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Mechanisms Leading to Co-Existence of Gas and Hydrate in Ocean Sediments

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MECHANISMS LEADING TO CO-EXISTENCE OF GAS AND HYDRATE IN OCEAN SEDIMENTS

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QUARTERLY PROGRESS REPORT
Reporting Period: 1 Oct 09 – 31 Dec 09

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Summary

Work during this period has focused on two areas:

(1) Extension of our grain-scale model of hydrate formation to account for fragile hydrate films at the gas-water interface
(2) Development of one-dimensional geologic bed-scale models of the conversion of methane to hydrate.

During this reporting period, we presented two papers at the SPE ATCE, one presentation and two posters at AGU, and an article in the Fire in the Ice Newsletter[1].

Our progress on the grain-scale model has allowed us to incorporate the potential instability of hydrate layers that form and grow at the gas-water interface. Such instabilities lead to rupture of the hydrate film, and subsequent imbibition events. The consequence of hydrate film rupture is that it accelerates the process of conversion to hydrate, since it removes the slow kinetic mass transfer across the hydrate layer (which thickens and becomes less porous with time). In current work, in collaboration with I-Ming Chou at USGS-Reston, we are trying to determine whether our model of film rupture is supported by experiments.

Our progress on the development of simplified bed-scale models has followed two tracks, consistent with the mechanisms learned during our work at the grain scale: (1) capillary dominated migration; (2) fracture-dominated migration.

For capillary-dominated migration, we present a simple 1D model for conversion to hydrate of an initial gas column that completely fills several sediment layers. Hydrate formation creates a void that causes gas to migrate vertically within the column. As the gas-water contact rises at the base of the column, sedimentological variation can cause the gas column to lose vertical communication. In contrast, the water phase is always connected to the water reservoir. Consequently the model predicts a nonuniform hydrate saturation even when the initial gas saturation is uniform. The vacancy caused by hydrate formation need not be filled only by free gas. Allowing both water and gas to invade yields a hydrate saturation profile in better agreement with field observations. The hydrate saturation from model prediction has a reasonable match with observations at Mt.

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[1] Peng, Y., Prodanović, M., and Bryant, S. "Improving Fidelity of Network Models for Drainage and Imbibition," SPE 124440, Proceedings of the 2009 SPE Annual Technical Conference and Exhibition held in New Orleans, Louisiana, USA, 4–7 October 2009.

Prodanović, M., Holder, J. and Bryant, S. "Coupling Capillarity-Controlled Fluid Displacement With Unconsolidated Sediment Mechanics: Grain Scale Fracture Opening," SPE 124717, Proceedings of the 2009 SPE Annual Technical Conference and Exhibition held in New Orleans, Louisiana, USA, 4–7 October 2009.

Peng, Y., Behseresht, J., Bryant, S. and Winters, W. "Sedimentological Control on Arctic Gas-Hydrate-Bearing Deposits," poster GC51A-0707, American Geophysical Union Fall Meeting, San Francisco, 14-18 Dec. 2009.

Holtzman, R., Juanes, R. “Hydrate Formation in Gas-Rich Marine Sediments: A Grain-Scale Model,” oral presentation, Abstract OS41A-08, American Geophysical Union Fall Meeting, San Francisco, 14-18 Dec. 2009.

Juanes, R., Bryant, S. “Models Provide Clues to How Methane Gas and Hydrate Coexist in Nature”, Fire in the Ice Newsletter, December 2009.

Elbert. In particular, a coarse-grained layer is correctly predicted to be only partially filled with large hydrate saturation.

For fracture-dominated migration, we present a conceptual model and some preliminary results that are based on the idea of gas transport through fractures in fine-grained sediments. Fractures open up and serve as conduits for vertical gas migration as a result of changes in the hydrostatic pressure at the top of the sediment column. The model has only a handful of parameters, and our preliminary results correlate very well with data of methane venting from Upper Mystic Lake, MA.

Activities in This Reporting Period

7.2 Coupled dynamics with fragile hydrate films: grain-scale model

Here, we report on investigations of the mode of hydrate growth in gas-rich sediment and the consequent distribution of the different methane phases in the pore space. We simulate the formation of a hydrate rind across the gas-water interface, highlighting the effect of mechanical instabilities of the shell as an essential mechanism for further growth. A grain-scale model based on recent experimental observations that suggest that mass transfer limitations control the growth of hydrate from free gas, has been introduced in the former report. Here, we present results from additional simulations and discuss the implications of these results regarding the distribution and saturation of hydrate and the sediment properties.

The simulations of hydrate growth begin from the drainage endpoint (Fig. 1). The three-dimensional model coupling two-phase flow and mechanical deformation introduced in former reports provides these initial conditions in the form of a detailed spatial description of the gas-water interface. We then simulate the growth of a thin hydrate film across the interface. Assuming a disconnected gas blob with fixed number of CH_4 moles, we estimate the gas pressure as methane diffuses across the interface and converts to hydrate, increasing the film's thickness. We use the ideal gas law to relate the conversion of gas to hydrate to the gas pressure drop. At every time step, we evaluate the mechanical stability of the shell at each pore, using linear-elastic buckling analysis of a spherical thin shell. The assumed mode of failure is implosion of the shell inwards, due to the reduction in gas pressure relative to the water pressure. Upon rupture of the film at a particular pore, we simulate the imbibition of water through the ruptured film. Imbibition stops when the pressure of the gas, which is now compressed into a smaller volume, suffices to resist further water flow.

