbf{u} \phi) + \frac{1}{P_{\phi}} \lambda^c \frac{\delta F}{\delta \phi} &= 0; \\
\frac{\partial c}{\partial t} + \nabla \cdot (\mathbf{u} c) - \frac{1}{P_{c}} \nabla \cdot (\lambda^c \nabla (\frac{\delta F}{\delta c})) &= 0,
\end{align*}
\]

with the following definition of permeability, viscosity and mobility:

\[
\begin{align*}
k(\phi) &= 0.1 + 0.9\phi; \\
\mu(\phi) &= e^{M(1-\phi)}; \\
\lambda^\phi &= \lambda^c = 0.01 + c(1-c)(0.5 + 0.5\phi),
\end{align*}
\]

and the definitions of potentials at a given point given as:

\[
\begin{align*}
\frac{\delta F}{\delta \phi} &= -\nabla^2 \phi + \frac{1}{\text{Ch}_b} W'(\phi) + \frac{1}{\text{Ch}_m^\phi} \left[ f_g(c) - f_i(c) \right] g'(\phi); \\
\frac{\delta F}{\delta c} &= -\nabla^2 c + \frac{1}{\text{Ch}_m^c} \left[ f_i'(c) (1 - g(\phi)) + f_g'(c) g(\phi) \right].
\end{align*}
\]

Note that here \( P \) is the modified pressure with respect to its hydrostatic datum: \( P = P_{\text{org.}} - \rho g z \). The system is controlled by five dimensionless parameters:

- **Phase-Peclet number:** \( P_{\phi} = \frac{u_c b}{\lambda_c \varepsilon_\phi^2 T / b^2} \)  
- **Concentration-Peclet number:** \( P_{\phi} = \frac{u_c b}{\lambda_c \varepsilon_\phi^2 T / b^2} \)  
- **Bulk Cahn number:** \( \text{Ch}_b = \frac{\varepsilon_\phi^2 / b^2}{\omega} = \frac{\text{surface energy}}{\text{bulk energy}} \)
Model simulation Equations (22)–(24) describe a flow and transport system that consists of two phases and two components; in addition to fluidic momentum effects, the system is also influenced by phase transitions driven by thermodynamic forces (gas dissolution and exsolution). Many parameters control the dynamics of this system; in addition to the give parameters listed in the previous section, the solubility of gas in liquid is also a key parameter. As described in previous report, we design the bulk free energies for pure liquid and gas phase using the following form:

\[
    f_l = c \log c + (1 - c) \log(1 - c) - c \log(c + \alpha_1 (1 - c)) - (1 - c) \log(1 - c + \alpha_2 c); \quad (27)
\]
\[
    f_g = c \log c + (1 - c) \log(1 - c) - c \log(c + \alpha_3 (1 - c)) - (1 - c) \log(1 - c + \alpha_4 c), \quad (28)
\]

which is controlled by four parameters as well: \( \alpha_1, \alpha_2, \alpha_3, \alpha_4 \). By constructing the common tangent of the two curves, \( f_l(c) \) and \( f_g(c) \), we can compute the gas solubility in liquid as well as the equilibrium vapor pressure in the gas phase. Conversely, we can design for a given gas solubility by tweaking the four \( \alpha \)'s. In the following, we use two examples to demonstrate that the system can behave quite differently even if only a few parameters are changed.

Inhibition of viscous fingering by gas dissolution We use the following example to illustrate the impact of gas miscibility on the dynamics of multiphase flow, as modeled by our current system. The initial condition of this example is shown in figure 2, where a less viscous band of gas is surrounded by a more viscous liquid phase (water). We impose a constant flow from left to right. Because the gas is less viscous than the liquid, it is more mobile than the ambient fluid. This leads to a viscous instability on the invasion front (the right interface in figure 2). This phenomenon is often referred to as viscous fingering because the unstable front eventually evolves into finger-like forms.

To simulate this system, we assume that the densities of gas and liquid are equal (or, alternatively, that flow is on the horizontal plane), so that there are no buoyancy effects. In figure 3, we show simulation results for a system where the gas is only weakly soluble within the liquid phase \( (c_{\text{solubility}} \approx 0.12) \). We observe that the model equations are able to reproduce the viscous fingering phenomenon as well as the pinch off of one gas patch from another (figure 3-d).

