

# PHYSICAL PROPERTIES OF HYDRATE-BEARING SEDIMENTS

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[1] Methane gas hydrates, crystalline inclusion compounds formed from methane and water, are found in marine continental margin and permafrost sediments worldwide. This article reviews the current understanding of phenomena involved in gas hydrate formation and the physical properties of hydrate-bearing sediments. Formation phenomena include pore-scale habit, solubility, spatial variability, and host sediment aggregate properties. Physical properties include thermal properties, permeability, electrical conductivity and permittivity, small-strain elastic  $P$  and  $S$  wave velocities, shear strength, and volume changes

resulting from hydrate dissociation. The magnitudes and interdependencies of these properties are critically important for predicting and quantifying macroscale responses of hydrate-bearing sediments to changes in mechanical, thermal, or chemical boundary conditions. These predictions are vital for mitigating borehole, local, and regional slope stability hazards; optimizing recovery techniques for extracting methane from hydrate-bearing sediments or sequestering carbon dioxide in gas hydrate; and evaluating the role of gas hydrate in the global carbon cycle.

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## 1. INTRODUCTION

[2] Gas hydrates are crystalline clathrates composed of low molecular weight gases, the most common of which is methane, encaged in a lattice of hydrogen-bonded water molecules. Methane gas hydrate, found beneath permafrost and in marine continental margin sediments worldwide [Kvenvolden and Lorenson, 2001], is the most common naturally occurring gas hydrate and has attracted interest as a possible energy resource [Collett, 2002; Dallimore and Collett, 2005; Grauls, 2001; Holder et al., 1984; Ruppel, 2007] and as a potential agent in climate change [Archer, 2007; Dickens et al., 1995; Ruppel and Pohlman, 2008] and seafloor instability [Kayen and Lee, 1991, 1993; McIver, 1982; Mienert et al., 2005; Nixon and Grozic, 2007].

[3] Gas hydrate research, as measured by publication numbers, has grown exponentially through the 20th century [Sloan, 2004]. Much of the measurement work has focused on gas hydrate as a pure material, referred to here as “hydrate,” and has been comprehensively reviewed by Sloan and Koh [2008]. As research shifts to hydrates in sediments, it is appropriate to review the current understanding of the evolution, behavior, and physical properties of hydrate-bearing sediments.

[4] Consider the process of methane recovery from hydrate-bearing sediments, discussed in sections 1.1–1.3 in terms of the critical roles physical properties play in the exploration, production, and reservoir management phases. Sections of this paper that address the corresponding governing parameters are given in parentheses.

### 1.1. Exploration

[5] Host sediment properties (section 6), particularly sediment grain size, play a prominent role in evaluating sites for their resource potential. Exploration for hydrate as an energy resource focuses on sands rather than fine-grained material to facilitate extraction while minimizing technical production challenges [Boswell and Collett, 2006; JIP Leg II Science Team, 2009]. A “petroleum systems” approach has been adopted to target sands with high hydrate saturations [Hutchinson et al., 2008; Jones et al., 2008]. One component of this approach is to identify sands that are linked to a methane source (section 2) via faults or other permeable pathways [Frye, 2008].

[6] Migration pathways and general reservoir properties (section 4) can be identified from seismic or other remote

sensing data [Hutchinson et al., 2008; Jones et al., 2008]. These mapping techniques rely on the effects of hydrates on sediment properties relative to hydrate-free sediment. Electrical survey data are sensitive to the resistivity increase as hydrate replaces conductive pore water in the sediment (section 9) [Weitemeyer et al., 2006], whereas seismic survey data are sensitive to the increase in wave velocity that hydrate imparts to the host sediment (section 10) [Dai et al., 2008b].

