# **Oil & Natural Gas Technology**

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## Quarterly Research Performance Progress Report (Period ending 3/31/2014)

## CONTROLS ON METHANE EXPULSION DURING MELTING OF NATURAL GAS HYDRATE SYSTEMS: TOPIC AREA 2

Project Period (9/30/2013 to 3/31/2014)

Submitted by: Peter B. Fleminas

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The University of Texas at Austin 101 East 27th Street, Suite 4.300 Austin, TX 78712-1500 e-mail: <u>pflemings@jsg.utexas.edu</u> Phone number: 512-475-9520

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**Office of Fossil Energy** 



## **1** ACCOMPLISHMENTS:

## 1.1 What are the major goals of the project?

The project goal is to predict, given characteristic climate-induced temperature change scenarios, the conditions under which gas will be expelled from existing accumulations of gas hydrate into the shallow ocean or directly to the atmosphere. When those conditions are met, the fraction of the gas accumulation that escapes and the rate of escape shall be quantified. The predictions shall be applicable in Arctic regions and in gas hydrate systems at the up dip limit of the stability zone on continental margins. The behavior shall be explored in response to two warming scenarios: longer term change due to sea level rise (e.g. 20 thousand years) and shorter term due to atmospheric warming by anthropogenic forcing (decadal time scale).

	Planned	Actual	Verification	Comments (progress toward achieving milestone, explanation of deviation from
Milestone Description	Completion	Completion	Method	plan, etc.)
<b>I.A</b> I-D simulation of gas hydrate	9/30/2013	9/30/2013	Report	we have completed this
dissociation in natural systems.				milestone and the results
				are documented in the
				continuation application.
<b>1.B</b> 1-D Simulation of gas hydrate	3/31/2014	11/1/2013	Report	We have completed this
dissociation in laboratory				milestone and the results
controlled conditions.				are documented in the
				continuation application.
1.C Model-based determination	3/31/2014	3/31/2014	Quarterly	We have completed this
of conditions required for gas not			Report	milestone and the results
to reach seafloor/atmosphere				are documented in the
from dissociating hydrate				continuation application.
accumulation.				
<b>1.D</b> Determination of what	12/31/2013	12/1/2013	Report	We have completed this
hydrate reservoirs are at three-				milestone and the results
phase equilibrium.				are documented in the
				continuation application.
<b>1.E</b> Demonstrate ability to create	9/30/2013	10/15/2013	Report	We have completed this
and dissociate methane hydrate				milestone and the results
within sediment columns under				are documented in the
conditions analogous to natural				continuation application.
systems.	0/20/2014			
<b>2.A</b> 1-D simulation of gas	9/29/2014		Report	Preliminary simulations
				produced
<b>2</b> B Determination of conditions	12/20/2014		Poport	Proliminary simulations
for which gas expulsion into	12/29/2014		кероп	produced
hydrate-stability zone is self-				produced
limiting.				
<b>2.C</b> Demonstration of reaction	9/30/2014		Quarterly	Currently developing/refining
transport experiment where gas	-,,		Report	remote sensing technologies.
invades hydrate stability zone and				Refining experimental design
creates three phase stability.				based on numerical simulation

2.D Demonstrate a 2D simulation	3/31/2015	Report	
of hydrate dissociation and gas			
expulsion.			

## 1.2 What was accomplished under these goals?

### 1.21 Task 1: Project Management and Planning:

Projected Finish: 9/30/15

Actual Finish: In process

- 1) An initial web-based kick off meeting was held on 11/07/2012.
- 2) Twice-monthly telephone conferences with all of our participants have been organized and held.
- 3) We recruited one post-doctoral scientist for the project (Dr. Kehua You) who arrived from Texas A&M on June 15, 2013.
- 4) We recruited 4 graduate students for the project.
- 5) Dylan Meyer (geoscience, started F 2012), Kris Darnell (geoscience, Fall 2012), Jason Sanford (geoscience, Spring 2014), Imran Khan (petroleum engineering, Spring 2014).
- 6) We organized travel and supported experiment at LBNL
  - a. Peter Polito, LBNL visit, Jan 2 4, 2013
  - b. Peter Polito, LBNL visit, July 7 12, 2013
  - c. Kehua You, LBNL visit, Sept 22 27, 2013
  - d. Steve Bryant, 2013 NCGC Symposium, Oct 29 30, 2013
  - e. Peter Polito & Dylan Meyer, LBNL visit, Dec 16 20, 2013
- 7) Completed Reports (as of the end of budget period one):
  - a. 5 Quarterly Research Performance Progress Reports
  - b. 17 Cost Accrual Reports
  - c. 5 SF-425 Federal Financial Reports
  - d. Continuation Application
  - e. Phase 1 Report
- 8) We purchased equipment for construction of a thermistor string. The thermistor string consists of ten 10 kΩ resistors epoxied ten centimeters apart inside a 0.25" OD stainless steel tube. External circuitry converts the temperature-controlled resistance drop in each loop to a DC voltage, which is recorded and converted to temperature by a LabVIEW program.
- 9) Organized and supported meetings to GordonResearch Conf?
- 10) Participated in powerpoint presentation on project continuation?

## 1.22 Task 2: Conceptual and Numerical Model Development -1D

Projected Finish: 3/31/14 Actual Finish: 3/31/14

#### Summary:

Task 2 has been completed. Significant accomplishments include that we completed development of two models: 1) An analytical 'box' model to describe hydrate formation in a specific volume; and 2) a one dimensional, fully coupled, transient numerical transport model that describes hydrate formation

and multi –phase (gas and water) flow. The 'box' model is used to design our experimental approach and to then understand the experimental results. The numerical model is used to simulate hydrate formation and dissociation both at the experimental and geological scales. A major computing challenge that was overcome was to stabilize and make more efficient the numerical model that we completed. We applied the 'numerical' and 'box' model to simulate the behavior we pursued in our laboratory experiments. The match between theory and observation was remarkable. We applied the coupled model to predict the effect of seafloor warming on marine hydrate deposits (2.3.2). A significant finding was that given a sufficient initial hydrate deposit, the methane that was disassociated would selfpropagate through the hydrate stability zone and vent to the ocean. The remaining subtask (2.3.1) that will be completed before 3/31/14 is to simulate the effect of warming on a deposit in a sub permafrost deposit.

#### Analytical 'box' model

Here we derive an analytical solution to calculate the maximum hydrate saturation and methane gas consumption during hydrate formation in sediments partially saturated with water and flooded with methane gas. We present examples where the pore fluid is assumed to both saline and fresh. This model is based on thermodynamic equilibrium among liquid phase, vapor phase and hydrate phase. Three components, water, salt and methane, are considered in the model. The calculations are based on mass conservations of water, salt and methane in the 'box'.

#### **Case 1: Saline solution**

Figure 1 shows the schematic diagram for this model. Initially, the sediment is filled with  $S_{g,i}$  methane gas (dimensionless, gas saturation) and  $S_{w,i}$  water (dimensionless, water saturation) with a salinity of  $X^{s}_{w,i}$  (wt.%). The initial pressure and temperature in the system is  $P_i$  (Pa) and  $T_i$  (°C), respectively. Methane hydrate starts to form when the system pressure and temperature decrease to the hydrate stable zone  $P_f$  (Pa) and  $T_f$  (°C), respectively. During hydrate formation, methane gas is allowed to freely flow into the sediment while no water reservoir is connected to the sediment.



Initial condition: Pi Ti

Figure 1: Schematic diagram of the 'box' model. G is gas or vapor phase. W is water or liquid phase. H is hydrate phase.  $P_i$  and  $T_i$  are the initial pressure and temperature, respectively.  $P_f$  and  $T_f$  are the final equilibrium pressure and temperature,

respectively.  $S_{g,i}$  and  $S_{w,i}$  are the initial gas and water saturations, respectively.  $S_{g,f}$ ,  $S_{w,f}$  and  $S_{h,f}$  are the final equilibrium gas, water and hydrate saturations, respectively.

Since salt is transported by water flow and there is no water flow that enters or leaves the system during the experiment, the total amount of salt initially in the sediment should equal that after hydrate formation. Therefore, one has

$$V_{tot}\phi S_{w,i}\rho_{w,i}X_{w,i}^{s} = V_{tot}\phi S_{w,f}\rho_{w,f}X_{w,e}^{s},$$
 Eq. 1

where  $V_{tot}$  is the total volume of the sediment (m<sup>3</sup>);  $\phi$  is porosity (dimensionless);  $X^{s}_{w,e}$  is the mass fraction of salt in brine at three phase equilibrium condition (wt.%), which can be calculated from the phase boundary curves of brine, gas and methane hydrate using  $P_{f}$  and  $T_{f}$  (Liu and Flemings 2007);  $\rho_{w,i}$ and  $\rho_{w,f}$  are the initial and final brine density in the sediment, which can be calculated using the initial and final pressure, temperature and salinity values, respectively (Liu and Flemings 2007). We reorganize Eq. (1) and obtain the final water saturation as

$$S_{w,f} = \frac{S_{w,i}\rho_{w,i}X_{w,i}^{s}}{\rho_{w,f}X_{w,e}^{s}}.$$
 Eq. 2

The maximum hydrate saturation is calculated from the mass conservation of fresh water in the sample. The initial mass of the fresh water in the brine should equal the final mass of the fresh water in the brine plus that in the hydrate, therefore, one has

$$V_{\text{tot}}\phi S_{w,i}\rho_{w,i}\left(1-X_{w,i}^{s}\right)\left(1-X_{w,i}^{m}\right) = V_{\text{tot}}\phi S_{w,f}\rho_{w,f}\left(1-X_{w,f}^{s}\right)\left(1-X_{w,e}^{m}\right) + \frac{V_{tot}\phi S_{h,f}}{M_{h}/\rho_{h}}NM_{w}, \quad \text{Eq. 3}$$

where  $X_{w,i}^{m}$  and  $X_{w,f}^{m}$  are the initial and final solubility of methane in the water (wt.%) As in Liu and Flemings (2007), the solubility of methane in water in presence of hydrate is calculated using the model of *Henry et al.* (1999), while the solubility of methane in water in absence of hydrate is calculated using the model of *Duan et al.* (1992).  $M_w$  and  $M_h$  are the molar weight of water (kg mol<sup>-1</sup>) and methane hydrate (kg mol<sup>-1</sup>), respectively;  $\rho_h$  is the methane hydrate density, and we used the value of 912 kg m<sup>-3</sup> in this study; *N* is the stoichiometric hydration number, which is assumed to be constant and equal to 5.75 in this study. We restate Eq. (3) and obtain the maximum hydrate saturation of

$$S_{h,f} = \frac{\left[S_{w,i}\rho_{w,i}\left(1 - X_{w,i}^{s}\right)\left(1 - X_{w,i}^{m}\right) - S_{w,f}\rho_{w,f}\left(1 - X_{w,f}^{s}\right)\left(1 - X_{w,e}^{m}\right)\right]M_{h}}{NM_{w}\rho_{h}}.$$
 Eq. 4