In figure 4, we show simulation results for a system where the gas is highly soluble in the liquid phase \( (c_{\text{solubility}} \approx 0.56) \). By comparing the results shown in figures 3 and 4, we demonstrate that when pushing a highly miscible gas phase through a liquid phase, even though the viscosity contrast remains high, the dissolution of gas phase can become a dominant aspect of the compositional flow, and eventually lead to inhibition of viscous fingering (figure 4), and ultimately a faster dissolution rate of gas.
Rising methane bubbles in water column  Once of the central questions of this project is how the survival rates of methane bubbles in the water column are affected by the presence of other bubbles, i.e., bubbles traveling as a plume rather than as an individual bubble. The hypothesis is that the survival rate of bubbles increases if they travel together. We test this hypothesis within our model for a simplified scenario of a small group of weakly soluble bubbles. The initial condition is shown in figure 5, where a group of six bubbles are released in undersaturated water. Figure 6 illustrates the rising and dissolution of the bubbles. Notice that in frames (c) and (d), the biggest bubble was traveling through a saturated area left behind by other bubbles, which might have slowed down the dissolution rate of the big bubble. Further analysis is needed to confirm this.

Future work  In the next reporting periods, we will extend the phase-field modeling framework to account for the hydrate phase in the system.
Figure 3: Viscous fingering with a weakly soluble gas. In each subfigure, the top frame represents $c$ and the bottom frame represents $\phi$. The snapshots are taken at (a) $t = 1.95$, (b) $t = 4.45$, (c) $t = 7.45$, (d) $t = 11.45$. 
Figure 4: Viscous fingering with a highly soluble gas. In each subfigure, the top frame represents $c$ and the bottom frame represents $\phi$. The snapshots are taken at (a) $t = 1.95$, (b) $t = 4.45$, (c) $t = 6.45$, (d) $t = 11.45$ (gas phase is completely dissolved).
Figure 5: Initial condition for a plume of bubbles: (a) concentration $c$, (b) gas volume fraction $\phi$. 
Figure 6: A series of snapshots showing the rising and dissolution of traveling bubbles. The top row shows concentration; the bottom row shows gas volume fraction. The snapshots are taken at (a) $t = 1.95$, (b) $t = 4.45$, (c) $t = 10.45$, (d) $t = 23.6$. 

methane concentration

gas volume fraction
Task 3.0: Laboratory experiments on hydrate armoring, rise rate, and gas loss from ascending bubbles

Subtask 3.1: Flow-loop design, fabrication and construction

Introduction. The USGS is constructing a high-pressure flow loop designed to “capture” gas bubbles for subsequent visual and acoustic imaging studies as well as bubble evolution and rise-rate measurements. The apparatus must be able to operate at pressures high enough for the gas to form hydrate. Xenon was chosen for the hydrate-forming gas, meaning hydrate can be formed at ~1.3 MPa (190 psi) at room temperature (21°C, 70°F), and at lower pressures when the system is cooled [Ohgaki et al., 2000].

Design Summary. The gas line responsible for generating the xenon bubble within the flow loop has been redesigned such that only a single 3/8” stainless steel tube penetrates the bubble-capture chamber. Design provides a compromise that retains tube stability while reducing fluid flow disruption due to bulky tube-support connections located within the flow loop chamber itself.

Fabrication Activities.

Bubble-capture chamber:
- The acrylic and stainless steel components of the bubble-capture chamber have been machined and/or fabricated.

Fluid flow and bubble injection:
- The 1” pipe water circulation lines connecting the bubble-capture chamber base to the circulating pump have been assembled and connected. This section of the flow loop contains temperature and pressure sensors as well as the water fill/drain port.
- Gravity-feed system for controlling the flow-loop water-filling process has been assembled.
- Gas injection line has been fabricated.