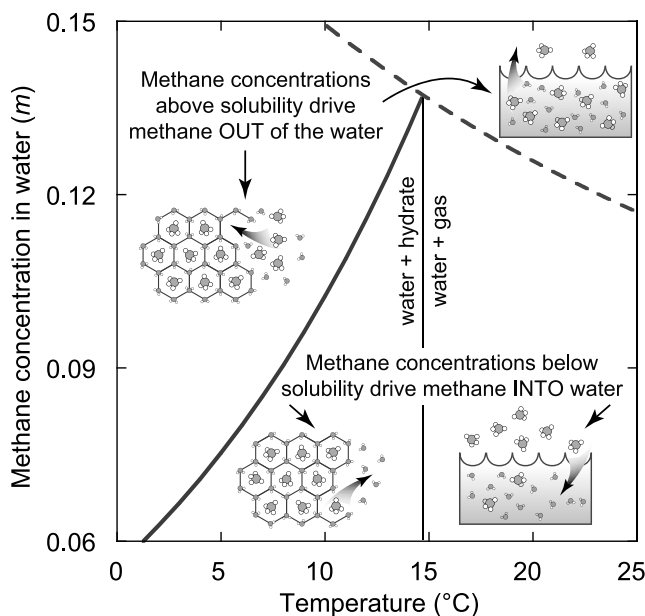
[7] The extent to which a given volume of hydrate alters the host sediment properties depends on where hydrate forms within the pore space (section 3) [Dvorkin et al., 2000]. Careful consideration must therefore be given in laboratory studies when mimicking hydrate-bearing sediments, when linking pore space hydrate saturations to measured physical properties (section 5), and when interpreting field data [Dai et al., 2008b].

### 1.2. Production

[8] Hydrate dissociation during drilling or production reduces the volume of a solid phase in the formation and converts it into a mixed fluid phase that is several times larger in volume, with immediate implications for fluid pressure, effective stress [Rutqvist et al., 2008], strength (section 11), and volumetric deformation (section 12) [Kwon et al., 2008]. Potential implications include the collapse of the production borehole [Birchwood et al., 2008]. Strength loss due to hydrate dissociation must also be considered while producing conventional hydrocarbons underlying hydrate-bearing strata as relatively warm hydrocarbons pumped through hydrate-bearing layers can destabilize hydrate surrounding the production well [Briaud and Chaouch, 1997; Hadley et al., 2008].

### 1.3. Reservoir Management

[9] The economical viability of a reservoir depends on a combination of several factors such as thermal properties, formation permeability, and sediment spatial variability. The rate at which dissociation can occur, for instance, is limited by the reservoir temperature and ability to conduct the heat needed to drive the endothermic dissociation of gas hydrate (section 7) [Anderson et al., 2008; Kneafsey et al., 2007]. The formation permeability and the relative permeability in the presence of gas and water (section 8) determine the ease with which methane can be transported into the production well [Sakamoto et al., 2008]. Sediment properties (section



**Figure 1.** Solubility curves for methane in water with hydrate (solid curve) and without hydrate (dashed curve). Pressure is assumed constant at 12 MPa. Depending on the temperature, a solution with excess methane will either precipitate hydrate or push methane into the gas phase (top schematics) until the methane concentration falls to the solubility value. A solution with a methane deficit will dissolve hydrate or absorb free gas (bottom schematics) until the solution's methane concentration rises to the solubility value. When methane is entering and exiting the solution at equal rates, the system is in dynamic equilibrium at the solubility concentration.

6) determine other production-related processes, such as fines migration during the production and clogging of permeable pathways around the production well [Valdes and Santamarina, 2007; Walsh et al., 2009]. Reservoir models used to optimize recovery strategies and forecast the economic potential of a given hydrate reservoir must properly account for interdependencies between physical properties in order to reliably capture the inherently coupled hydromechanical, thermomechanical, and chemomechanical processes that govern the behavior of hydrate-bearing sediment [Anderson et al., 2008; Walsh et al., 2009; Wilder et al., 2008].

[10] The production example given in section 1.2 is not merely hypothetical. The Chevron–Department of Energy (DOE) Joint Industry Project (JIP) in the Gulf of Mexico completed a drilling program in May 2009 to test whether the “petroleum system” approach mentioned in section 1.1 is applicable to locating sand units with high hydrate saturations [JIP Leg II Science Team, 2009]. On Alaska's North Slope, a ConocoPhillips–DOE JIP is planning a long-term production test from a subpermafrost hydrate-bearing sand [ConocoPhillips–University of Bergen Hydrates Team, 2008]. Several countries are currently exploring for hydrate-bearing reservoirs [Expert Panel on Gas Hydrates, 2008], and Japan aims to produce methane

from hydrate at a commercial scale by 2016 [Sakamoto et al., 2008].

[11] In support of ongoing efforts in hydrate exploration, reservoir assessment, analyses of gas hydrate's role in climate change, and evaluation of seafloor instability conditions, this review collects the current understanding of physical properties of hydrate-bearing sediment. Where possible, connections are made between these properties to indicate the ways in which hydrate-bearing sediment evolves in response to changes in its surroundings.