The final gas saturation can be written as

$$S_{g,f} = 1 - S_{w,f} - S_{h,f} \,. \label{eq:gg}$$
 Eq. 5

Mass conservation of methane is used to calculate the methane gas consumption in the sample. Initially, the methane is distributed in water and gas phase. At three phase equilibrium condition, the methane is distributed in water, gas and hydrate phases, therefore, one has

where  $\Delta m$  is the mass of methane gas consumed during hydrate formation (kg);  $m_{w,f}^m$ ,  $m_{g,f}^m$ ,  $m_{h,f}^m$  are the mass of methane (kg) in the final water, gas and hydrate phases, respectively;  $m_{w,i}^m$  and  $m_{g,i}^m$  are the mass of methane (kg) in the initial water and gas phases, respectively. They are calculated as

$$m_{w,f}^{m} = V_{tot} \phi S_{w,f} \rho_{w,f} X_{w,f}^{m}$$
, Eq. 7

$$m_{g,f}^{m} = V_{tot} \phi S_{g,f} \rho_{g,f},$$
 Eq. 8

$$m_{h,f}^{m} = \frac{V_{tot}\phi S_{h,f}\rho_{h}}{M_{h}}M_{m}, \qquad \text{Eq. 9}$$

$$m_{w,i}^{m} = V_{tot} \phi S_{w,i} \rho_{w,i} X_{w,i}^{m},$$
 Eq. 10

where  $M_m$  is the molar weight of methane (kg mol<sup>-1</sup>);  $\rho_{g,i}$  and  $\rho_{g,f}$  are the initial and final gas density (kg m<sup>-3</sup>), respectively, which can be calculated from the initial and final temperature and pressure, respectively (Liu and Flemings 2007). Substitute Eqs. (7)-(11) into Eq. (6), one can obtain the methane gas consumption during methane hydrate formation at the final pressure and temperature of  $P_f$  and  $T_f$ , respectively.

#### Case 2: Fresh water

In this case, methane hydrate is formed in a sediment column initially partially saturated with fresh water and flooded with the methane gas. Under the same three phase equilibrium pressure and temperature condition for saline water  $P_f$  and  $T_f$  as discussed above, the fresh water system reaches liquid and hydrate stable zone. However, since the sediment is connected with a methane gas reservoir, and water is limited, theoretically all the water initially in the sediment should be converted to hydrate. Therefore, one has

$$S_{w,f} = 0$$
. Eq. 12

By conservation of water mass, we find

$$V_{tot}\phi S_{w,i}\rho_{w,i}(1-X_{w,i}^{m}) = \frac{V_{tot}\phi S_{h,f}}{M_{h}/\rho_{h}} NM_{w}.$$
 Eq. 13

We reorganize Eq. (13) and obtain the maximum hydrate saturation for the case of fresh water

$$S_{h,f} = \frac{S_{w,i}\rho_{w,i}(1 - X_{w,i}^{m})M_{h}}{NM_{w}\rho_{h}}.$$
 Eq. 14

The final gas saturation is calculated by Eq. (5). According to the mass conservation of methane, one can calculate the methane gas consumption for the fresh water case as follows

$$\Delta m = m_{g,f}^m + m_{h,f}^m - m_{w,i}^m - m_{g,i}^m.$$
Eq. 15  

$$m_{g,f}^m, m_{h,f}^m, m_{w,i}^m \text{ and } m_{g,i}^m \text{ can be calculated by Eqs. (8)-(11), respectively.}$$

Matlab programs SH\_BRINE and SH\_FRESH have been developed to assist the above calculations for the saline water and fresh water cases, respectively.

#### Numerical model

This numerical model considers the fully coupled multiphase, multicomponent fluid flow, solute transport and heat flow. It was originally developed by *Liu* (2006) and has been described in *Liu and Flemings* (2007). The downward direction is set as positive direction. This model is based on local thermodynamic equilibrium among the liquid, vapor, and hydrate phases. Three components, water, salt and methane, are considered in the model. Fluid flow in the system includes viscous flow (pressure driven), capillary flow (saturation-gradient driven) and gravity flow (buoyancy driven). Heat is transported by conduction and advection.

The following assumptions are used in the model: (1) Darcy's law describes multiphase fluid flow in the uniform porous media. (2) There is no sedimentation and erosion. (3) There is no in situ biogenic methane. (4) Methane is the only hydrate-forming gas. (5) Salt is confined to the liquid phase. (6) Methane is assumed to be the only component in the gas phase. (7) Hydrate is a solid phase and only two-phase (vapor+liquid) capillary pressure is considered. (8) The temperature among each phase is locally in equilibrium.

Appling mass conservation to each component, one can get the mass balance equation for methane as

$$\phi \frac{\partial \left(\sum_{\beta=l,\nu,h} \rho_{\beta} S_{\beta} X_{\beta}^{m}\right)}{\partial t} - \sum_{\beta=l,\nu} \nabla \left\{ \frac{kk_{r\beta}}{\mu_{\beta}} \left( \nabla P_{\beta} - \rho_{\beta} g \right) \rho_{\beta} X_{\beta}^{m} \right\} - \nabla \left\{ \phi^{2} D_{l0}^{m} \rho_{l} \nabla X_{l}^{m} \right\} - q^{m} = 0.$$
 Eq. 16

The mass balance equation for water is

$$\phi \frac{\partial \left(\sum_{\beta=l,h} \rho_{\beta} S_{\beta} X_{\beta}^{w}\right)}{\partial t} - \sum_{\beta=l} \nabla \left\{ \frac{kk_{r\beta}}{\mu_{\beta}} \left( \nabla P_{\beta} - \rho_{\beta} g \right) \rho_{\beta} X_{\beta}^{w} \right\} - \nabla \left\{ \phi^{2} D_{l0}^{w} \rho_{l} \nabla X_{l}^{w} \right\} - q^{w} = 0.$$
 Eq. 17

The mass balance equation for salt is

$$\phi \frac{\partial \left(\sum_{\beta=l} \rho_{\beta} S_{\beta} X_{\beta}^{s}\right)}{\partial t} - \sum_{\beta=l} \nabla \left\{ \frac{kk_{r\beta}}{\mu_{\beta}} \left( \nabla P_{\beta} - \rho_{\beta} g \right) \rho_{\beta} X_{\beta}^{s} \right\} - \nabla \left\{ \phi^{2} D_{l0}^{s} \rho_{l} \nabla X_{l}^{s} \right\} - q^{s} = 0.$$
 Eq. 18

In the above three equations, the superscripts m, w and s denote methane, water and salt, respectively. The subscripts I, v and h denote liquid, vapor and hydrate phases, respectively.

 $\phi$  is porosity (dimensionless). *t* is time (sec). *k* is sediment permeability (m<sup>2</sup>).  $\rho_{\beta}$ ,  $S_{\beta}$ ,  $\mu_{\beta}$ ,  $P_{\beta}$  and  $k_{r\beta}$  are the density (kg m<sup>-3</sup>), saturation (dimensionless), dynamic viscosity (Pa sec), pressure (Pa) and relative permeability of  $\beta$  phase, respectively.  $X_{\beta}^{m}$ ,  $X_{\beta}^{w}$  and  $X_{\beta}^{s}$  are the mass fractions of methane, water and salt in  $\beta$  phase, respectively. *g* is acceleration due to gravity (m s<sup>-2</sup>).  $D_{l0}^{m}$ ,  $D_{l0}^{w}$  and  $D_{l0}^{s}$  are the molecular diffusion coefficient (m<sup>2</sup> s<sup>-1</sup>) of methane, water and salt, respectively.  $q^{m}$ ,  $q^{w}$  and  $q^{s}$  are the sources or sinks of methane, water and salt, respectively.

The energy balance equation (superscript e) is

$$\frac{\partial \left( (1-\phi)\rho_{R}C_{R}T + \sum_{\beta=l,\nu,h}\phi\rho_{\beta}S_{\beta}u_{\beta} \right)}{\partial t} - \sum_{\beta=l,\nu}\nabla \left\{ \frac{kk_{r\beta}}{\mu_{\beta}} \left( \nabla P_{\beta} - \rho_{\beta}g \right)\rho_{\beta}h_{\beta} \right\} - \nabla \left\{ \lambda \nabla T \right\} - q^{e} = 0, \quad \text{Eq. 19}$$

where the subscript *R* denotes the solid grain. *T* is temperature (°C).  $\lambda$  is the bulk thermal conductivity of the porous media (W m<sup>-1</sup> °C<sup>-1</sup>), and  $\lambda = (1 - \phi)\lambda_R + \phi \sum_{\beta = l, v, h} S_\beta \lambda_\beta$ .  $\lambda_\beta$ ,  $u_\beta$  and  $h_\beta$  are the thermal conductivity (W m<sup>-1</sup> °C<sup>-1</sup>), specific internal energy (J kg<sup>-1</sup>) and specific enthalpy (J kg<sup>-1</sup>) of phase  $\beta$ , respectively.

Duan et al.'s (1992) model is used to calculate the methane solubility in water in absence of methane hydrate. Henry et al.'s (1999) model is used to calculate the methane solubility is water in presence of methane hydrate. The Leverett J-function is used to describe the relationship between capillary pressure and pore fluid saturation (Bear 1972). Corey's model is used to calculate the relative water and gas permeability (Bear 1972).