References.
Task 4.0: Field data analysis to link models and laboratory data to real world gas hydrate dynamics

Subtask 4.1: Quantitative analysis of newly-discovered US Atlantic margin methane plumes

We are currently working toward an in-depth analysis of split-beam echosounder (SBES) and multibeam echosounder (MBES) data corresponding to seeps along the US Atlantic margin (Skarke et al., 2013). In particular, we are interested in using these data to constrain the fate of methane gas bubbles as they rise through the water column. Our intended approach is to use a bubble evolution model that is based on the work in described in subtasks 2.1 and 3.1 and/or published models such as that described by McGinnis et al. (2006). Such a modeling effort requires knowledge (or reasonable constrains) on several parameters including

- The size distribution of the bubbles at the source
- The gas transfer rate across the bubble-wall boundary for various gas constituents (e.g., CH4 out, O2 in), for both hydrate coated and ‘free’ bubbles
- The rise speed of the bubbles with both immobile (i.e., hydrate coated) boundaries and free boundaries

With these and a few other parameters in hand, we can then predict the evolution of the bubble size as they rise through the water column, and by using a model of the acoustic response of the bubble we can then predict the relative acoustic target strength of the bubble plume as a function of depth. For those parameters that can be only constrained (e.g., the source size distribution), we anticipate this resulting in a family of acoustic target strength profiles.

We can narrow down the size of the model family, and verify the model in general, with SBES and MBES observations collected from a variety of depths on the Atlantic margin. To do so, great care needs to be taken when extracting the empirical seep TS profiles from the SBES and MBES data. The ‘raw’ plume observations have been extracted from the overall acoustic data set as part of the year 1 activities, and the current focus is refining these seep profiles. This refinement step is motivated by the example seeps shown in figure 1. For the seep on the left-hand side of Figure 1, the gas-bubble plume target strengths are significantly higher than the background noise and can, to first order, be separated from the background noise using a simple thresholding routine such as that described by Jerram et al. (accepted). However, several of the gas bubble plume observations have target distributions that stochastically overlap with the background noise, such that a simple thresholding routine would result in TS-depth profiles that, unrealistically, follow the background noise. We are fortunate to be able to know the statistics of the background noise (from direct observations) and to be able to predict the type of distribution that the gas seep targets follows (Rayleigh, at least for the strongest seeps). This makes it possible to work towards separating the seep target distribution from the seep-plus-noise distribution, ultimately resulting in a more accurate profile describing the change in seep TS with depth. We are currently exploring the possibility of performing this separation using an expectation-maximization algorithm (Moon, 1996).
Figure 1. Example data from methane gas seeps observed in on the US Atlantic margin. The gas-bubble targets observed on the left are sufficiently strong that they can be rather simply separated from the background noise profile using a noise-thresholding approach. The gas-bubble targets on the right, however, have target strengths that overlap considerably with the background noise. Efforts are currently underway to develop an algorithmic approach to separating the gas-bubble targets from the background noise so that accurate TS-depth profiles can be extracted from these types of data.

Subtask 4.2: Place US Atlantic margin seeps in regional and global context of gas hydrate system dynamics.

To supplement the CTD-based database of bottom water temperatures on the Atlantic margin, the USGS has been working on bottom water temperature data acquired on the R/V Endeavor in July 2014 (John Kessler, Rochester, Project Director for NSF) during a cruise in which UNH and the USGS both participated. On that cruise, we visited Hudson Canyon, where Skarke et al. (2014) document about 50 seeps in an area that had long been suspected of seepage, but where actual seeps had never before been identified. A particular feature of about half of these seeps is their occurrence exactly at the updip theoretical limit of gas hydrate in Hudson Canyon, roughly between 505 and 550 m water depth.
Using an EK80 installed on the R/V Endeavor, Weber identified other seeps in the canyon’s thalweg in addition to the 50 documented in Skarke et al (2014). Tracking the bottom water temperature variations recorded by CTDs taken during the cruise in space and time reveals a juxtaposition of seafloor seepage areas where temperatures are just inside or just outside the gas hydrate stability field. In one location, we documented cooling of seafloor temperatures by about 1°C over the course of half a day. This attests to the dynamism of near-seafloor temperatures at intermediate water depths, particularly within the complicated current regime of large shelf-break canyons. The near-seafloor temperatures may also be affected by seep fluids. Results comparing these near-seafloor temperature regimes on the Atlantic margin and the Beaufort margin were presented as the lead talk in a special session at the Fall AGU Meeting (Ruppel et al., 2014). Further work in Hudson Canyon is expected during a September 2015 DOE-funded coring cruise as part of an agreement with SMU/USGS/OSU.