## 2. SOLUBILITY OF HYDRATE-FORMING GAS IN AQUEOUS SYSTEMS

[12] Hydrate forms in the presence of water when there is enough hydrate-forming gas and both pressure and temperature are conducive to hydrate stability. Conversely, the hydrate crystal may break down and release methane by either dissolution, when there is not enough hydrate-forming gas in the surrounding water, or dissociation, when the pressure and temperature requirements for stability are not met. Whereas hydrate dissolution results in only a small net volume increase [Lu et al., 2008; Sultan et al., 2004a], dissociation generates a free methane gas phase and a much larger volume increase [Kwon et al., 2008; Xu and Germainovich, 2006].

[13] The equilibrium concentration of hydrate-forming gas (the solute) in the surrounding water or aqueous system (the solvent) is given in units of molarity,  $M$ , defined as moles of solute per liter of solution. Solute concentration can also be given in terms of molality,  $m$ , defined as the moles of solute per kilogram of solvent. For simplicity, the solute considered herein is methane,  $\text{CH}_4$ .

[14] Dissolution and precipitation occur when hydrate is in contact with water. During dissolution, hydrate dissolves into the water phase, increasing the methane concentration in the water. During precipitation, hydrate formation extracts methane from the water phase, lowering the methane concentration in the water. In the presence of hydrate, dissolution and precipitation occur at the same rate when the concentration of methane in the water reaches the solubility limit. In the absence of hydrate, methane molecules move at equal rates between the free gas phase and the dissolved phase when the concentration of methane in water reaches the solubility limit (Figure 1).

### 2.1. Theoretical Determination of Solubility Concentrations

[15] The solubility of each chemical species in the gaseous, liquid, and hydrate phases can be calculated from thermodynamic properties by minimizing the system's Gibbs free energy or, equivalently, equating the potential energy changes in the system, as shown in Table 1 [Sun and Duan, 2007; Zatsepina and Buffett, 1998]. In step 3 in Table 1, the Trebble and Bishnoi [1987] equation of state has been shown to work well for the methane-water system [Englezos and Bishnoi, 1988; Zatsepina and Buffett, 1998]. Solubility can also be estimated directly from fugacity-based models,

**TABLE 1. Obtaining the Equilibrium Solubility Concentration,  $x_i^j$ , of Species  $i$  in Phase  $j$  From Minimizing Gibbs Free Energy,  $G^a$** 

Step	Process	Equation
1	minimize Gibbs free energy, $G$ , or equate chemical potentials, $\mu$	$G = \sum_{i,j} n_i^j \mu_i^j$ or $\Delta \mu_w^H = \mu_w^\beta - \mu_w^H = \mu_w^\beta - \mu_w^L = \Delta \mu_w^L$
2	relate chemical potential to activity, $a$ , or fugacity, $f$	$\mu_i^j - \mu_i^0 + RT \cdot \ln(a_i^j) = \mu_i^0 + RT \cdot \ln\left(\frac{f_i^j}{f_i^0}\right)$
3	relate activity or fugacity to concentration, $x$	$a_i^j = \frac{f_i^j}{f_i^0} = \nu_i^j x_i^j$

<sup>a</sup>Notation is as follows:  $n$  is number of moles;  $\mu_i^j$  is chemical potential or free energy per mole of species  $i$  in phase  $j$ , with  $j = 0$  representing a convenient reference state; activity,  $a$ , is a measure of how nonideal molecules such as methane and water interact; fugacity,  $f$ , is a measure of how stable a species is in a given phase; ideal gas constant  $R = 8.314 \text{ J (mol K)}^{-1}$ ;  $T$  is temperature in kelvins; and  $\nu$  is the activity coefficient determined from an equation of state. Subscript  $w$  refers to water. Superscripts  $H$ ,  $\beta$ , and  $L$  refer to water in the hydrate phase, in a hypothetical empty hydrate with no guest molecules, and in the liquid phase, respectively.

though expressions for activity and fugacity can be complex when the combined effects of temperature, pressure, salinity, and pore size are included. Solubility “calculators” that account for some of these effects can be found online ([http://www.geochem-model.org/?page\\_id=48](http://www.geochem-model.org/?page_id=48)) [Duan and Mao, 2006; Sun and Duan, 2007].