Porosity is defined as the pore volume fraction filled with fluid phases (liquid and vapor). As hydrate forms, porosity is reduced as  $\phi = \phi_0 (1 - S_h)$ , where  $\phi_0$  is the porosity (dimensionless) in absence of hydrate. The decrease of porosity leads to the decrease of intrinsic permeability, which is described by the model of *Kleinberg et al.* (2003), where hydrate is assumed to form in the center of the pores. The decrease in porosity and permeability can change the capillary pressure, which is calculated as

 $P_c = \sqrt{k_0 \phi / \phi_0 k} P_{c0}$ , where  $k_0$  and  $P_{c0}$  are the intrinsic permeability (m<sup>2</sup>) and capillary pressure (Pa) in absence of hydrate, respectively.

The numerical model is solved by fully implicit block-centered finite-difference method. Upstream weighting is used to calculate the phase mobility, and harmonic weighting is used to calculate the

intrinsic permeability. Newton\_Raphson method is used to iteratively solve the nonlinear equations. Primary variables switching method is used in case of the appearance or disappearance of phases. The Matlab program originally developed by *Liu* (2006) for this numerical model can only simulate the case when the sediment is initially 100% saturated with water. We modified the input files and the files calculating the Jacobian and residual matrixes for solving the nonlinear equations to extend the program to more general cases of any arbitrary initial water, gas or hydrate saturations. Besides, we added a dynamic time-step choice to improve the numerical stability. With the dynamic time-step choice, the simulation starts with a big time-step value. This value will be cut down to a smaller one whenever the calculation cannot be converged or when it is converged to unreasonable situations, for example, when the saturations are less than zero or greater than 100%. At the new time, the time-step will get back to the original big value to guarantee the efficiency of the simulation. We also added the choice of manually controlling the sediment temperature and fixed gas pressure boundary condition to simulate the laboratory experiment.

#### 1.22a Subtask 2.1 - Dissociation of 1D vertical hydrate accumulation

Milestone 1.A 1-D simulation of gas hydrate dissociation in natural systems.

### 1.22b Subtask 2.2 - Apply 1D model to laboratory experiment

Milestone 1.B 1-D Simulation of gas hydrate formation in laboratory controlled conditions.

In this section, we apply the 1D numerical model to simulate the hydrate solidification front advancing in our second experiment described in section 1.24b. The column is filled with sand and placed vertically. The sediment has a porosity of 36%, intrinsic permeability of 0.83 Darcy and capillary entry pressure of 0.02 MPa. Initially, the sediment is saturated with brine having a salinity of 7.0 wt.%. The water pressure in the sample is hydrostatic, with a pressure of 6.89 MPa at the top of the sample. The temperature is uniformly 4 °C. The gas pressure at the top boundary is fixed at 6.94 MPa. At the bottom boundary, we apply a constant water flux of 50 g hour<sup>-1</sup> m<sup>-2</sup>.

As we gradually pulls water from the bottom, methane gas slowly flows into the sample from the top (Figure 2). Methane hydrate starts to form from the top of the sample, increasing the local salinity there from 7 wt.% (Figures 2 and 3). When the local salinity reaches 10.9 wt.%, the local thermal state hits the three-phase equilibrium phase boundary. No more hydrate can be formed locally. Methane gas moves further into the water column, and the hydrate solidification front moves downward (Figure 2). Methane hydrate, brine and methane gas coexist, and salinity equals 10.9 wt.% behind the hydrate solidification front. Before the hydrate solidification front, salinity gradually decreases from 10.9 to 7.0 wt.% due to the advection and diffusion transport of salt (Figure 3). The hydrate solidification front reaches the bottom of the sample at 136 hours (Figure 2), when the salinity is uniformly 10.9 wt.% across the sample (Figure 3). During hydrate formation, as brine is pulled out from the sample with a constant rate, the total methane mass in the sample gradually increases from zero to nearly steady-state value of 56 g at 136 hours (Figure 4).



Figure 2: The distribution of methane hydrate (green), gas (red) and water (blue) saturations across the sample at 5, 10, 15, 20, 30, 50, 70, 90, 110 and 136 hours.



Figure 3: The distribution of salinity across the sample at 5, 10, 15, 20, 30, 50, 70, 90, 110 and 136 hours.



Figure 4: Time change of the total methane and total water mass in the sample during hydrate formation.

## 1.22c Subtask 2.3 - 1D models of natural examples Subtask 2.3.1 Hydrate accumulations below permafrost

Subtask 2.3.2 - 1D model application to deposits near up-dip limit of stability zone on continental margins

Milestone 1.C Model-based determination of conditions required for gas not to reach seafloor/atmosphere from dissociating hydrate accumulation.

#### Transient venting in natural systems

We have extended the results from our previous numerical simulations of gas venting to the ocean. We now characterize gas venting for generic environments. Our analysis shows that the behavior previously described as "transient venting" is a consequence of the changes in volume that occur during the reorganization of the hydrate system in response to warming. We have shown that the salinity increase that occurs during secondary hydrate formation is the control on the three-phase behavior. Thus, we can simply calculate the changes in the hydrate stability zone for a given warming, and assess the hydrate re-organization. The threshold for transient venting as we have shown happens when the amount of dissociated hydrate exceeds the amount of hydrate required to elevate the salinity in the shortened hydrate stability zone to the three-phase equilibrium. This basic analysis demonstrates that the transient venting is a potential mechanism for venting across a wide range of water depths and temperature changes.



Figure 5: Gas venting potential under a given temperature increase (from assumed 0 C) and at a given water depth. The gradient shows the minimum hydrate saturation within the dissociated zone necessary to produce transient venting.

### 1.23 Task 3: Categorize stability of known hydrate reservoirs

Projected Finish: 9/30/13 Actual Finish: 9/30/13

Milestone 1.D Determination of what hydrate reservoirs are at three-phase equilibrium.

#### Summary

We constrained the in situ temperature, pressure, and salinity at NGHP Site 01-10A (Krishna-Godavari Basin, off the eastern coast of India). NGHP Site 01-10A has elevated in situ salinities near or at the three-phase boundary for a large portion of the GHSZ, indicating these portions of this system is at three-phase equilibrium: salinity is elevated enough that gas, water, and hydrate can be present. We further analyze the available well log, pressure core, lithology, and model data to better characterize the in situ conditions (pressure, temperature, and salinity) within the GHSZ.

#### Determination of in situ hydrate saturation and pressure, temperature, and salinity conditions

In order to assess the overall thermodynamic state of a hydrate system, the in-situ pressure, temperature, and salinity must be determined throughout the GHSZ. The in-situ pressure and temperature are used to define the salinity required for three-phase equilibrium, which marks the boundary between the hydrate stable and gas stable zones. The in-situ salinity can then be compared to the three-phase salinity to determine the thermodynamic state of the hydrate system with depth.

#### Determination of in-situ pressure and temperature

We follow the common assumption of previous research and assume a hydrostatic gradient and that no overpressure is developing within the sediments. Therefore, we calculate pore pressure (u) at a particular depth within the GHSZ using Equation 20:

$$u = (\rho_{sw} \cdot g \cdot Z_{wd}) + (\rho_{pw} \cdot g \cdot Z) = \rho_{sw} \cdot g \cdot (Z + Z_{wd}).$$
 Eq. 20

 $Z_{wd}$  is the water depth at the site, Z is the depth within the GHSZ,  $\rho_{sw}$  is the average density of seawater (1.023 g/cm<sup>3</sup>), g is gravitational acceleration (9.81 m/s<sup>2</sup>), and  $\rho_{pw}$  is the assumed density of the porewater. The density of water can vary depending on its salinity and temperature. The potential effect of this density change on the pore pressure, however, is relatively small, so we assume that the pore-water density is equal to seawater density.

We calculate the in-situ temperature (T) at a particular depth within the GHSZ using Equation 21:

$$T = T_b + (Z \cdot G_g).$$
 Eq. 21

 $T_b$  is the temperature at the seafloor, and  $G_g$  is the geothermal gradient for the site. Geothermal gradient is controlled by the thermal conductivity and heat flow of the material below the seafloor (Henninges et al. 2005) and can be determined using downhole temperature probes.

#### Determination of in-situ salinity

The core-derived salinities are usually presumed to equal the in-situ values. The presence of hydrate, however, can result in elevated in-situ salinities. The dissociation of that hydrate releases fresh water back into the pore space, decreasing the salinity and invalidating this assumption. In this case, we determine the in-situ salinity using a method similar to that implemented by Malinverno, et al. (2008),

which calculated the in-situ hydrate saturation from pore-water freshening. We assume a two-phase system where only free water, of saturation  $S_w$ , and hydrate, of saturation  $S_h$ , exist, such that:

$$S_h = 1 - S_w.$$
 Eq. 22

We also assume that the total pore volume does not change with hydrate formation and that the system is closed to diffusion and advection, meaning that the salt is immobile (Liu and Flemings 2006). With these assumptions, we calculate the in-situ salinity ( $C_{in-situ}$ ) with a volumetric correction (Eq. 23) between the core-derived salinity ( $C_0$ ) and the water saturation:

$$C_{in-situ} = \frac{C_0}{1-S_h} = \frac{C_0}{S_w}.$$
 Eq. 23

#### 2.3 Determination of in-situ water saturation

We determine the water saturation using Archie's Law (Archie 1941):

$$S_w = \sqrt[N]{\frac{a \cdot \rho_w}{n^m \cdot \rho_t}}.$$
 Eq. 24

*N* is the saturation exponent, *a* is the tortuosity coefficient,  $\rho_w$  is the pore-water resistivity, *n* is the porosity, *m* is the cementation exponent, and  $\rho_t$  is the formation resistivity. We use the RING resistivity log from the Logging-While-Drilling (LWD) data as a good estimate of the true formation resistivity (Cook et al. 2012). Porosity is calculated using a density equation:

$$n = \frac{(\rho_m - \rho_b)}{(\rho_m - \rho_f)}$$
. Eq. 25

Where  $\rho_m$  is the average grain density derived from the core moisture and density data,  $\rho_f$  is the assumed constant fluid density for each study site, and  $\rho_b$  is the bulk density derived from the LWD density log.