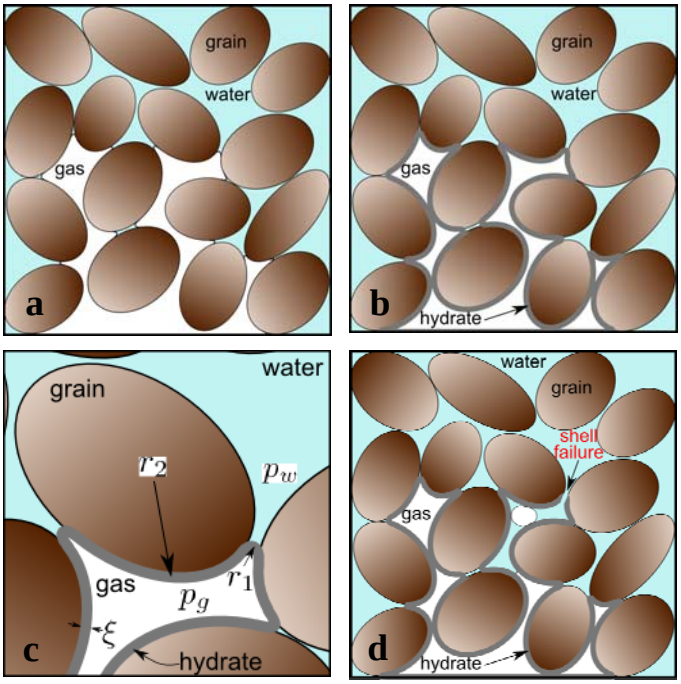


Figure 1: Schematic of hydrate growth mechanism. The starting point for the simulations is the gas-water interface location (pore occupancy at drainage endpoint) from the drainage simulations (a). A thin hydrate film grows across the interface (b). By evaluating the drop in gas pressure as it converts to hydrate, increasing the film's width, we determine the mechanical stability of the film in each pore, using linear-elastic buckling analysis (c). Upon rupture of the hydrate film, water imbibes, regaining connectivity with the gas and forming new gas-water interfaces (d). This enhances the $CH_{4(g)} \rightarrow CH_{4(aq)}$ conversion rate, which otherwise vanishes quickly due to mass-transfer limitations. Additional consequence of imbibition is trapping of gas bubbles, reducing the connectivity of the gas body.

The invasion pattern at the percolation threshold and the distribution of the hydrate throats are shown in Fig. 2. These simulations were performed on two samples containing about 14,300 grains, with average grain size of 100 and 0.1µm, hereafter referred to as coarse- and find-grained. In the coarse-grained sample, the large pore sizes lead to multiple rupture-imbibition-growth cycles, increasing the number of pore throats containing a hydrate film from ~2,600 right after the drainage endpoint to ~4,100. On the other hand, the hydrate film (formed in ~900 throats) in the fine-grained sample remains intact, and the conversion of the gas-filled fracture into hydrate stops quickly. The hydrate shell acts to preserve the gas in its own phase, and the gas body remains connected.

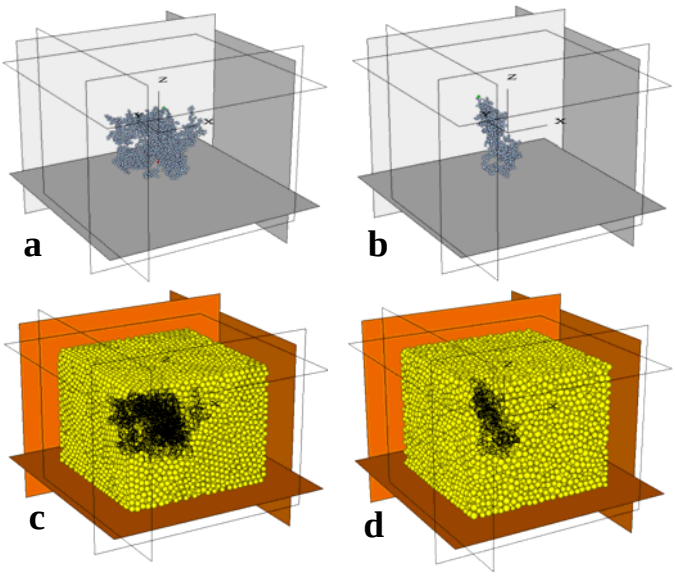


Figure 2: Results of simulations of drainage followed by hydrate growth along the gas-water interface in coarse- and fine-grained sediment. Top row: invasion pattern (grey=drained pores, solid grains and undrained pores not shown) at the drainage endpoint in the coarse-grained (a) and fine-grained (b) samples, with saturations of 17 and 4% and percolation pressures of 4.4KPa and 3.5MPa, respectively. Bottom row: hydrate film (black line represents a hydrate across a pore throat) formed within the coarse-grained (c) and fine-grained (d) sediment (yellow spheres = sediment grains), with about 4,100 and 900 throats coated by hydrate, respectively.