## 2.2. Data

[16] Experimental measurements and theoretical estimates for methane solubility in water with and without hydrate are compiled in Tables 2a–2c. Here we summarize the dependence of methane solubility in water on temperature, pressure, salinity, capillary pressure, and pore size.

### 2.2.1. Temperature

[17] The solubility of methane in water is primarily controlled by temperature and the presence of hydrate. In the absence of hydrate (dashed curve in Figure 1), methane becomes less soluble as the temperature increases because the increasing kinetic energy allows molecules to break intermolecular bonds in the liquid water and move into the gas phase. The same general concept applies in the presence of hydrate, where increasing temperature means more energetic methane molecules can break out of the solid hydrate and enter the liquid water, increasing the water’s methane concentration (solid curve in Figure 1) [Subramanian and Sloan, 2002].

### 2.2.2. Pressure

[18] In the absence of hydrate, the solubility rises with increasing pressure, indicating an increased preference for methane to exist in the dissolved phase rather than the gas phase [Servio and Englezos, 2002]. In the presence of hydrate, solubility falls slightly with increasing pressure, indicating a preference for methane to exist in the hydrate rather than the water phase [Lu et al., 2008].

### 2.2.3. Salinity

[19] The addition of salt drives methane out of solution, shifting the curves in Figure 1 to lower values. Methane is forced into hydrate if it is present or into the gas phase in the absence of hydrate [Davie et al., 2004; Sun and Duan, 2007; Tishchenko et al., 2005; Zatsepina and Buffett, 1998]. Solubility changes due to salt are secondary to those of temperature in natural settings but are important in flow assurance applications, such as preventing hydrate formation in pipelines, where electrolytes and other chemical inhibitors are used extensively [Sloan and Koh, 2008].

### 2.2.4. Capillary Pressure and Pore Size

[20] Capillary pressure is the pressure difference across an interface between two immiscible phases, such as water and hydrate or water and gas. The capillary pressure,  $\Delta P$ , across a spherical interface of radius  $r$  and interfacial tension  $\gamma_{i,w}$  between species  $i$  (hydrate or free methane gas in this case) and water is

$$\Delta P = P_i - P_w = \gamma_{i,w} \left( \frac{2}{r} \right). \quad (1)$$

The pressure,  $P_i$ , in the hydrate or free gas bubble is therefore higher than the pressure in the water,  $P_w$ , by an amount equal to the capillary pressure,  $\Delta P$ . Equation (1) indicates that the capillary pressure increases with decreasing radius of interfacial curvature.

[21] Like the capillary pressure, the chemical potential in a hydrate crystal or free gas bubble scales inversely with the radius of curvature [Clennell et al., 1999]. Smaller hydrate crystals or free gas bubbles therefore have higher chemical potentials than their larger counterparts and require higher methane concentrations in the surrounding water to balance that chemical potential [Henry et al., 1999; Kwon et al., 2008]. This process is only significant in small pores, which would need to have radii <18 nm for this solubility increase

**TABLE 2A. Solubility References for Hydrate-Forming Gas in Water in the Presence of Hydrate: Methane and Pure Water**

$P$ (MPa)	$T$ (K)	Reference <sup>a</sup>
0.1–50	273–278	Handa [1990], M
0.1–200	273–573	Duan and Mao [2006], M
0.6–8.9	274–282	Englezos et al. [1987], E and M
1–18	275–313	Mohammadi et al. [2006], E and M
1–35	283–318	Chapoy et al. [2003], E and M
2.7–78	274–302	Hashemi et al. [2006], M
3–50	273–293	Tishchenko et al. [2005], M
3.5–6.5	274–285	Servio and Englezos [2002], E
3.5–6.5	274–285	Bergeron et al. [2007], M
3.5–30	273–291	Sun and Duan [2007], M
5–20	276–282	Kim et al. [2003], E and M
6–20	274–286	Seo et al. [2002], E
10–30	273–300	Davie et al. [2004], M
10–40	277–295	Lu et al. [2008], E and M
10–60	324.65	Masoudi et al. [2004], M
20	273–300	Zatsepina and Buffett [1997, 1998], M

<sup>a</sup>E, experiment; M, model.