The pore-water resistivity is dependent upon the temperature and salinity of the water and is calculated using Arps' Equation (Arps 1953):

$$\rho_w = 0.0123 + \left( \left( \frac{3647.5}{C^{0.955}} \right) \cdot \frac{45.4}{(T_f + 21.5)} \right).$$
Eq. 26

Where  $T_f$  is the fluid temperature, determined using Equation 21, and *C* is the salinity of the water. We determine the tortuosity coefficient (*a*) and cementation exponent (*m*) for each site based on resistivity and porosity measurements where water is the only phase present ( $S_w = 1$ ). With this assumption, Equation 24 simplifies to:

$$F = \frac{\rho_t}{\rho_w} = a \cdot n^{-m} \,. \tag{Eq. 27}$$

Where *F*, termed the formation factor, is the ratio of formation resistivity to pore-water resistivity. A power law regression is taken from a cross-plot between porosity and formation factor (Pickett plot) and

is used to infer the values of a and m. We limited the values of a and m to be between 0.5 – 1.5 and to be greater than 1, respectively (Crain 2013).

To ensure that the points chosen to determine *a* and *m* are from material that is fully water saturated, we only use data points that are from below the GHSZ and that are not associated with anomalously low log-derived density. We also remove data points that have a bulk density correction log greater than  $\pm 0.25$  g/cm<sup>3</sup> or a caliper log that exceeds the bit diameter by greater than 1 cm (0.394 in). These conditions are applied not only to ensure that the points represent water-saturated sediments, but also to remove points where borehole conditions may have compromised the log data accuracy.

The value of the saturation exponent in hydrate-saturated sediments is a topic of considerable debate. Pearson, et al. (1983) shows that *N* was equal to approximately 2 for various water-saturated sandstones. Hydrate-bearing sediment, however, experiences physical changes as hydrate precipitates and therefore does not act like a clean, water-saturated sandstone. Spangenberg (2001) suggested that *N* can range from 0.5 to 4 and that the value was dependent on many factors, including: whether hydrates are isopachous or pore-filling, the degree of hydrate saturation, and the significance of capillary effects. Spangenberg suggests that, regardless of the other factors, *N* increases at greater hydrate saturations. We assume an *N*-value of 4 for all study sites, because our region of interest is associated with significant hydrate saturations.

We use an iterative application of Archie's Law (Eq. 24) and the salinity correction (Eq. 23) to determine the in-situ water saturation and salinity. The water saturation is calculated for the first iteration using the core-derived salinity. This salinity is then corrected and used in the following iteration to recalculate the water saturation. The saturation from the current iteration is then used to re-correct the corederived salinity for the following iteration. This process is repeated for 10 iterations, though we found that the calculated water saturation and in-situ salinity leveled off ( $\Delta S_w < 1\%$ ) after 4 to 5 iterations. During this procedure, linear interpolation was required to account for the different sampling resolutions of the log and core-derived data. The logged data resolution ranged from 3.05 – 15.24 cm (1.2 - 6 in), depending on the site and logging tool, while the core was sampled every 208 - 493 cm(81.9 – 194.1 in). To account for this difference, this iterative application of Archie's law is run using two modes of linear interpolation at each site. The first mode interpolates between the core-derived salinities to determine a unique salinity value for each resistivity data point. This method produces a hydrate saturation and salinity curve at the same resolution as the resistivity data. The second mode interpolates between the resistivity measurements to determine a unique resistivity value for each salinity sample. This mode produces a hydrate saturation and salinity profile for each available salinity data point. The results from both of these interpolation modes are shown in the results for each site as gray or black lines for the resistivity resolution data and red dots for the salinity resolution data.

#### **Determination of three-phase salinity**

We calculate the salinity necessary to maintain three-phase equilibrium throughout the GHSZ for the interpreted temperature and pressure profiles at each study site. At any particular depth, we define this salinity as the point where the solubility of methane gas in water in a liquid-gas phase system (Duan et al. 1992) and liquid-hydrate phase system (Henry et al. 1999), at the unique in-situ pressure and temperature conditions, are equal. This model was described by Liu and Flemings (2006) and showed good agreement with stability conditions produced by the CSMHYD hydrate program (Sloan 1998).

#### **Study Site**

#### Analysis of well log and core-derived data

Each study site was chosen for the availability of necessary log and core data as well as the confirmed presence of hydrate within the logged portion of the well. The standard suite of log data included the gamma ray, caliper, resistivity, bulk density, photoelectric factor, and neutron porosity tools. Some logs were not essential to our calculations and are therefore are not displayed in the well log montages. We analyze the LWD and core data to infer the presence of hydrate and the dominant lithology and to determine if salt diffusion or advection is significantly affecting the in-situ salinity.

Hydrate presence is inferred using the resistivity and bulk density logs. Gas hydrate is a highly resistive material that complicates the conductive pathway, increasing tortuosity and the measured resistivity (Collett and Ladd 2000, Cook et al. 2010, Pearson et al. 1983). Also, gas hydrate has a density equal to approximately 0.925 (Collett et al. 2012), which is less than seawater. The formation of gas hydrate could result in a decrease in measured bulk density as the greater density pore fluid is replaced by the significantly less dense hydrate. Therefore, we infer the presence of hydrate wherever the resistivity increases and bulk density decreases together.

The general lithological trends within a well are determined from the gamma ray log and core samples. The gamma ray tool responds to changes in grain size distribution, recording larger gamma ray values (GAPI) in finer-grained sediment (Serra 1984). This information is used to identify interbedded fine-grained and coarse-grained material and directional-fining sequences. The core samples allow for a more complete characterization of the lithology, but sacrifice data resolution. These data are used to calibrate and confirm the analysis performed on the gamma ray log.

We determine the validity of the "closed system" assumption from the core-derived salinities. In an open system, the excess in-situ salt will be reduced back to baseline values through diffusion and advection, while in a closed system it will remain in the pore space. When the core is removed from the in-situ conditions and hydrate dissociates, fresh water will flow back into the pore space, freshening the pore-water. With open conditions the core-derived salinities would be significantly below seawater, while with closed conditions the pore-water would freshen back to the baseline salinity. Therefore, we interpret the system to be "closed" if the core-derived salinities are around seawater.

#### NGHP Site 01-10A

NGHP Site 01-10A (Figure 6) was drilled in the Krishna-Godavari Basin, off of the eastern coast of India (15° 51.857'N, 81° 50.079'E) to investigate the distribution of methane hydrate resources available in that region. Site 10A is located approximately 150 kilometers southeast of Guntur, India in 1049.3 meters of water. The well was drilled to a total depth of 205.5 mbsf and penetrated the BSR at 160 mbsf (NGHP Expedition 01 Scientists 2007). A standard suite of LWD tools was run for the entire well; the relevant LWD and core-derived data from this borehole are presented in Figure 7. Archie's parameters, *a* and *m*, were determined to equal 1.50 and 1.62, respectively (Table 1, Figure 8). To avoid washout near the seafloor, the first 30 mbsf of the hole were drilled with low flow, rotation, and penetration rates. After 30 mbsf, the flow rate was increased until all LWD tools were activated (NGHP Expedition 01 Scientists 2007). As a result, the data required for our calculation was only available below 22 mbsf.

The resistivity log for Site 10A increases from a baseline value of 0.94 ohmm starting at 28 mbsf, reaching a maximum value of 130 ohmm at 48 mbsf. Between 48 - 160 mbsf, the resistivity drops log-linearly from the peak value back to the baseline, excluding the region between 89 - 125 mbsf, where the resistivity drops an average of 8.3 ohmm below the this trend. Where data was available, the bulk density log ranges from 1240 - 1820 kg/m<sup>3</sup> with a baseline density of 1800 kg/m<sup>3</sup>. Above the BSR, the

bulk density decreased significantly from the baseline between 22 - 89 and 125 - 160 mbsf. Below the BSR, the density alternated between the baseline and a bulk density of approximately  $1500 \text{ kg/m}^3$ , which could either indicate the presence of free gas or be the result of poor borehole conditions. These data indicate that hydrate exists between 28 - 160 mbsf, but that greater saturations of hydrate occur between 45 - 90 and 125 - 160 mbsf. The occurrence of hydrate at Site 10A was confirmed in core sample cuts, infrared imaging data, and the occurrence of soupy or "mousse-like" textured sediment as a result of hydrate dissociation in core samples. Gas hydrate was observed as solid nodules, disseminated throughout the pore space, and within high-angle fractures (NGHP Expedition 01 Scientists 2007).

The gamma ray log for Site 10A ranges between 60 -100 GAPI from 28 – 160 mbsf, with an average value of 82 GAPI, indicating that the lithology is primarily fine-grained material. The lithology from recovered cores supports this interpretation, defining a single lithological unit consisting of a clay matrix with varying occurrence of nannofossils. The core lithology also indicated the presence of authigenic carbonate cements in large portions on the well (NGHP Expedition 01 Scientists 2007). The core-derived salinities for NGHP Site 10A range from 397.6 - 634 mM Cl<sup>-</sup>, averaging 526.6 mM Cl<sup>-</sup> with a standard deviation of  $\pm 65.3$  mM Cl<sup>-</sup>. The range of salinity values are relatively well distributed throughout the well, showing no particular trends correlated with lithology or hydrate presence. The close proximity of the salinities to the baseline salinity indicates that the system was closed during hydrate formation.



Figure 6: NGHP Site 01-10A is located approximately 150 km southeast of Guntur, India in about 1050m of water. Bathymetry data from IOC, et al. (2003).



Figure 7: Montage of core and LWD data from NGHP Site 01-10A in the Krishna-Godavari Basin. Track 1: Gamma ray and caliper log (dashed line indicates bit size); Track 2: RING resistivity log; Track 3: Core-derived and LWD bulk density. Equivalent porosity scale (assuming  $\rho g = 2.72$  g/cm3 and  $\rho w = 1.023$  g/cm3) is included for reference; Track 4: Core-derived chloride concentration. Dashed line represents average salinity of 526.4 mM Cl-.



Figure 8: Pickett plot for NGHP 01-10A. The best fit linear regression line using water-saturated points yields the cementation exponent (m = 1.62) and tortuosity coefficient (a = 1.50).