The effect of rupture and imbibition is two-fold: (a) overcoming the mass-balance limitation associated with diffusion across the increasingly thick and dense hydrate film [Taylor *et al*., 2007] by creating new gas-water interfaces; and (b) trapping of gas bubbles by snap-off, reducing the connectivity of gas. Thus, in coarse-grained sediment the rate of gas conversion and hydrate formation will remain high, while in fine-grained media the growth rate will diminish as the hydrate layer thickens. The fate of the gas-filled fracture will depend on the boundary conditions indicated by the geologic settings: if gas is recharged, the well-connected (thus with high relative permeability) gas body could traverse the sediment, eventually making its way to the water column. If, on the other hand, the gas remains trapped in the fracture for longer periods with no further recharge, it will eventually convert entirely into hydrate, forming the vein-filling hydrate deposits which are frequently-encountered in fine-grained layers [Abegg *et al*., 2008; Obzhirov *et al*., 2009]. The insights gained from our grain-scale model could be used to explain the correlation between hydrate saturation and fraction of coarse-grains in the sediment [Torres *et al*., 2008]. Finally, experimental investigation of the mechanisms involved in hydrate growth from gas bubbles, in particular the fate of the hydrate rind formed at the gas-water interface, is the subject of our current efforts. Identifying the mode of mechanical instability that allows rapid conversion of gas to hydrate is a necessary step towards a comprehensive understanding of the dynamics of hydrate-bearing sediments.

Bibliography

Abegg, F., Bohrmann, G., Freitag, J., and Kuhs, W. (2007). Fabric of gas hydrate in sediments from Hydrate Ridge—results from ODP Leg 204 samples Geo-Mar. Lett., 27:269–277.

Obzhirov, A. (2009). Methane Fluxes and Gas Hydrates in the Sea Of Okhotsk. Fire in the Ice, Spring 2009, NETL.

Taylor, C.J., Miller, K.T., Koh, C.A,. and Sloan, E.D. (2007). Macroscopic investigation of hydrate film growth at the hydrocarbon/water interface. Chem. Eng. Sci., 62: 6524–6533.

Torres, M.E., Wallman, K., Trehu , A.M., Bohrmann, G., Borowski, W.S., and Tomaru, H. (2004). Methane hydrate formation in turbidite sediments of northern Cascadia, IODP Expedition 311. Earth Planet. Sci. Lett., 226:225– 241.

Task 8.0 - Modeling methane transport at the bed scale

Capillary-Dominated Migration Model

Conceptual Model

The preferential accumulation of gas hydrate in coarse-grained rather than fine-grained layers of sediment is well known. But observations of hydrate that only partially fills coarse-grained layers require further explanation. We argue that this type of hydrate occurrence is consistent with the establishment of a gas phase saturation within the sediment when the base of gas hydrate stability zone (BGHSZ) was located above the sediment package. Gas is presumed to have migrated from a source below, and is trapped below sedimentological seals (i.e. layers with smaller grain size) (Figure 1).

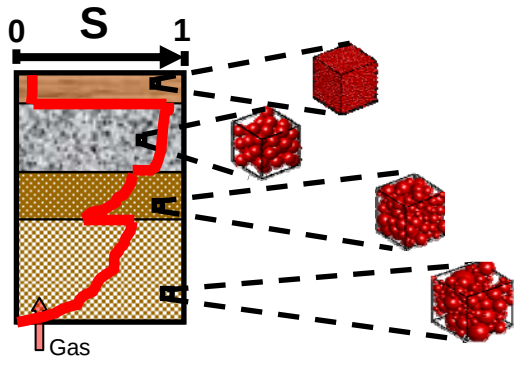


Figure 1. Rising gas accumulates below the finest-grained formation (the seal at top of package) at saturations that vary with grain size distribution.

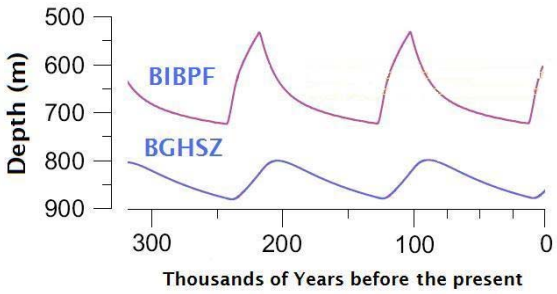


Figure 2. BGHSZ (base of gas hydrate stability zone) and BIBPF (base of ice-bearing permafrost) cycle with geological time.

The accumulated gas saturation is converted to hydrate as the BGHSZ moves down through the gas accumulation. Subsequently hydrate dissociates if the BGHSZ moves upwards, leaving the gas bearing region out of HSZ. Cycles of hydrate formation and dissociation would take place during geological time with BGHSZ ascending and descending periodically (Figure 2).

Here we focus on the case in which BGHSZ descends after gas column is formed. We develop a simple quantitative model and compute the saturation of gas hydrate as a function of depth. Such model accounts for the volume change from two phase system (CH4+H2O) to three phase system (CH4+H2O+methane hydrate), as well as the vertical transportation of methane. We validate this model with data from the Mt. Elbert well on the Alaskan North Slope.