**TABLE 2B. Solubility References for Hydrate-Forming Gas in Water in the Presence of Hydrate: Methane, Pure Water, and Salt<sup>a</sup>**

$P$ (MPa)	$T$ (K)	Salt Content <sup>b</sup>	Reference <sup>c</sup>
0.1–50	273–278	3.5%	Handa [1990], M
0.1–200	273–573	0–6 $m$ (0%–26%)	Duan and Mao [2006], M
5–50	273–293	2%, 3.5%, 5%, and 7%	Tishchenko et al. [2005], M
10–30	273–283	3% and 3.5%	Sun and Duan [2007], M
10–60	324.65	1 and 4 $M$ (6% and 23%)	Masoudi et al. [2004], M

<sup>a</sup>Salt is NaCl.<sup>b</sup>Original units are given. Results given in molarity ( $M$ ) or molality ( $m$ ) are also converted to percent (grams of salt per 100 grams of solution).<sup>c</sup>M, model.

to balance the solubility decrease caused by the salinity in a standard seawater solution of 3.5 wt % salt [Sun and Duan, 2007]. By comparison, the pore space distribution in fine-grained hydrate-bearing sediment at Blake Ridge Ocean Drilling Program Hole 995A peaked near a radius of 100 nm [Clennell et al., 1999]. The capillary pressure effect is even smaller in clean sands, where sediment grains are larger than 75  $\mu\text{m}$  and pore sizes generally exceed  $\sim 50 \mu\text{m}$ .

### 2.3. Geologic Implications

[22] In natural systems, the solubility of methane increases with depth, as shown in Figure 2 [Nimblett and Ruppel, 2003; Xu and Ruppel, 1999]. The solubility is nearly constant below the depth at which hydrate is no longer stable because the solubility increase with increasing pressure and decrease with increasing temperature nearly balance in the absence of hydrate.

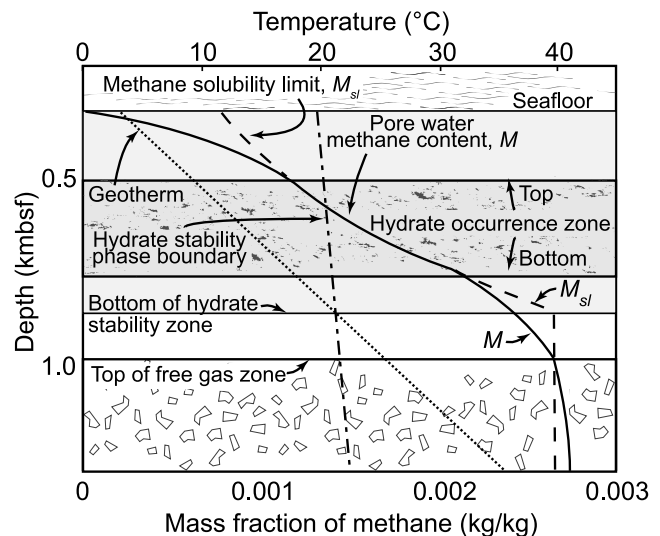
[23] Fluid migrating up through the sediment column may not be fully saturated with methane at depth and hence cannot begin precipitating hydrate until it passes through the depth at which the solubility limit is low enough to equal the methane concentration in the rising fluid (bottom of hydrate occurrence zone in Figure 2). The actual base of hydrate occurrence is therefore often shallower than would be predicted from pressure and temperature considerations alone [Xu and Ruppel, 1999]. These concepts have been captured in numerical models predicting the hydrate distribution formed by methane dissolved in upwelling fluid over geologic time [Garg et al., 2008; Nimblett and Ruppel, 2003] and when the rising fluid contains free methane gas [Liu and Flemings, 2007].

[24] While seafloor conditions may be within the stability field, hydrate does not tend to form at or close to the seafloor (top of hydrate occurrence zone in Figure 2) for

three reasons [Egorov et al., 1999; Haeckel et al., 2004; MacDonald et al., 1994]: (1) methane in upwelling water is consumed by hydrate formation at depth [Xu and Ruppel, 1999]; (2) sulfate reduction, anaerobic methane oxidation, and other chemical processes active in the shallow sediment consume available methane [Egorov et al., 1999; Malinverno et al., 2008; Nimblett and Ruppel, 2003; Rehder et al., 2004]; and (3) low methane concentrations in seawater cause rapid hydrate dissolution [Rehder et al., 2004]. Thus, hydrate outcrops at the seafloor tend to occur in conjunction with active methane gas vents that can sustain the hydrate outcrop.