#### Results

#### NGHP Site 01-10A

At Site 10A, there are four distinct zones of varying hydrate saturation: Zone 1, from 28 - 45 mbsf; Zone 2, from 45 - 90 mbsf; Zone 3, from 90 - 123 mbsf; and Zone 4, from 123 - 160 mbsf. These zones are identified by significant changes in the average value of the hydrate saturations between zones. Zone 1 – 4 have average hydrate saturations of 0.526, 0.7, 0.382, and 0.413, respectively, with a peak saturation of 0.817 at 48.4 mbsf (Figure 9; Track 3). The hydrate saturations in Zones 2 and 4 are consistently high and follow a relatively linear decline in value with depth. The hydrate saturation drops rapidly from 0.40 – 0 in the last 3 meters above the BSR. Zones 1 and 3 exhibit lower hydrate saturations relative to the proximal zones as well as a similar decrease in saturation with depth. Elevated salinities are identified throughout zones 1 - 4, averaging 1181, 1922, 876.6, and 872 mM Cl<sup>-</sup>, respectively, ranging between 1.66 – 3.65 times greater than the baseline salinity (Figure 9; Track 4).

We qualitatively interpret Zones 2 and 4, where in-situ salinities are at or exceed the three-phase salinity, to be near to or at three-phase equilibrium. Between 46 - 57 mbsf, the in-situ salinities calculated at the log data resolution (gray line) were far greater than the three-phase salinity. At the pressure and temperature conditions at this depth, hydrate would not be stable under these conditions. We attribute these anomalously high values to the lack of core-derived salinities within this section. The interpolation of salinity values between the available salinity data above and below this region results in an average salinity 94.6 mM Cl<sup>-</sup> greater than the baseline. If the baseline salinity were used in this region, the in-situ salinities would decrease by between 270 - 530 mM Cl<sup>-</sup>.



Figure 9: Results from NGHP Site 01-10A. Track 1: Occurrence of carbonate cement derived from recovered cores (NGHP Expedition 01 Scientists 2007); Track 2: RING (black line) and propagation resistivity curves (colored lines) at 2MHz and electrode spacing ranging from 16 – 40 inches; Track 3: Resistivity- (black line) and salinity-interpolated (red dots), Archie-derived hydrate saturation, pressure core-derived hydrate saturations (NGHP Expedition 01 Scientists 2007, Rees, Kneafsey and Seol 2011a), and modeled hydrate saturations incorporating resistivity anisotropy (Cook et al. 2010); Track 4: Core-derived salinity (NGHP Expedition 01 Scientists 2007), resistivity- (gray line) and salinity-interpolated (red dots) in-situ salinities, and the salinity required for three-phase equilibrium (dashed line). Red shading show quantitatively interpreted three-phase equilibrium zones

#### Discussion

#### **Historic Data**

Five pressure cores, 10B-08Y (50.1 mbsf), 10B-15P (98.2 mbsf), 10B-18Y (117.4 mbsf), 10D-12E (77.8 mbsf), and 10D-22E (145.1 mbsf), were recovered from within the GHSZ while drilling sites 10B and 10D and were used to determine the in-situ hydrate saturation. The resulting saturation values from these analyses are plotted with the calculated hydrate saturations in Figure 9. Core 10D-12E (Fig. 9, purple dots) had substantial mechanical complications during recovery and storage that resulted in significant hydrate dissociation and gross underestimation of in-situ hydrate saturation (NGHP Expedition 01 Scientists 2007).

Core 10B-08Y (Fig. 9, orange dot) was rapidly depressurized on deck, segmented into four sections, and then stored in liquid nitrogen to preserve the hydrate present in the core. Each of the segments were then place in a micro-CT scanner at atmospheric pressure and room temperature to record three-dimension density contrast images. From this data, the hydrate saturation of the core was estimated at 25 percent, which is significant lower than the Archie-derived saturations. As a result of the depressurization, handling, and storage, however, approximately 32 percent of the core was air voided with from hydrate dissociation and gas devolution, which could have caused significant underestimation of the hydrate saturation (Rees, Priest and Clayton 2011b).

The final three pressure cores (Fig. 9, purple dots) underwent controlled degassing on deck, such that the hydrate saturation could be determined from the amount of gas released during the experiment. Although each of these cores were associated with varying amounts of hydrate dissociation during recovery, resulting in lower calculated in-situ hydrate saturations, the saturations derived from these three pressure cores are correlated relatively well with the Archie-derived hydrate saturations we present here. The average saturation of these pressure cores was 16.3 percent lower than calculated, which can be attributed to the standard error  $(-5\% S_h)$  associated with pressure cores (Lee and Collett, 2009) and the dissociation of hydrate during recovery and handling.

Along with the pressure cores, Cook, et al. (2010) modeled hydrate saturations (Fig. 9, blue dots) from resistivity data, taking into account anisotropic conditions due to high-angle, hydrate-filled fractures. This study compared the modeled propagation resistivity response to fractures of different angles to the actual response recorded in the LWD propagation resistivity curves (Fig. 9, Track 2), to estimate the hydrate saturation at that depth. The hydrate saturation was estimated to be 96 percent at the middle depth. This anomalously high saturation is explained by model limitations concerning the fracture angle and the relative depths of investigation of the Resistivity-At-Bit and propagation resistivity tools. The other two modeled saturations, however, correlated well with the Archie-derived saturation, with an average saturation of 3 percent lower. The pressure core and modeled hydrate saturations generally support the saturations we present for Zones 3 and 4, despite the effects of hydrate-filled fractures on the resistivity anisotropy.

#### Resistivity anisotropy from hydrate-filled fractures

Both of the study sites have been associated with the presence of high-angle, hydrate-filled fractures (Cook et al. 2010, Lee and Collett 2009, Weinberger and Brown 2006). It has been suggested that these fractures create an anisotropic medium that could result in overestimates of hydrate saturation, when using isotropic petrophysical methods (Kennedy and Herrick, Lee and Collett 2009). In isotropic media, the measured resistivity is the same regardless of the direction in which the measurement is taken. In the presence of alternating layers of materials with distinctly different resistivities, however, the

measured resistivity perpendicular ( $R_{\perp}$ ) to the layers tends to be far greater than the resistivity parallel ( $R_{\parallel}$ ) to the layers (Cook et al. 2012, Kennedy and Herrick 2003). With an isotropic model, this increase in resistivity is attributed to greater hydrate saturation, despite the fact that hydrate-filled fractures contribute little additional hydrate saturation to the sediment. We critically evaluate the distribution and character of the fracture network at each study site to determine if fractures are affecting our results.

Hydrate-filled fractures are identified from recovered core samples and from the Resistivity-At-Bit (RAB) images and the propagation resistivity data collected during LWD acquisition. In the core samples, curators observe concentrated hydrate in fractures and identify the massive presence of hydrate using thermal infrared imaging to detect negative thermal anomalies (NGHP Expedition 01 Scientists 2007, Shipboard Scientific Party 2003). The RAB imaging system records the resistivity of the borehole wall in all directions, creating a three-dimensional look at how resistivity changes across the borehole. Hydrate-filled fractures appear as sinusoidal layers with high resistivity, because the fracture intersects the borehole wall at two different depths along the strike orientation. The dip of the fracture ( $\vartheta$ ) can be calculated from the borehole diameter (D) and amplitude of the fracture (A) on the RAB image (Weinberger and Brown 2006):

$$\theta = tan^{-1} \left(\frac{A}{D}\right).$$
 Eq. 28

The propagation resistivity tool records the phase-shift and attenuation resistivity at two frequencies and three source-receiver spacings and has been used to infer information about  $R_{\parallel}$  and  $R_{\perp}$  in the borehole (Ellis and Singer 2007). Fractures are identified in the phase-shift propagation resistivity data from separation between the resistivity curves, caused by increasing resistivity at greater depths of investigation. Greater separation between the propagation resistivity curves indicates more anisotropic conditions, potentially due to the presence of fractures (Cook et al. 2010). This tool is not only used to identify the presence of fractures, but also provides a qualitative assessment of the degree to which anisotropy is affecting the bulk resistivity measurement.

At NGHP Site 01-10A, the infrared scanner identified large amounts of hydrate distributed throughout the well, though none of these occurrences were associated with fractures. The RAB image revealed the presence of hydrate-filled fractures concentrated between 90 – 124 mbsf, with sporadic fractures in other regions of the well (Cook et al. 2010, NGHP Expedition 01 Scientists 2007). The phase-shift propagation resistivity curves (Figure 9; Track 2) show separation in Zones 1, 3, and 4, with concentrated separation in Zone 3. This indicates the presence of resistive fractures in these regions, supports the results from the RAB image, and suggests that Zone 2 can be considered isotropic. Cook, et al. (2010) used a one-dimensional forward fracture model to predict the bulk hydrate saturation at three depths, incorporating the effects of resistivity anisotropy. Two of the saturations predicted from this model correlated well with our Archie-calculated saturations (Figure 9; Track 3), suggesting that Archie's law could be valid in anisotropic conditions (Lee and Collett 2009). These results suggest that the hydrate saturation and salinity we calculated in Zones 2 and 4 accurately represent the in-situ conditions and that, although the conditions at Zones 1 and 3 are affected by anisotropy, the in-situ conditions are well represented using Archie's Law.

#### Limitations on hydrate formation and distribution

Within the regions interpreted to be at three-phase equilibrium, hydrate formation is buffered by the insitu salinity. Salinity increases as hydrate forms until it reaches the value required for three-phase stability, which is controlled by the in-situ pressure and temperature conditions. In the zones interpreted to be at two-phase equilibrium, however, hydrate formation could be limited by an absence of gas or by the presence of carbonate cements.

At NGHP Site 01-10A, the recovered core was also used to identify the presence of carbonate cements (Figure 9; Track 1), which frequently complicates the pore structure and decreases permeability (Lucia 1983). From 0 – 90 mbsf, Zones 1 and 2, core recovery was 64.6 percent and carbonate occurrence was reported in 26.4 percent of the core. Between 90 – 160 mbsf, Zones 3 and 4, core recovery was 67.4 percent with reported carbonate occurrence in 66.1 percent of the core (NGHP Expedition 01 Scientists 2007). The lower hydrate saturations in Zones 3 could be related to the increased presence of carbonate cements. Either the decreased permeability is reducing the gas saturation and limiting hydrate formation, or it is increasing capillary effects, which decrease hydrate stability (Clennell et al. 1999, Liu and Flemings 2011) and the three-phase salinity.