Volume Changes Associated with Equilibration of the CH4-H2O-Methane Hydrate system

First we review the results reported previously on the volume change accompanying hydrate formation. We use a simple box model to account for the volume change as hydrate forms. The box (with a volume V0) is originally filled only by methane and water (Figure 3a). Hydrate forms at the fluid/fluid interface (Figure 3b). We assume T and P do not change during hydrate formation. Thus gas and water phases have constant density, and hydrate formation therefore causes a volume change. The volume change can cause two phenomena: (1) sediment grains rearrange their positions, and (2) fluid phases leave/enter as needed to maintain pressure. Here we do not consider the grain rearrangement. The system volume change is computed for two scenarios: when gas is stoichiometrically limiting (excess water), and vice versa (excess gas).

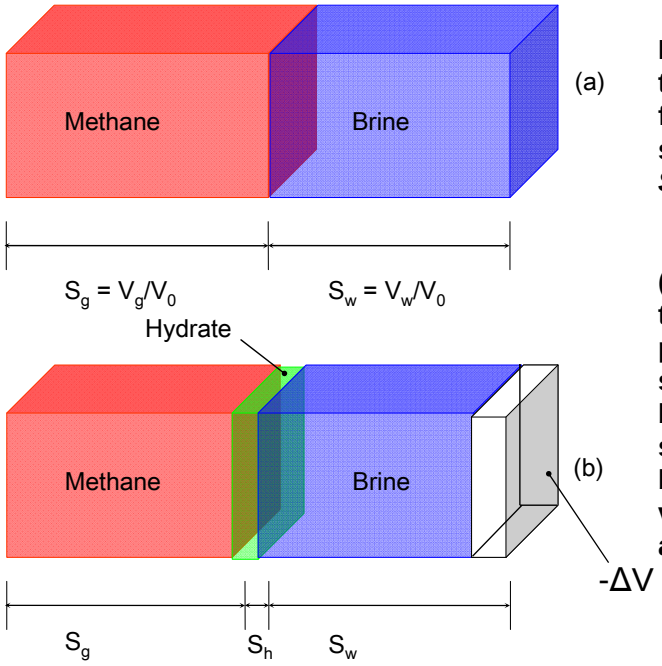


Figure 3. The box model to compute the volume change due to hydrate formation. (a) The initial gas/water saturations are fixed, and $S_w = 1 - S_g$. No hydrate is present initially.

(b) An increment of hydrate forms at the interface between gas and water phases. Hydrate formation results in system volume reduction, as shown by the blank box at the right hand side of brine. Such reduction is because the hydrate occupies less volume than the converted water and gas.

Scenario 1: Limited Methane/Water

In this scenario, the amounts of methane and water are limited to the initial values, and no fluid enters or leaves the system. The volume change is computed when water (Eq. 1) or methane (Eq. 2) is in stoichiometric excess.

Excess water:
$$\frac{\Delta V}{V} = S_g \left(\frac{\rho_g}{\rho_h} \frac{M_g + NM_w}{M_g} - \left(1 + \frac{\rho_g}{\rho_w} \frac{NM_w}{M_g} \right) \right) \quad (1)$$

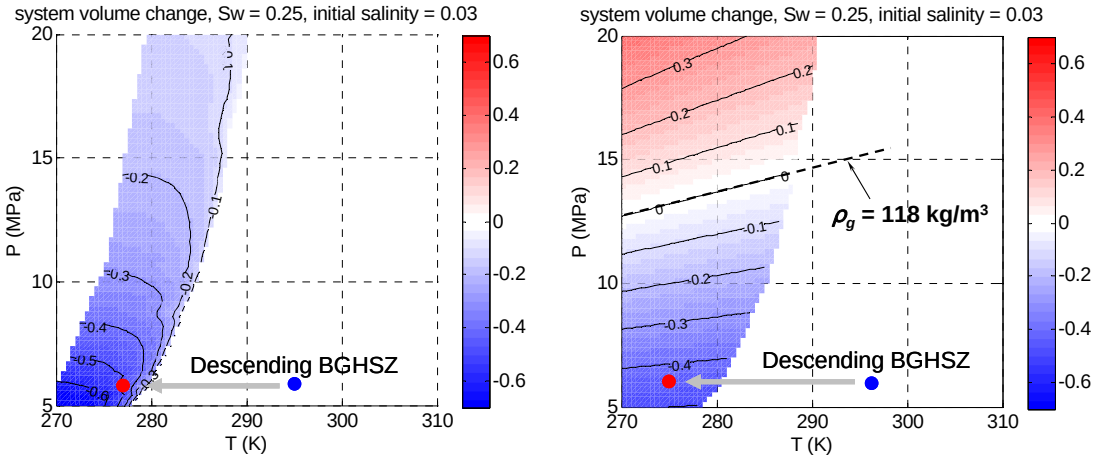
Excess gas:
$$\frac{\Delta V}{V} = S_w \left(1 - \frac{Sal}{MSal} \right) \left(1 + \frac{u}{V_w \rho_w} \right) \times \left(\frac{\rho_w}{\rho_h} \frac{M_g + NM_w}{NM_w} - \left(1 + \frac{\rho_w}{\rho_g} \frac{M_g}{NM_w} \right) \right) \quad (2)$$

Scenario 2: Limited Methane and Unlimited Water

Methane is limited to the amount initially present, but water can be supplied from outside the system, and is always in stoichiometric excess. We assume the salt ion dissipation speed is much greater than hydrate formation speed, so that salt will not accumulate to inhibit the hydrate formation.

$$\frac{\Delta V}{V} = S_g \left(\frac{\rho_g}{\rho_h} \frac{M_g + NM_w}{M_g} - 1 \right) \quad (3)$$

The volume change predicted by the box model for these two scenarios is shown in Figure 4 for a range of temperature and pressure and an initial S_w of 0.25. The volume change is positive in scenario 2 wherever (T, P) yield gas densities greater than 118 kg/m^3.