### 3. HYDRATE FORMATION IN SEDIMENT

[25] The pore-scale location of hydrate exerts a strong control on the macroscale physical properties of hydrate-

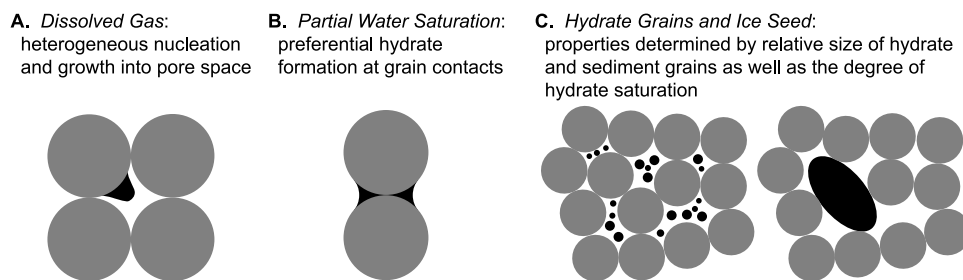


**Figure 2.** The zone in which methane gas hydrate occurs can be thinner than the stability zone. Fluid with a methane concentration  $M$  must rise to the depth at which the local solubility limit,  $M_{sl}$ , is less than  $M$  in order for hydrate to precipitate and form the base of hydrate occurrence. The top of hydrate occurrence is often below the seafloor even when hydrate is thermodynamically stable because methane consumption drives the methane concentration below the local solubility limit. Modified from Xu and Ruppel [1999], who assumed a water depth of 2500 m.

**TABLE 2C. Solubility References for Hydrate-Forming Gas in Water in the Presence of Hydrate: Methane, Pure Water, Salt, and Pore Size<sup>a</sup>**

$P$ (MPa)	$T$ (K)	Salt Content (%)	Pore Size (nm)	Reference <sup>b</sup>
5–50	273–294	3.5	5–50	Sun and Duan [2007], M
3–14	271–287	0	9–30	Anderson et al. [2003], E
3–8	259–283	0	4–100	Uchida et al. [2002], E

<sup>a</sup>Salt is NaCl.<sup>b</sup>E, experiment; M, model.



**Figure 3.** Dependence of hydrate habit on hydrate formation technique. Physical properties of hydrate-bearing sediments depend on the size and distribution of hydrate (black) relative to the sediment grains (gray).

bearing sediments. Pore-scale habits of hydrates, hydrate formation techniques used in the laboratory, and observations based on natural hydrate-bearing sediments are reviewed in sections 3.1–3.4 in the context of their impact on measured physical properties (based on J. Jang (personal communication, 2008) and *Lee et al.* [2007]).

### 3.1. Hydrate in Pores

[26] The effects of hydrate on host sediment properties depend on where hydrate forms in the pore space. The three most commonly discussed hydrate habits are as follows:

[27] The first habit is pore filling. Hydrates nucleate on sediment grain boundaries and grow freely into pore spaces without bridging two or more particles together. In this case, hydrate primarily affects the pore fluid bulk stiffness and fluid conduction properties [*Helgerud et al.*, 1999].

[28] The second habit is load bearing. Hydrate bridges neighboring grains and contributes mechanical stability to the granular skeleton by becoming part of the load-bearing framework. Pore-filling hydrate naturally turns into load-bearing hydrate when the pore space hydrate saturation exceeds  $S_h = 25\%–40\%$  [*Berge et al.*, 1999; *Yun et al.*, 2005, 2007].

[29] The third habit is cementation. Hydrate cements intergranular contacts. Even a small amount of hydrate can dramatically increase the sediment shear and bulk stiffnesses by bonding adjacent grains together [*Dvorkin et al.*, 1999].

[30] Hydrate nucleation and growth processes govern which hydrate habit occurs. As a result, different laboratory methodologies for forming hydrate can result in different hydrate habits and hence different physical properties for identical sediments with equal hydrate saturations, as discussed in sections 8, 10, and 11.

### 3.2. Hydrate Formation in the Laboratory

[31] The controlled synthesis of methane hydrate in sediments is challenging owing to methane's low solubility in water. Even for water in contact with hydrate at 4°C, there are ~750 water molecules per methane molecule [*Lu et al.*, 2008], as compared to ~6 water molecules per methane molecule required in the methane hydrate structure. Hydrate formation from methane gas dissolved in water is thus a slow process for laboratory studies, and more expedient techniques have been developed. These laboratory methods

produce different pore-scale growth habits [*Ebinuma et al.*, 2005; *Spangenberg et al.*, 2005; *Zhong and Rogers*, 2000].