#### Conclusions

We present the in-situ hydrate saturation and salinity at four hydrate-bearing sites, calculated using an iterative application of Archie's Law and a salinity correction. We calculate the salinity required for three-phase equilibrium at the in-situ pressure and temperature using a thermodynamic model. We compare the in-situ salinity to the three-phase salinity at each site to determine the thermodynamic state throughout the GHSZ. We conclude that:

- NGHP Site 01-10A contains thick regions within the GHSZ where the in-situ pressure, temperature, and salinity conditions suggests that the system is at three-phase equilibrium.
- At NGHP Site 01-10A, the propagation resistivity curve indicates that Zone 2, interpreted to be at three-phase equilibrium, is not associated with resistivity anisotropy, suggesting that the use of Archie's Law here accurately calculates water saturation. We believe that this is due to both a lower occurrence of hydrate-filled fractures, as well as a lower discrepancy between the fracture and matrix resistivities within this region.
- Within Zones 3 and 4, at NGHP Site 01-10A, the presence of carbonate cement could be limiting the formation of hydrate and, therefore, the development of elevated in-situ salinities.
- At NGHP Site 01-10A, although there are fractures present, our saturations correlate well with those from pressure cores and forward fracture models, indicating that the Archie parameters used are attributing for some anisotropic effects.

## 1.24 Task 4: Laboratory Evaluation of Hydrate Dissociation

Projected Finish: 3/31/14 Actual Finish: 6/1/14

#### Summary

During this quarter, we have further refined our analysis from our original set of experiments, we have set up for a new experiment, and we have run simulations for this experiment.

Subtask 4.1 - Freezing to 3 phase stability conditions, followed by melting from above

Milestone 1.E Demonstrate ability to create and dissociate methane hydrate within sediment columns under conditions analogous to natural systems.

#### Discussion of 1<sup>st</sup> step experiment:

#### Mass transport during hydrate formation:

More hydrate formed on the left side than the right side of our apparatus. We interpret that hydrate nucleated first on the left hand side (Figure 10a). We interpret that this happened because coolant flowed from left to right, resulting in a slight thermal gradient, and greater subcooling on the left side.

Greater hydrate formation on the left side must have occurred due to transport of water from right to left. Our broad picture is as follows. Hydrate initiation on the left side increased salinity and lowered the gas and water pressure (Figure 10a). This drove water and gas to the left (Figure 10a). Salt diffused down the concentration gradient to the right (Figure 10a). Further hydrate formation was slowed down due to decreased gas permeability and increased difficulty to obtain methane. In addition, the pore size would be smaller in the left due to hydrate growth. Therefore, capillary pressure would be higher in the left, pulling water with lower-than-equilibrium salinity to the left and promoting further hydrate formation there (Figure 10b). This core-scale migration of water induced by capillary pressure has also been observed by Kneafsey et al. (2007) and Rees et al. (2011a) in fresh water systems. Clennell et al. (1999) theoretically discussed the effect of brine migration on hydrate formation. Oswald ripening resulted in continued higher hydration formation on the left and along the central axis of the sample throughout the hydrate formation phase (Figure 10b). At three-phase equilibrium condition, a small salinity gradient would exist toward right side due to slightly higher water pressure (lower capillary pressure) there (Figure 10c). However, the hydrate saturation is high at the interface between the left and right sides, resulting in a significantly reduced salt diffusivity and a negligible salt diffusion toward left (Figure 10c).

#### Geological Application:

This work is broadly motivated by geological observations and theoretical models in gas-rich geological systems, such as gas chimneys at Southern Hydrate Ridge (Milkov et al. 2004, Liu and Flemings 2007), and gas hydrate formation along the conduits of mud volcanos (Clennell et al. 1999, Milkov 2000). Reproduce of the three-phase equilibrium behavior or salinity-buffered hydrate behavior in laboratory provides a fundamental understanding of these systems and an evidence for the theoretical models. In these systems, free gas rapidly enters the gas hydrate stability zone. Gas hydrate forms and increases the in situ salinities. This drives the system to three-phase equilibrium. Further hydrate formation is limited by the rate of salt to leave the system. The three-phase equilibrium creates a gas pathway through the gas hydrate stability zone and can lead to gas venting at sea floor. This concept is fundamentally different from the gas chimneys created by sediment failures due to overpressure (Cathles, Su and Chen 2010) or gas venting at the edge of gas hydrate stability zone along continental slopes (Westbrook et al. 2009).



## (a) First hydrate nucleation

Figure 10: Conceptual model for hydrate nucleation and growth in this experiment. (a) Hydrate nucleated first on the left side sample. This decreased the water and gas pressure significantly there, and pulled gas and water to the left. This also increased salinity in the left and drove salt to diffuse to right. (b) Further hydrate grew across the entire sample. This decreased the pore size and gas permeability, decreasing the rate of hydrate formation. Capillary pressure drew water toward the place with greater hydrate saturation (left side). Oswald ripening resulted in higher hydrate formation on the left and along the central axis of the sample. (c) At three-phase equilibrium, hydrate concentrated in the left and along the central axis of the sample. Slightly higher water pressure resulted in a slight salinity gradient toward right and very slow salt diffusion toward left. S is solid grain. W is water phase. H is hydrate phase. G is gas phase.

## 1.24a Subtask 4.2 - Freezing to L+H condition, warming from above

We are currently embarking on a 2<sup>nd</sup> set of experiments that will be in a 1 meter long core. This experiment will allow us to perform warming from both above and below. Our plans are described under expected outcomes.

## 1.24b Subtask 4.3 - Freezing to L+H condition, warming from below

We prepared the second experimental set-up. This set-up consists of a 2" diameter x 6" long sandpack. Embedded inside the sand pack are two electrodes spaced 4" apart (and 1" from each end of the sand pack) and 5 type-J thermocouples spaced 1" apart beginning at 0.5" from the end of the san pack (Figure 11). At present, there is significant leaking occurring through this instrument string. Attempts have been made to repair the instrument string. Concurrently, we constructed a second instrument string using a low-viscosity epoxy which will fill in the interstitial space of the string, thereby reducing leaks substantially. This second string was constructed at UT and sent to LBNL where it awaits installation.

We are currently embarking on a 2<sup>nd</sup> set of experiments that will be in a 1 meter long core. This experiment will allow us to perform warming from both above and below. Our plans are described under expected outcomes.



Figure 11: Schematic of the experimental setup. T means thermocouples. P means pressure transducers. E means electrodes measuring the bulk resistivity of the sample.

Here is the detailed experimental plan:

- 1) Collect 10 kg dirt sand from natural sediment.
- 2) With temperature and resistivity probe passing through the lower end cap, pack sand 1 cm at a time into a vertically oriented 12.7 cm vessel until it is full. Add 3 tbsp of sand into vessel, pack, and repeat 100 times.
- 3) Insert sample spring and seal vessel (install second end cap).
- 4) Draw vacuum from the bottom of the sample for 10 minutes and then flood the sample with CO<sub>2</sub> from above. Repeat this process a minimum of three times to purge the sample of error.
- 5) After drawing vacuum from the sample a final time, flood the sample with a 7.0 wt.% brine (NaCl) solution.

- 6) Attach a constant flow rate water fluid line at the bottom of the sample, a constant gas pressure fluid line at the top of the sample, and ensure that all pressure sensors, resistivity leads, and thermocouples are acquiring data properly.
- 7) Slowly ramp up pore pressure to 6.89 MPa at the top of the sample at a rate not to exceed 6895 Pa s<sup>-1</sup> (or 1 psi s<sup>-1</sup>). Flood the core from the upper-most pore fluid port.
- 8) Perform system leak test.
- 9) Place vessel onto CT Scanning mount and make initial CT scan of sample. If CT images reveal major density heterogeneities (i.e. clear and obvious layering) repeat steps 1-3. Subtle layers will always exist and are acceptable.
- 10) Cool sample from room temperature (17 °C) to 4 °C homogeneously across the sample (subcooling about 3 °C).
- 11) Pull water from the downstream end of the sample with a rate of 50 g hour<sup>-1</sup> m<sup>-2</sup>. At the same time, keep the gas pressure at the upstream end being 6.94 MPa. Continuously monitor the system temperature, pressure, and resistivity. Collect CT images when desired. Observe the gradual downward moving of hydrate solidification front.
- 12) After system reaches steady state, heat the top of the sample to 10 °C through the heater connected to the upstream end of the sample. Continuously monitor the system temperature, pressure, and resistivity. Collect CT images when desired. Observe the gradual downward moving of hydrate melting front.

## **1.3** What opportunities for training and professional development has the project provided?

There has been strong interaction between UT and LBNL over this past quarter. Our graduate students and our post-doctoral scientist are now fully working with both institutions. A particularly ripe interface is that our students and post-doc are working closely with experimental efforts at LBNL. There is continuous interaction between petroleum engineering and geosciences as we address this problem.

## 1.4 How have the results been disseminated to communities of interest?

Abstract and Paper Submissions

- Bhandari, A., Cronin, M., Polito, P., Flemings, P.B., Bryant, S., 2013, Mass Transport Properties in the Matrix of the Barnett Shale, Abstract submitted to be presented at *2013 Fall Meeting, AGU*, San Francisco, Calif., 9-13 Dec.
- Darnell, K., Flemings, P.B., Bryant, S., 2014, Simulations of seafloor methane venting from warming-induced hydrate destabilization, Abstract submitted to be presented at 8th International Conference on Gas Hydrates Beijing, China, 28 July to 1 August 2014.
- Darnell, K., Flemings, P.B., 2013, Methane hydrate destabilization sensitivity to physical complexity and initial conditions in a numerical model, Abstract submitted to be presented at *2013 Fall Meeting*, AGU, San Francisco, Calif., 9-13 Dec.
- Kneafsey, T., Flemings, P.B., Bryant, S., You, K., Polito, P., 2013, Preliminary Experimental Examination Of Controls On Methane Expulsion During Melting Of Natural Gas Hydrate Systems, Abstract submitted to be presented at *2013 Fall Meeting*, *AGU*, San Francisco, Calif., 9-13 Dec.
- Meyer, D., Flemings, P.B., 2013, Thermodynamic state of hydrate-bearing sediments on continental margins around the world, Abstract submitted to be presented at 2013 Fall Meeting, AGU, San Francisco, Calif., 9-13 Dec.