Scenario 1. limited methane and water **Scenario 2. limited methane and unlimited water**

Figure 4. Fractional volume changes accompanying hydrate formation computed from Eqs (1) and (2) for a range of *T* and *P*. The initial gas accumulation below BGHSZ is at conditions corresponding to the blue dot. When BGHSZ descends, temperature decreases (pressure remains constant), and the region moves from blue to red dot. Hydrate will form once temperature and pressure are inside HSZ.

Conversion of Gas Accumulation to Hydrate

The diagrams in Figure 5 show how a void forms when the BGHSZ moves incrementally down into an accumulation of gas ($S_g = 1 - S_{w,irr}$). The volume change will depend on the temperature and pressure of the formation. In this diagram, the gas accumulation is assumed to be disconnected from the original source and from other, lower accumulations.

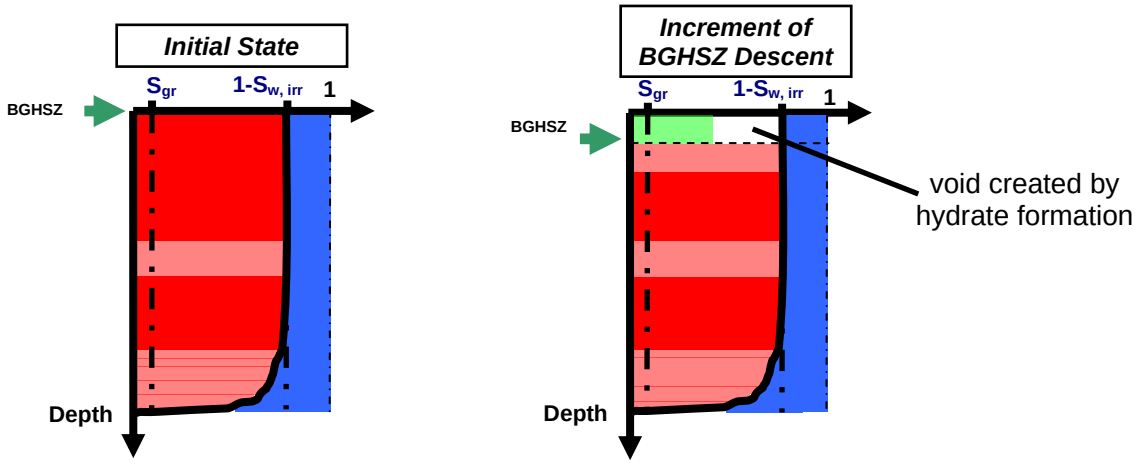


Figure 5. (L) Gas accumulation (pink) established below a seal, and base of gas hydrate stability zone (BGHSZ) has descended to the top of the accumulation. (R) When the BGHSZ falls an incremental distance into the accumulation, the conversion of existing gas to hydrate (green) leaves a void (white). This void must be filled by other fluids or by grain rearrangement to reduce porosity.

The void will be filled in one of two ways: either the grains of the sediment will re-arrange to reduce the porosity, or fluids (gas and/or water phases) will flow into that part of the sediment. For deep sediments that have already undergone compaction, only the movement of fluids is likely to make a significant contribution to void filling. We consider three cases: all the void is filled by gas rising from lower parts of the accumulation; all the void is filled by water imbibing into the region from above or from below; the void is filled partly by gas and partly by water. Figure 6 shows the result of the continued descent of the BGHSZ for each of these cases.