#### 3.2.1. Dissolved Gas Method

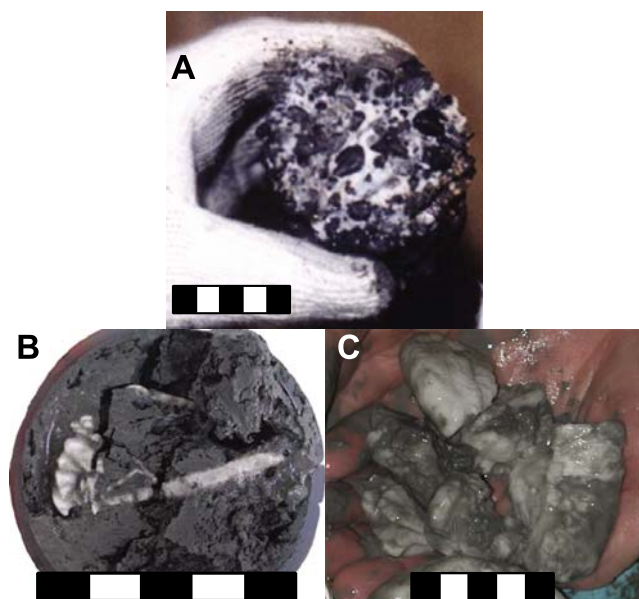
[32] Water saturated with a hydrate-forming gas is circulated through sediment that is held within the hydrate pressure and temperature stability field. The hydrate growth rate is limited by the concentration of hydrate former in the water, so many of these experiments use carbon dioxide, CO<sub>2</sub> [*Katsuki et al.*, 2006; *Tohidi et al.*, 2001; *Zatsepina and Buffett*, 2001] due to its higher solubility in water relative to methane [e.g., *Spangenberg et al.*, 2005].

[33] Regardless of the hydrate former, bringing the system into the hydrate stability field does not immediately result in a measurable quantity of hydrate. Hydrate crystals must first nucleate, and then these nuclei must grow before the hydrate formation can be detected. The induction time, the delay between imposing hydrate stability conditions and observing hydrate formation [*Sloan and Koh*, 2008], can be quite long when forming hydrate from dissolved phase gases. Surfactants have been used to promote hydrate nucleation [*Zhong and Rogers*, 2000], and induction times have also been reduced by flowing fluid through hydrate granules stored in a separate chamber, thereby entraining hydrate nuclei that can facilitate hydrate growth once they reach the test sediment [*Waite et al.*, 2008].

[34] Heterogeneous nucleation in the dissolved gas method may occur anywhere on the mineral surface, with subsequent growth into the pore space (Figure 3a). Conceptually, the dissolved gas method is limited to forming hydrate saturations  $S_h$  below ~60%–70% for which water remains a percolating phase and can continue to circulate, though saturations have been reported as high as 95% after ~50 days of circulation [*Spangenberg et al.*, 2005].

#### 3.2.2. Partial Water Saturation Method

[35] Soil grains are mixed with a limited amount of water and packed to form a partially water-saturated sediment. The system is pressurized with methane gas and cooled into the stability field to promote hydrate formation. Depending on the initial water saturation, this method can take just a few days to form hydrate-bearing sediments [*Kneafsey et al.*, 2007; *Waite et al.*, 2004]. Alternatively, the sample can be fully water saturated initially and have methane introduced as a bubble phase prior to cooling [*Winters et al.*, 2002]. Unlike the dissolved gas method, however, both partial water saturation approaches lead to preferential



**Figure 4.** Modes of hydrate occurrence: (a) Hydrate (white) saturating pore space of a coarse-grained sample from the 1998 Mallik 2L-38 permafrost hydrate research well. (b) Veined hydrate (white) in fine-grained sediment from the Krishna Godavari Basin, offshore India. (c) Sediment-coated hydrate chunks from fine-grained sediment in the Gulf of Mexico. Photos in Figures 4a and 4c by W. Winters, U.S. Geological Survey. Photo in Figure 4b courtesy of the National Gas Hydrate Program (NGHP) Expedition 01 Scientific Party. Scale bars indicate 5 cm.

hydrate formation at contacts and stiffening of the sediment framework (Figure 3b) [Chuvilin *et al.*, 2003; Ebinuma *et al.*, 2005; Klapproth *et al.*, 2007; Kneafsey *et al.*, 2005, 2007; Kono and Budhijanto, 2002; Masui *et al.*, 2005; Priest *et al.*, 2005].