- Meyer, D., Flemings, P.B., 2014, Thermodynamic State of Hydrate-Bearing Sediments on Continental Margins Around the World, Abstract submitted to be presented at 2014 Offshore Technology Conference, Houston, TX, 5-8 May.
- You, K., Flemings, P.B., Bryant, S., Kneafsey, T., Polito, P., 2014, Methane Hydrate Formation and Dissociation at Three-Phase Equilibrium at Constant Pressure, Abstract submitted to be presented at *8th International Conference on Gas Hydrates*, Beijing, China, 28 July to 1 August 2014.
- You, K., Flemings, P.B., Bryant, S., Kneafsey, T., Polito, P., 2014, Methane Hydrate Formation And Dissociation At Three-Phase Equilibrium At Constant Pressure, Abstract submitted to be presented at *Gordon Research Conference: Natural Gas Hydrate Systems*, Galveston, TX, 23-28 March.
- You, K., Flemings, P.B., Bryant, S., Kneafsey, T., Polito, P., 2014, Salinity-buffered methane hydrate formation and dissociation in gas-rich systems, *Journal of Geophysical Research: Solid Earth*, in review.

## 1.5 What do you plan to do during the next reporting period to accomplish the goals?

## 1.51 Task 5.00: Gas expulsion modeling

Subtask 5.10: Develop 1D model of gas exp. into water-sat. hydrate-stability zone Subtask 5.20: Apply 1D expulsion to laboratory experiments

We have developed the model for laboratory experiments and plan to summarize in the next Quarterly report. If our experiment is finished by the end of the period, we will appy the model to the real experimental data.

Subtask 5.30: Apply 1D model to natural hydrate accumulations

We are revising the 1D model to include the ice phase and are going to apply the revised model to natural hydrate accumulations underlying permafrost. Will produce a map of the arctic showing the requirements necessary for transient venting. Will continue work on the manuscript to be submitted to Geophysical Research Letters on the topic of transient venting from marine deposits.

## 1.52 Task 6.00: Gas expulsion experiments

Subtask 6.10: Gas invasion into water-saturated hydrate saturated zone Subtask 6.20: Gas invasion from melting hydrate into water saturated HSZ

We will build resistivity and temperature sensing components to be used in experiments under that fall under Task 6.0. If need be, staff will travel to LBNL and assist in the installation, testing, and calibration of the components as well as supply technical expertise in the design and running of Task 6.0 experiments.

## 1.53 Task 7.00: 2D model

Subtask 7.10: Hydrate dissociation in 2D systems Subtask 7.20: Gas expulsion in 2D systems Subtask 7.30: Apply 2D, gas expulsion model to natural examples Subtask 7.31: Pleistocene to Holocene Sea level rise Subtask 7.32: Recent warming

## 2 **PRODUCTS**:

#### 2.1 What has the project produced?

We have now produced a one dimensional, coupled; hydrate formation code that simulates the thermochemical response of a hydrate system to perturbation. We have demonstrated three-phase stability through experimental analysis and we have modeled the behavior. We have also characterized the insitu thermodynamic state of a number of hydrate locations around the world and shown that in at least two locations, local thermodynamic conditions are altered by high salinity.

## **3 PARTICIPANTS & OTHER COLLABORATING ORGANIZATIONS:**

### 3.1 What individuals have worked on the project?

Provide the following information for: (1) principal investigator(s)/project director(s) (PIs/PDs); and (2) each person who has worked at least one person month per year on the project during the reporting period, regardless of the source of compensation (a person month equals approximately 160 hours of effort).

Name	Peter Flemings	Steve Bryant	Tim Kneafsey	Dylan Meyer	Ebrahim
					Roasromani
Project Role	Principal	Co-Principal	Co-Principal	Graduate	Graduate
	Investigator	Investigator	Investigator	Student	Student
Nearest person	.25	.25	1.25	1	1
month worked					
Contribution	Advised graduate student Meyer, managed project, and recruited students. Worked with technicians for thermistor development.	Advised graduate student Meyer on analysis of models of pore space alteration due to hydrate growth and its effect on saturation exponent.	Set up experiment, ran tests, and analyzed data.	Performed analysis of thermodynamic state of 4 locations.	Performed analysis of data.
Funding Support	The University of Texas	The University of Texas	Lawrence Berkeley National Lab	JSG Fellowship	The University of Texas
Collaborated with individual in foreign country	No	No	No	No	No

Name	Peter Polito	Kris Darnell	Kehua You	Tessa Green
Project Role	Laboratory	Graduate	Post Doc	Project
	Manager	Student		Coordinator
Nearest person	1.5	1	3	1
month worked				

Contribution	Participated in conference calls on experimental design. Ran experimental tests.	Performed literature review and theoretical calculation to prepare for laboratory	Performed literature review and theoretical calculation to prepare for	Coordinate meeting logistics, archive documents, and manage	
		experiments	laboratory	financials.	
Eunding Support	The University of	The University of	The University	The University	
Funding Support	Tawaa	The University of	of Towns	of Toward	
	Texas	Texas	or rexas	or rexas	
Collaborated	No	No	No	No	
with individual					
in foreign					
country					

## 3.2 What other organizations have been involved as partners?

Organization Name: Lawrence Berkeley National Lab Location of Organization: Berkeley, CA

Partner's contribution to the project (identify one or more)

- In-kind support: partner makes lab space and equipment available for experiments. (e.g., partner makes software, computers, equipment, etc., available to project staff);
- Facilities: Experiments are performed in partner's lab space using equipment largely supplied by the partner (e.g., project staff use the partner's facilities for project activities);
- Collaborative research: Partner collaborates with the project staff. (e.g., partner's staff work with project staff on the project); and

## 3.3 Have other collaborators or contacts been involved?

No

## 4 IMPACT:

## 4.1 What is the impact on the development of the principal discipline(s) of the project?

Geological models of gas transport and hydrate melting and solidification have suggested that free gas cannot migrate through the hydrate stability zone during melting. In contrast, we suggest that free gas can migrate through the hydrate stability zone by altering the conditions of hydrate stability to a state of three-phase equilibrium through the elevation of salinity and possibly temperature. This results in fundamentally different macro-scale behavior during melting and may result in greater gas venting than has been previously demonstrated. If this hypothesis is correct, it may engender a new generation of field and laboratory investigations to document this behavior in both the field of geosciences and petroleum engineering. Second, the project links theoretical development with laboratory modeling because the concepts can be applied at the laboratory scale as well as the field scale. The laboratory experiments to be conducted will enable validation of the mechanisms incorporated in the models. These laboratory experiments will play a key role in demonstrating the processes.

## 4.2 What is the impact on other disciplines?

A likely outcome of our work is a more quantitative prediction of the magnitude of methane flux from the earth to the atmosphere over human (decadal) timescales and geological timescales (10,000 years). These will serve as boundary conditions for atmospheric climate models. In turn, these results may guide policy decisions.

## 4.3 What is the impact on the development of human resources?

We are working at the interface of geosciences and engineering. We are coupling theory and laboratory experiments to address macro-scale geologic problems. This is training a new generation of geoscientists and engineers to think with a systems-based approach that links observation with theory.

The results are being applied in the classroom and the support is training several graduate students.

## 4.4 What is the impact on physical, institutional, and information resources that form infrastructure?

The project is strengthening the experimental efforts and capability at UT as it is our job to develop sensor equipment. The project is strengthening development at LBNL where primary experimental work is occurring.

### 4.5 What is the impact on technology transfer?

We are presenting our research to approximately 100 industry members at our GeoFluids consortium and we will be presenting at a range of national and international meetings. We will also present our results at the upcoming OTC conference in Spring 2014.

## 4.6 What is the impact on society beyond science and technology?

A likely outcome of our work is a more quantitative prediction of the magnitude of methane flux from the earth to the atmosphere over human (decadal) timescales and geological timescales (10,000 years). These will serve as boundary conditions for atmospheric climate models. In turn, these results may guide policy decisions.

## 4.7 What dollar amount of the award's budget is being spent in foreign country(ies)?

Zero percent of the award's budget is being spent in foreign countries.

## **5 CHANGES/PROBLEMS:**

## 5.1 Changes in approach and reasons for change

There are no changes in approach to report for this reporting period.

## 5.2 Actual or anticipated problems or delays and actions or plans to resolve them

No problems or delays to report for this reporting period.

#### 5.3 Changes that have a significant impact on expenditures

No changes in approach to report for this reporting period.