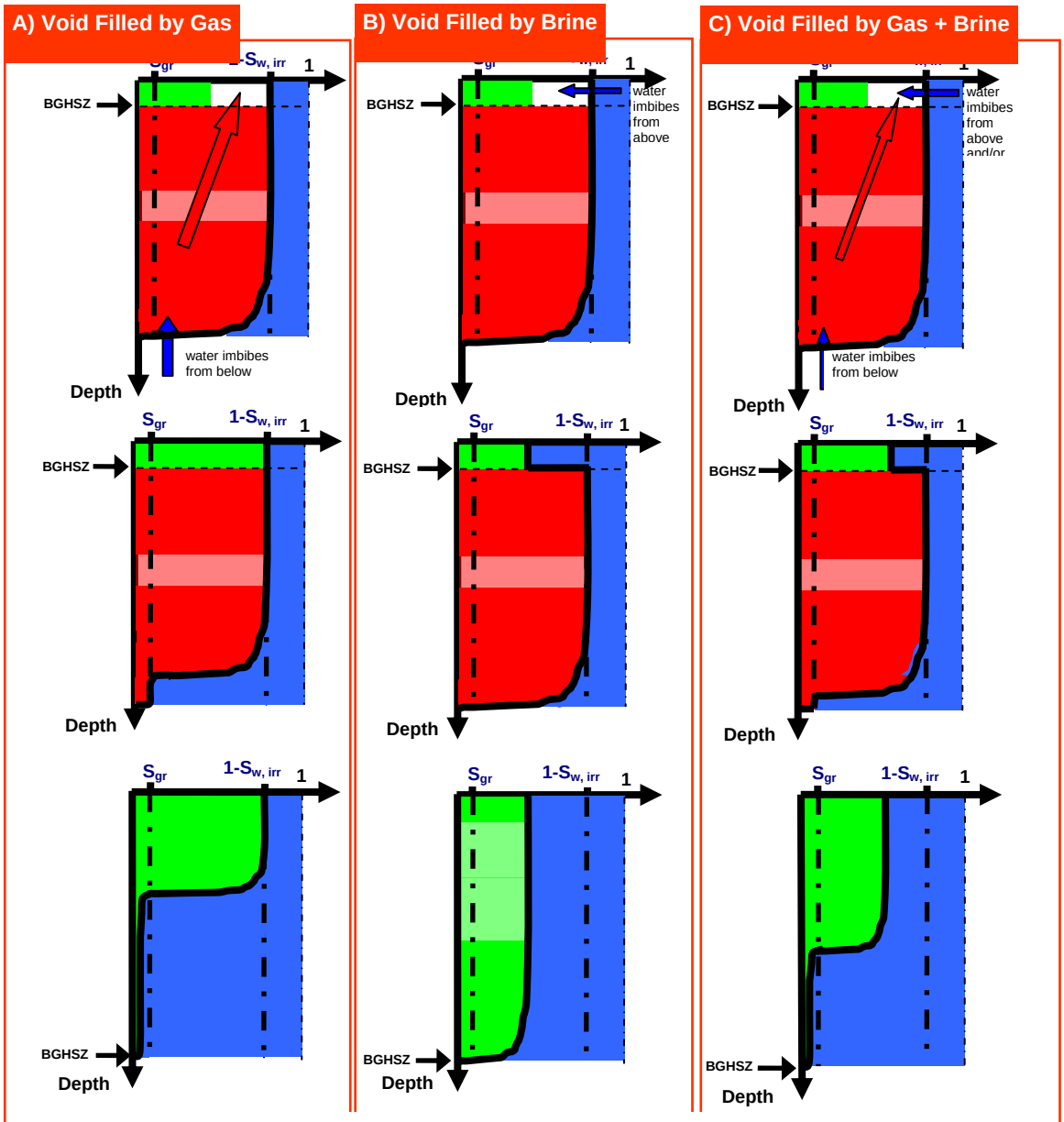


Figure 6. Schematic of the development of hydrate saturation as BGHSZ descends through an existing accumulation of gas. The three panels show the result of filling the void resulting from hydrate formation (L) entirely by gas moving from below; (M) entirely by water moving from below or above; and (R) partly by gas and partly by water.

If only gas migrates to fill the void, a large hydrate saturation forms in the upper part of the original gas accumulation. Only a small hydrate saturation forms in the lower part of the accumulation. This saturation is the consequence of converting residual gas to hydrate. The residual gas in the lower part of the accumulation is established as water imbibes in to replace the gas that moved upward to fill the hydrate void.

The situation is qualitatively different if only water migrates to fill the void. A moderate, uniform saturation of hydrate forms throughout the original accumulation. This is the result of complete conversion of original gas saturation. If both fluids move, the hydrate saturation profile is intermediate between the two limiting cases.

We remark that our previously reported work demonstrating the competition between sediment fracturing and sediment drainage can be integrated into this model. The creation of a fracture will establish only a small gas saturation. The conversion of this gas to hydrate will likewise yield a small

Field Implications

Crucially, this simple model predicts highly nonuniform hydrate saturation *even in the absence of lithological variation*. In other words, the convention wisdom that hydrates form in sand-rich sediments and do not form in clay-rich sediments is not entirely true. Even sand-rich sediments may exhibit small hydrate saturations in this model. Moreover, the same model provides a mechanism for the occurrence of large (>60%) saturations of hydrate in sediment, namely the conversion of existing gas into hydrate under conditions in which gas migrates faster than water within the accumulation, so that the void is filled by gas which itself turns to hydrate.

This model is consistent with the observation of incomplete filling of the Unit D sand with hydrate in the Mt. Elbert well. The log-derived saturation profile (Boswell et al., 2009) and corresponding model predictions are shown in Figure 7. The model assumed that the initial gas accumulation filled Units C and D completely, but did not extend farther down.