As part of this project and in preparation for an April 2015 cruise being carried out by the USGS under its core Interagency agreement with DOE, the USGS is currently sifting through existing Atlantic margin upper continental slope MCS data released through the USGS NAMSS framework and identifying areas with robust BSRs or indicators of gas. While uppermost slope gas hydrates tend not to be associated with BSRs, knowing their locations on mid to lower continental slopes is important to devising appropriate upper slope surveys in seep and non-seep areas.

Figure 2. Hudson Canyon seeps (colored dots) mapped by Skarke et al. (2014) and available in the database published with that paper. The pockmark locations are based on a paper by D. Brothers et al. (2014). Image from USGS website: http://woodshole.er.usgs.gov/project-pages/hydrates/seeps.html
References:


Jerram, K, Weber, T., and Beaudoin, J.. (accepted Jan 2015), Split-beam echo sounder observations of natural methane seep variability in the northern Gulf of Mexico, Geochemistry, Geophysics, Geosystems.


2.3 Opportunities for training and professional development

The project has offered opportunities for training of our graduate students Amir Pahlavan (MIT), Xiaojing Fu (MIT), Ben Scandella (MIT), and Liam Pillsbury (UNH).

2.4 Dissemination of results to communities of interest

Several of the PIs and graduate students have, during this reporting period, presented abstracts to the 2014 AGU Fall Meeting. See the Products section (Section 3.1.3). These include:


2.5 Plans for the next reporting period

The project is progressing according to the anticipated plan, with the exception of the construction and validation of the flow loop for hydrate formation using Xenon as hydrate former. We are currently addressing some of the fabrication issues. In the next reporting period we will continue to work on the following tasks:

- Subtask 2.2: Model of buoyant hydrate-coated gas bubble
- Subtask 3.1: Laboratory experiments — flow-loop design, fabrication and construction
- Subtask 3.2: Laboratory experiments — acoustic signature due to hydrate formation
- Subtask 4.2: Estimate of methane flux from Atlantic margin
3 Products

3.1 Journal publications, conference papers, and presentations

3.1.1 Journal publications


3.1.2 Conference papers

Nothing to report.

3.1.3 Presentations


• Ruppel, Weber, Kessler, Pohlman, and Skarke, Methane hydrate dissociation and gas seepage on global upper continental slopes driven by intermediate ocean warming, EOS Trans. AGU, OS11C-01, AGU Fall Meeting.


• Ruppel, Skarke, Kodis, D. Brothers, and Lobecker, 2014, Methane seepage at ~600 newly-discovered sites between Cape Hatteras and Georges Bank, URI Graduate School of Oceanography weekly seminar series, October 2014.


3.2 Website(s) or other Internet site(s)
Nothing to report.

3.3 Technologies or techniques
Nothing to report.

3.4 Inventions, patent applications, and/or licenses
Nothing to report.

3.5 Other products
(such as data or databases, physical collections, audio or video products, software or NetWare, models, educational aids or curricula, instruments, or equipment)


4 Participants and collaborating organizations

4.1 Individuals working on the Project

- Name: Ruben Juanes  
  Project Role: Principal Investigator / Project Director  
  Nearest person month worked: 1  
  Contribution to Project: Ruben Juanes, as project director, is responsible for overall coordination of the effort and for the technology transfer activities, including progress and topical reports, and project review presentations. He takes the lead in the modeling and simulation of hydrate formation and dissociation in rising methane bubbles (Task 2.0), and advises the MIT graduate student responsible for doing the modeling. He also serves as primary advisor to the MIT student who conducts the laboratory experiments of bubble rise and hydrate formation with analogue multiphase fluids (Task 3.0), in collaboration with Waite (USGS).  
  Funding Support: MIT academic-year salary / DOE summer salary  
  Collaborated with individual in foreign country: No  
  Country(ies) of foreign collaborator: Not applicable  
  Travelled to foreign country: Not applicable  
  Duration of stay in foreign country(ies): Not applicable