## 5.4 Significant changes in use or care of human subjects, vertebrate animals, and/or Biohazards

Nothing to report

## 5.5 Change of primary performance site location from that originally proposed

Nothing to report

#### **6 BUDGETARY INFORMATION:**

				Budge	t Period 1			
	D	,1	Q	2	0	33	0	14
Baseline Reporting (10/1/12 - 6/30/13)	10/1/12	- 2/15/13	2/16/13-6	/30/2013	7/1/2013-	11/15/2013	11/16/2013	3-3/31/2014
		Cumulative		Cumulative				
	Q1	Total	Q2	Total	Q3	<b>Cumulative Total</b>	Q4	<b>Cumulative Total</b>
Baseline Cost Plan								
Federal Share	\$ 136,111.50	\$ 136,111.50	\$ 175,000.50	\$ 311,112.00	\$ 175,000.50	\$ 486,112.50	\$ 175,000.50	\$ 661,113.00
Non-Federal Share	\$ 43,568.75	\$ 43,568.75	\$ 43,568.75	\$ 87,137.50	\$ 43,568.75	\$ 130,706.25	\$ 43,568.75	\$ 174,275.00
Total Planned	\$ 179,680.25	\$ 179,680.25	\$ 218,569.25	\$ 398,249.50	\$ 218,569.25	\$ 616,818.75	\$ 218,569.25	\$ 835,388.00
Actual Incurred Cost								
Federal Share	\$ 45,506.00	\$ 45,506.00	\$ 67,607.00	\$ 113,113.00	\$ 258,059.00	\$ 371,172.00	\$ 137,004.00	\$ 508,176.00
Non-Federal Share	- \$	\$ -	\$ 81,202.43	\$ 81,202.43	\$ 26,527.09	\$ 107,729.52	\$ 10,775.81	\$ 118,505.33
Total Incurred Cost	\$ 45,506.00	\$ 45,506.00	\$ 148,809.43	\$ 194,315.43	\$ 284,586.09	\$ 478,901.52	\$ 147,779.81	\$ 626,681.33
Variance								
Federal Share	\$ (90,605.50)	\$ (90,605.50)	\$ (107,393.50)	\$ (197,999.00)	\$ 83,058.50	\$ (114,940.50)	\$ (37,996.50)	\$ (152,937.00)
Non-Federal Share	\$ (43,568.75)	\$ (43,568.75)	\$ 37,633.68	\$ (5,935.07)	\$ (17,041.66)	\$ (22,976.73)	\$ (32,792.94)	\$ (55,769.67)
Total Variances	\$ (134,174.25)	\$ (134,174.25)	\$ (69,759.82)	\$ (203,934.07)	\$ 66,016.84	\$ (137,917.23)	\$ (70,789.44)	\$ (208,706.67)
				Budge	t Period 2			
	Ω	1	Q	2		23	0	14
	4/1/2014-	8/15/2014	8/16/2014-:	12/31/2014	1/1/2015	-5/15/2015	5/16/2015	-9/30/2015
	2	Cumulative	8	Cumulative	2	) - - - -		- : :
	Ļ	וטנמו	ş	IVIAI	Ę		Ļ.	
Baseline Cost Plan								
Federal Share	\$ 127,422.00	\$ 661,113.00	\$ 127,422.00	\$ 788,535.00	\$ 127,422.00	\$ 915,957.00	\$ 127,422.00	\$ 1,043,379.00
Non-Federal Share	\$ 34,048.50	\$ 174,275.00	\$ 34,048.50	\$ 208,323.50	\$ 34,048.50	\$ 242,372.00	\$ 34,048.50	\$ 276,420.50
Total Planned	\$ 161,470.50	\$ 835,388.00	\$ 161,470.50	\$ 996,858.50	\$ 161,470.50	\$ 1,158,329.00	\$ 161,470.50	\$ 1,319,799.50
Actual Incurred Cost								
Federal Share	\$ '	\$ 508,176.00	\$ -	\$ 508,176.00	\$ -	\$ 508,176.00	\$ -	\$ 508,176.00
Non-Federal Share	\$ -	\$ 118,505.33	\$ -	\$ 118,505.33	\$ -	\$ 118,505.33	\$ -	\$ 118,505.33
Total Incurred Cost	- Ş	\$ 626,681.33	, Ş	\$ 626,681.33	÷	\$ 626,681.33	÷	\$ 626,681.33
Variance								
Federal Share	\$ (127,422.00)	\$ (152,937.00)	\$ (127,422.00)	\$ (280,359.00)	\$ (127,422.00)	\$ (407,781.00)	\$(127,422.00)	\$ (535,203.00)
Non-Federal Share	\$ (34,048.50)	\$ (55,769.67)	\$ (34,048.50)	\$ (89,818.17)	\$ (34,048.50)	\$ (123,866.67)	\$ (34,048.50)	\$ (157,915.17)
Total Variances	\$ (161,470.50)	\$ (208,706.67)	\$(161,470.50)	\$(370,177.17)	\$ (161,470.50)	\$ (531,647.67)	\$(161,470.50)	\$ (693,118.17)

## 7 References

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#### 8 Nomenclatures

G	Free gas phase
Н	Hydrate phase
L	Liquid phase
и	Pore pressure (MPa)
$ ho_{\scriptscriptstyle SW}$	Seawater Density $(g/cm^3)$
$ ho_{pw}$	Pore water density $(g/cm^3)$
$ ho_f$	Fluid density $(g/cm^3)$
$ ho_b$	Bulk density (g/cm <sup>3</sup> )
$\rho_m$	Grain density (g/cm <sup>3</sup> )
$Z_{wd}$	Water depth (m)
$\Delta Z$	Depth within the GHSZ (m)
Ζ	GHSZ thickness (m)
g	Gravitational acceleration $(m/s^2)$
$T_f$	Formation temperature (°C)
$T_b$	Seafloor temperature (°C)
$G_g$	Geothermal gradient (°C/km)
$S_h$	Hydrate saturation (dimensionless)
$S_w$	Water saturation (dimensionless)
$C_{in-situ}$	In-situ salinity (dimensionless)
$C_0$	Core-derived salinity (dimensionless)
С	Salinity (dimensionless)
Ν	Saturation exponent (dimensionless)
a	Tortuosity coefficient (dimensionless)
т	Cementation exponent (dimensionless)
n	Porosity (dimensionless)
$ ho_w$	Fluid resistivity (Ωm)
$\rho_t$	Formation resistivity ( $\Omega m$ )
F	Formation factor (dimensionless)
Analytical model	
$M_m$	molar weight of methane (kg mol <sup>-1</sup> )

$M_m$	molar weight of methane (kg mol <sup>-1</sup> )
$M_w$	molar weight of water (kg mol <sup>-1</sup> )
$M_h$	molar weight of hydrate (kg mol <sup>-1</sup> )
$m_{g,f}^m$	methane mass in the final gas phase (kg)
$m_{h,f}^m$	methane mass in the final hydrate phase (kg)
$m^m_{w,f}$	methane mass in the final water phase (kg)
$m_{g,i}^m$	methane mass in the initial gas phase (kg)
$m_{w,i}^m$	methane mass in the initial water phase (kg)
Ν	stoichiometric hydration number (dimensionless)
P <sub>f</sub>	final pressure (Pa)
$P_i$	initial pressure (Pa)
$T_f$	final temperature (K)
$T_i$	initial temperature (K)
S <sub>g,i</sub>	initial gas saturation (dimensionless)

S <sub>a,f</sub>	final gas saturation (dimensionless)
S <sub>h,f</sub>	maximum hydrate saturation (dimensionless)
S <sub>w,i</sub>	initial water saturation (dimensionless)
S <sub>w,f</sub>	final water saturation (dimensionless)
$V_{\rm tot}$	total volume of the sediment (m <sup>3</sup> )
$X^{m}_{w,f}$	final solubility of methane in water (wt.%)
X <sup>m</sup> <sub>w,i</sub>	initial solubility of methane in water (wt.%)
X <sup>s</sup> <sub>w,i</sub>	initial mass fraction of salt in brine (wt.%)
$X^{s}_{w,f}$	final mass fraction of salt in brine (wt.%)
$ ho_{\scriptscriptstyle w,f}$	initial brine density (kg m <sup>-3</sup> )
$ ho_{\scriptscriptstyle w,i}$	final brine density (kg $m^{-3}$ )
$ ho_{g,i}$	initial gas density (kg m <sup>-3</sup> )
$ ho_{g,f}$	final gas density (kg m <sup>-3</sup> )
$ ho_h$	methane hydrate density (kg m <sup>-3</sup> )
$\phi$	porosity of the sediment (dimensionless)
$\Delta m$	mass of methane gas consumed during hydrate formation (kg)

#### Numerical model

β	phase
е	energy component
g	gas phase
h	hydrate phase
K	component
Ι	liquid phase
т	methane component
S	salt component
V	vapor phase
W	water component
$C_R$	heat capacity of the solid grain (J kg <sup>-1</sup> oC <sup>-1</sup> )
$D_{l0}^{\kappa}$	molecular diffusion coefficient of component k in free water (m <sup>2</sup> s <sup>-1</sup> )
$\phi$	porosity of the sediment (dimensionless)
$\phi_0$	porosity in the absence of hydrate (dimensionless)
g	acceleration due to gravity (m $s^{-2}$ )
$h_{eta}$	specific enthalpy of phase $eta$ (J kg $^{-1}$ )
k	intrinsic permeability (m <sup>2</sup> )
<i>k</i> <sub>0</sub>	permeability in the absence of hydrate (m <sup>2</sup> )
$k_{r\beta}$	relative permeability of phase $eta$ (dimensionless)
λ	overall thermal conductivity of porous media (W m <sup>-1</sup> °C <sup>-1</sup> )
$\lambda_eta$	thermal conductivity of phase $\beta$ (W m <sup>-1 o</sup> C <sup>-1</sup> )
$\lambda_{R}$	thermal conductivity of grain (W $m^{-1} {}^{o}C^{-1}$ )
$\mu_{eta}$	viscosity of phase $eta$ (Pa s)
P <sub>c</sub>	capillary pressure (Pa)
<i>P</i> <sub>c0</sub>	capillary pressure in the absence of hydrate (Pa)

$P_{\beta}$	eta phase pressure (Pa)
$q^e$ $q^{\kappa}$	generation rate of energy (J m <sup>-3</sup> s <sup>-1</sup> ) generation rate of component $\kappa$ (kg m <sup>-3</sup> s <sup>-1</sup> )
$ ho_eta$	density of phase $eta$ (kg m <sup>-3</sup> )
$S_{\beta}$	saturation of phase $eta$ (dimensionless)
Т	temperature (°C)
t	time (s)
$u_{\beta}$	specific internal energy of phase $eta$ (J kg $^{-1}$ )
$X^{k}_{\beta}$	mass fraction of component $\kappa$ in phase $eta$ (dimensionless)

## National Energy Technology Laboratory

626 Cochrans Mill Road P.O. Box 10940 Pittsburgh, PA 15236-0940

3610 Collins Ferry Road P.O. Box 880 Morgantown, WV 26507-0880

13131 Dairy Ashford Road, Suite 225 Sugar Land, TX 77478

1450 Queen Avenue SW Albany, OR 97321-2198

Arctic Energy Office 420 L Street, Suite 305 Anchorage, AK 99501

Visit the NETL website at: www.netl.doe.gov

Customer Service Line: 1-800-553-7681