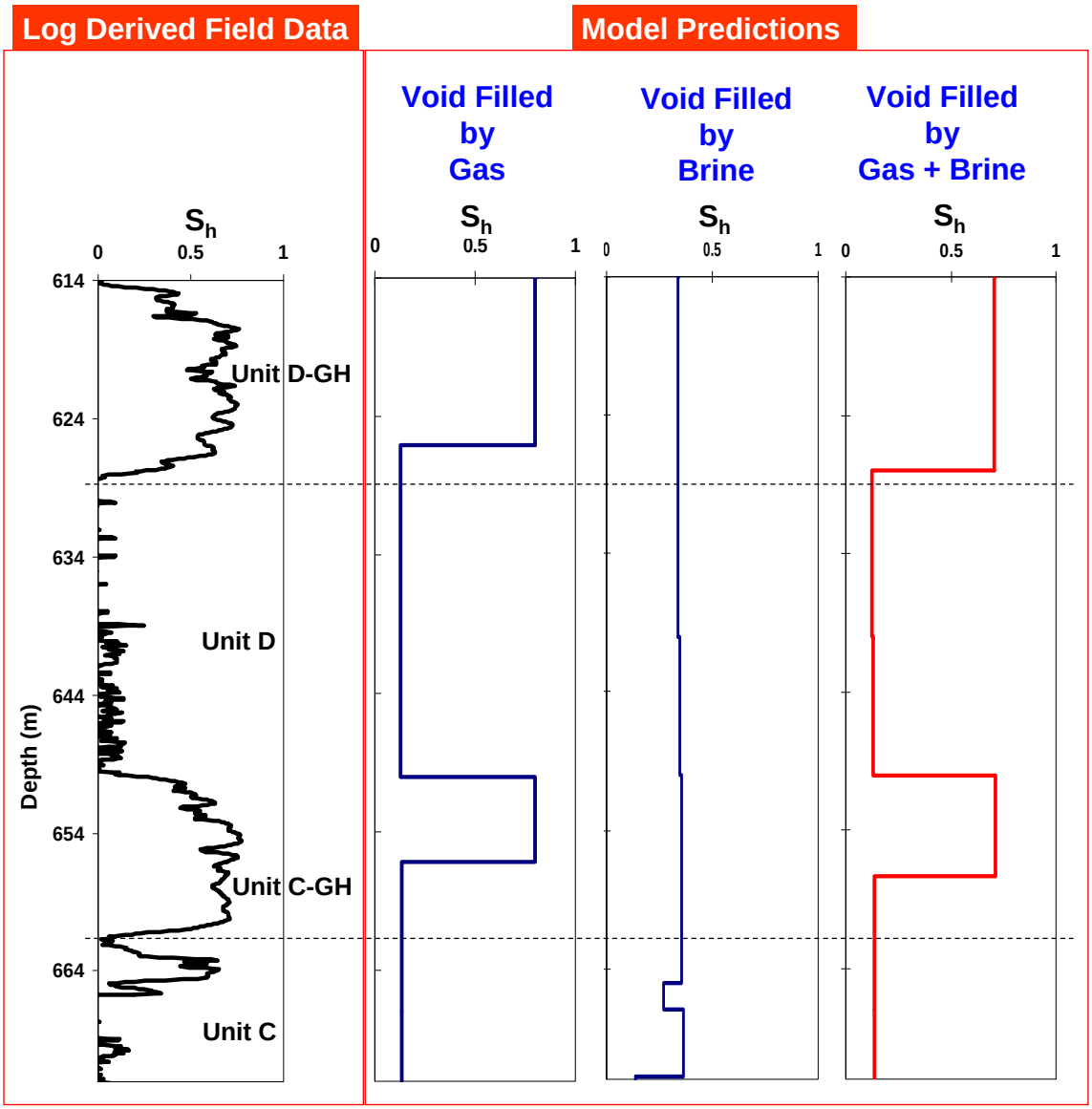


Figure 7. (L) Gas hydrate saturation in the Mt. Elbert well inferred from wireline logs shows large accumulation in the top of unit D and the top of unit C, but with little accumulation in the remaining parts of those units. (R) Model predictions that involve gas migration within the accumulation (left and right panels) as BGHSZ descends are consistent with the observed profile.

Fracture-Dominated Migration Model

We have started the development of a one-dimensional model of methane migration through a sediment column, in which the main transport mechanism is that of advection of methane through fractures, in its own gas phase. For now, we have restricted the developments to methane transport outside the hydrate stability zone.

We have recently obtained quantitative evidence for this mechanism (gas transport through fractures) in recent records of methane venting (and corresponding time series of methane fluxes) in Upper Mystic Lake, MA (Varadharajan, 2009). The key observation is that venting events are correlated with periods of low hydrostatic pressure (combined atmospheric pressure and water level), and these events occur simultaneously, in discrete places, throughout the bottom of the lake (Fig. 1).

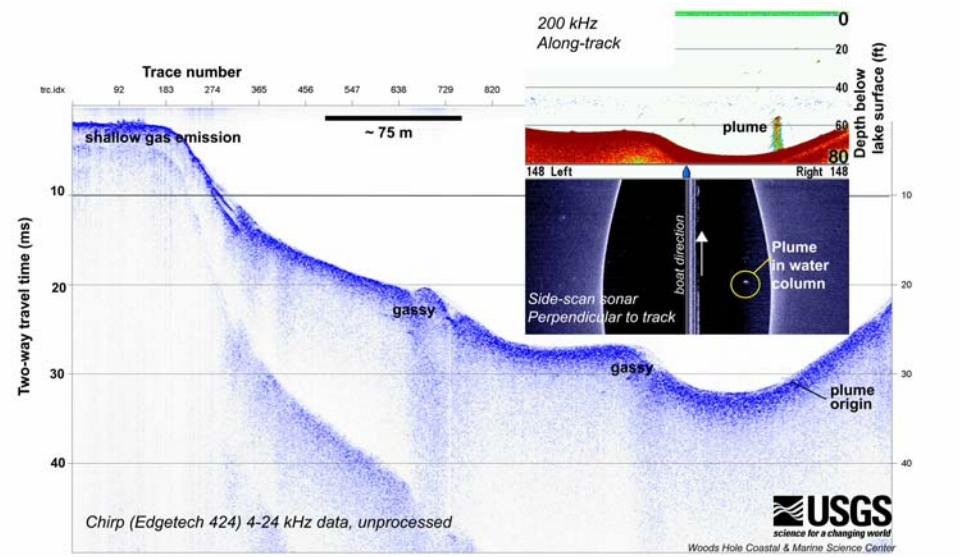


Figure 1. Seismic and sonar traces from Upper Mystic Lake, MA. The inset shows the trace of a methane gas plume rising up the water column and disappearing before reaching the surface. Preliminary data courtesy of Carolyn Ruppel, USGS.