- Name: Thomas Weber  
  Project Role: Co-Principal Investigator  
  Nearest person month worked: 1  
  Contribution to Project: Thomas Weber leads the field component of the project (Task 4.0), particularly the quantitative analysis of existing public domain data for northeast Atlantic margin bubble plumes. He also advises a graduate student at UNH. Weber also assists with the acoustics aspects of the laboratory experiments (Task 3.0), both in design of the acoustic component and the interpretation of the resulting data.  
  Funding Support: MIT academic-year salary / DOE summer salary  
  Collaborated with individual in foreign country: No  
  Country(ies) of foreign collaborator: Not applicable  
  Travelled to foreign country: Not applicable  
  Duration of stay in foreign country(ies): Not applicable

- Name: Carolyn Ruppel  
  Project Role: Co-Principal Investigator  
  Nearest person month worked: 1  
  Contribution to Project: Carolyn Ruppel has responsibility for keeping the project grounded in natural gas hydrates systems and in the issues of greatest relevance for the US gas hydrates research community, particularly the part of the community focused on the environmental impact of methane emissions from gas hydrate deposits. She is also responsible for ensuring that appropriate resources (salary support) are allocated to herself, Waite, and the USGS engineers supporting this project and interacts frequently with Juanes and his students at MIT, where she maintains a second office. She is also responsible for regional analysis and integration of observational data related to
hydrate-derived seeps and plumes on the U.S. Atlantic margin and for linking the newly emerging observational data to other existing data sets (e.g., BOEMs gas hydrates assessment of the Atlantic margin) in this area and in other areas worldwide (Task 4.0).

Funding Support: USGS salary
Collaborated with individual in foreign country: No
Country(ies) of foreign collaborator: Not applicable
Travelled to foreign country: Not applicable
Duration of stay in foreign country(ies): Not applicable

- Name: William Waite
  Project Role: Co-Principal Investigator
  Nearest person month worked: 1
  Contribution to Project: William Waite leads the lab component of the project (Task 3.0) and has primary responsibility for design and construction oversight of the xenon hydrate lab apparatus. He interacts with the USGS engineers, visits UNH to see existing devices at Webers lab, and meets with MIT staff to understand the parameters for the cell installation at MIT. After completion of the testing phase of the laboratory work at the USGS, Waite is responsible for moving the apparatus to MIT. Waite takes on primary responsibility for developing the collaboration among MIT, UNH, and the USGS for the multifaceted lab experiments and working directly with the MIT graduate student on the experiments at MIT.
  Funding Support: USGS salary
  Collaborated with individual in foreign country: No
  Country(ies) of foreign collaborator: Not applicable
  Travelled to foreign country: Not applicable
  Duration of stay in foreign country(ies): Not applicable

- Name: Amir Pahlavan
  Project Role: Graduate Student at MIT
  Nearest person month worked: 3
  Contribution to Project: Amir Pahlavan works on Task 2.0: Theoretical and computational models of coupled bubble rise and hydrate formation and dissociation.
  Funding Support: DOE
  Collaborated with individual in foreign country: No
  Country(ies) of foreign collaborator: Not applicable
  Travelled to foreign country: Not applicable
  Duration of stay in foreign country(ies): Not applicable

- Name: Xiaojing Fu
  Project Role: Graduate Student at MIT
  Nearest person month worked: 0
  Contribution to Project: Xiaojing Fu works on Task 2.0: Theoretical and computational models of coupled bubble rise and hydrate formation and dissociation.
  Funding Support: DOE
  Collaborated with individual in foreign country: No
• Name: Liam Pillsbury
  Project Role: Graduate Student at UNH
  Nearest person month worked: 0
  Contribution to Project: Liam Pillsbury works on Task 4.0: Field data analysis to link models and laboratory data to real world gas hydrate dynamics.
  Funding Support: DOE
  Collaborated with individual in foreign country: No
  Country(ies) of foreign collaborator: Not applicable
  Travelled to foreign country: Not applicable
  Duration of stay in foreign country(ies): Not applicable

4.2 Other organizations involved as partners

Nothing to report.