Such observations suggest that the mechanism responsible for methane venting is the episodic release of methane gas through fractures that open up in response to exceeding the horizontal effective stress in the sediment.

We have developed a simple one-dimensional mathematical model that accounts for these effects. The conceptual model is illustrated in Fig. 2. The essential ingredients of the model are the following:

- The model considers only the generation and flow of free-phase gas
- Dynamic fractures respond to hydrostatic pressure change
- The gas pressure is constrained by water pressure and horizontal stress
- The amount of methane is a function of the volumetric generation rate

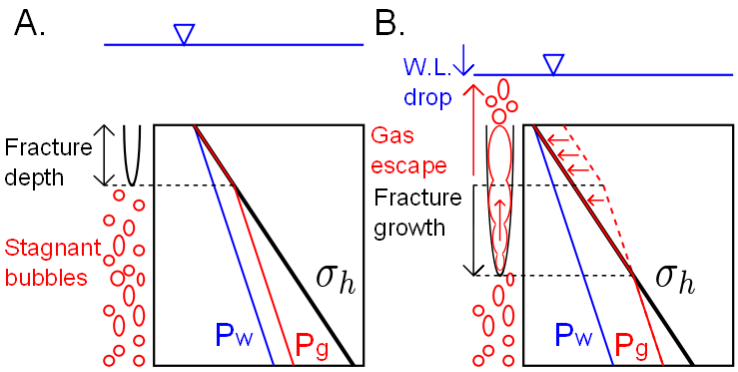


Figure 2. Conceptual model of methane migration in a lake or ocean sediment. Shown is the mechanism for the opening of a fracture and subsequent upward migration of methane gas (see text for a description).

With these basic elements, we formulate a mathematical model that predicts the dynamics of fracture formation and the episodic release of methane gas in response to hydrostatic pressure forcing. To illustrate the behavior of the model in a real case, we compare the results from our model with actual data collected at Upper Mystic Lake (Fig. 3). The model allows explaining the observations, and matches well both in terms of cumulative methane release, and the fine-scale episodic structure of the methane venting record. In subsequent reports and publications we will give the complete details of the model, and a thorough validation with data from Mystic Lake and elsewhere.

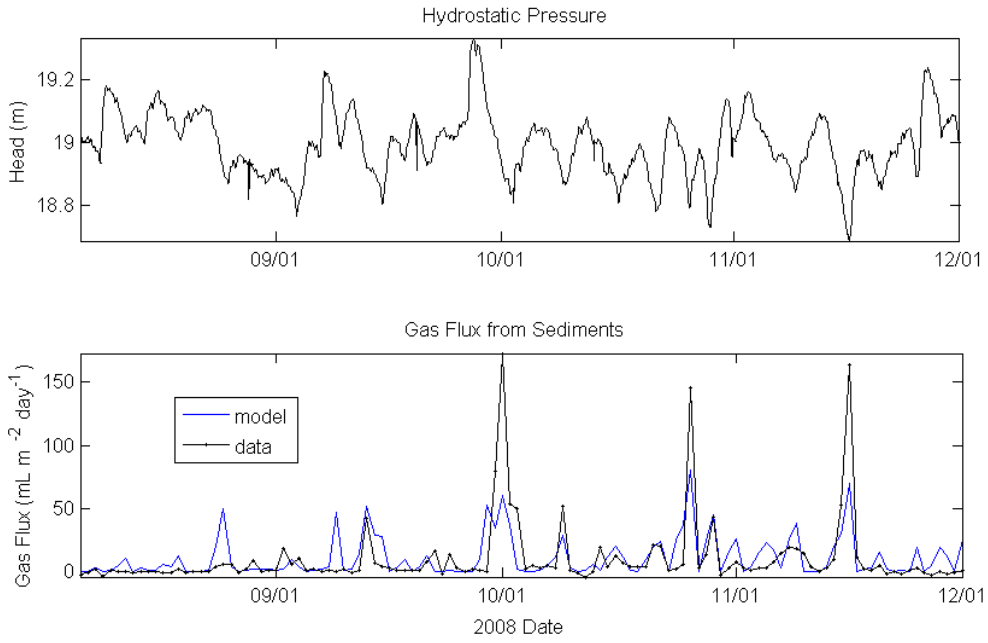


Figure 3. Preliminary results of the application of the model to methane fluxes in Mystic Lake. Note the excellent correlation between data and model in terms of the timing and magnitude of the methane venting events. Data from Varadharajan (2009).

Bibliography

Varadharajan, C. (2009). Magnitude and Spatio-Temporal Variability of Methane Emissions from a Eutrophic Freshwater Lake. Ph.D. Dissertation. Massachusetts Institute of Technology.

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