4.3 Other collaborators or contacts

We have established a collaboration with Dr. Luis Cueto-Felgueroso, formerly a research scientist in Juanes’s group and currently a researcher at the Technical University of Madrid, and with Prof. Hector Gomez, at the University of La Coruña and who has visited MIT on several occasions and has published joint papers with Juanes. Both researchers are experts in phase-field modeling, and the collaboration will bring new perspectives on the mathematical aspects of multiphase-multicomponent flows.

We have also established contact with Prof. Carolyn Koh’s group at Colorado School of Mines, where they have built an experimental system that is related to the one proposed in our project. William Waite has already visited their group and we anticipate that this contact will be very beneficial for the experimental aspects of the project.

Ruppel continues to make plans to visit some of the deepwater Nantucket seeps on the R/V Endeavor in July 2014 as part of a NSF cruise funded to Prof. J. Kessler (U. Rochester).

We have established a collaboration with Dr. Ann Blomberg, a post-doctoral researcher at the University of Oslo. Dr. Blomberg, who has funding through the Norwegian Research Council, has an interest in acoustic detection and classification of methane gas seeps and brings an expertise in sonar signal processing. She has been working closely with us on several aspects of the data analysis for the US Atlantic margin observations as part of Task 4.1.
5  Impact

5.1  Impact on the principal discipline of the Project
No impact to report yet.

5.2  Impact on other disciplines
No impact to report yet.

5.3  Impact on the development of human resources
The project is supporting the training of graduate students.

5.4  Impact on physical, institutional, and information resources that form infrastructure
Nothing to report yet.

5.5  Impact on technology transfer
Nothing to report yet.

5.6  Impact on society beyond science and technology
No impact to report yet.

5.7  Dollar amount of the awards budget spent in foreign country(ies)
Zero.
6 Changes and problems

Nothing to report.

7 Special reporting requirements

Nothing to report.

8 Budgetary information

The Cost Plan is included as Appendix 2.
<table>
<thead>
<tr>
<th>Milestone</th>
<th>Task/Project Milestone</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
<th>Planned</th>
<th>Planned</th>
<th>Actual</th>
<th>Actual</th>
<th>Comments (notes, explanation)</th>
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<td>Q1</td>
<td>Q2</td>
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<td>Q1</td>
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<td>1</td>
<td>1.0 Revise PMP</td>
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<td></td>
<td>1-Oct-13 31-Dec-13 1-Oct-13 3-Dec-13 Revised PMP sent by email on Dec 3, 2013</td>
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<tr>
<td>2</td>
<td>1.0 Kick-off meeting</td>
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<td></td>
<td>1-Oct-13 31-Dec-13 1-Oct-13 3-Dec-13 Webex meeting on Nov 14, 2013</td>
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<tr>
<td>3</td>
<td>2.1 Model of static gas bubble in 3D</td>
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<td>slight delay in flow-loop construction</td>
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<td>4</td>
<td>3.1 Verify flow-loop</td>
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<td>5</td>
<td>4.1 Extract MBES/SBES seep parameters</td>
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<td>3.2 Acoustic signature due to hydrate formation</td>
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<td>4.2 Estimate of methane flux from Atlantic</td>
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<td>8</td>
<td>2.2 Model of buoyant hydrate-coated gas bubble</td>
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<td>3.3 Measure gas-loss rate at low initial pressures</td>
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<td>4.1 Analyze plume data acquired by NOAA OE</td>
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<td>11</td>
<td>2.3 Model of bubble-bubble interactions</td>
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<td>3.3 Measure gas-loss rate at high initial pressures</td>
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<td>13</td>
<td>4.2 Extend bottom water temperature database</td>
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<td>2.4 Model formulation and comparison with field observations</td>
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<td>all Manuscripts submitted / Final project synthesis and report</td>
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