### 3.2.3. Ice-Seeding Method

[36] Cooled soil grains are mixed with small ice grains. The mixture is pressurized into the hydrate stability field with methane. The temperature is slowly increased. Hydrate nucleation is facilitated by the existing ice lattice, and hydrate can grow rapidly from the water liberated as the ice melts [Stern *et al.*, 1996, 1998]. Depending on the gas pressure, this method can be run to completion within a few days. As shown in Figure 3c, the relative size and volume fraction of mineral and hydrate grains will determine their relative load-bearing contribution to the mineral framework. Additionally, as with the partial saturation method, meltwater may accumulate at sediment grain contacts prior to hydrate formation (Figure 3b) [Circone *et al.*, 2004; Ebinuma *et al.*, 2005; Holder and Kamath, 1984; Kamath *et al.*, 1991; Klapproth *et al.*, 2007; Masui *et al.*, 2005; Stern *et al.*, 1998; Ullerich *et al.*, 1987; Waite *et al.*, 2002; Yoon *et al.*, 2004].

### 3.2.4. Hydrate Premixing Method

[37] Granular methane hydrate is prepared by spraying misted water in a pure methane gas atmosphere under phase equilibrium conditions [Hyodo *et al.*, 2005] or by melting small ice particles in the presence of methane at 25–30 MPa pressure [Stern *et al.*, 1998]. The methane hydrate granules

are mixed with sediment at very low temperature and consolidated at the target effective stress for a few hours. The temperature of the prepared specimen is maintained within the stability field but briefly raised near the hydrate phase boundary to eliminate excess moisture and allow for hydrate annealing [Hyodo *et al.*, 2005]. As with the ice-seeding method, the load distribution within the hydrate-bearing sediment depends on the relative size of the hydrate granules and sediment grains (Figure 3c).

### 3.3. Hydrate Formation in Nature

[38] The formation patterns of naturally occurring hydrate are varied, with an observable distinction between disseminated, pore-filling hydrate in coarse sands compared to veined or nodule-type hydrate occurrences in fine-grained sediments (Figure 4). While the formation of hydrate near faults and at the base of the hydrate stability zone may take place in the presence of free gas, hydrate formation in sediments within the gas hydrate stability zone most likely utilizes dissolved, aqueous phase methane [e.g., Buffett and Zatsepina, 2000]. This requires a methane source within the sediment such as biogenic, microbial activity and/or the transport of either biogenic or thermogenic methane via diffusion or advection from deeper strata.

[39] Hydrate occurrences in the Nankai Trough offshore Japan have been characterized as pore filling [Murray *et al.*, 2006]. In the Blake Ridge, off the southeast coast of the United States, hydrate has been characterized as cementing by Guerin *et al.* [1999] but as load bearing by Helgerud *et al.* [1999]. As a rule of thumb, however, acoustic, electrical, or nuclear magnetic resonance (NMR) estimates of hydrate saturation suggest hydrate in sands can be characterized with load-bearing models when the hydrate saturation exceeds 25%–30% [Kleinberg and Dai, 2005; Lee and Waite, 2008] except in high gas flux areas [Bohrmann *et al.*, 1998] or where gas is recycled into the hydrate stability zone, allowing hydrate to form as a cement [Guerin *et al.*, 1999; Yuan *et al.*, 1999].

### 3.4. Laboratory Formation of Analog Hydrate

[40] Tetrahydrofuran ( $C_4H_8O$ , hereinafter referred to as THF) hydrate has been used in place of methane hydrate in laboratory studies [Handa *et al.*, 1984; Leaist *et al.*, 1982; Lee *et al.*, 2007; Rueff and Sloan, 1985; Yun *et al.*, 2005, 2007; Cortes *et al.*, 2009]. Concerns related to the polar nature of the THF molecule compared to the nonpolar nature of the methane molecule have been raised, but this polarity difference between THF and methane loses relevance in the context of hydration processes because the large size and structure of the THF molecule significantly weaken polarity-based ionic interactions between water and THF. Implications of THF's polar nature regarding hydrate research are discussed by Lee *et al.* [2007].

[41] The main advantage of THF relative to methane is its complete miscibility in water, which enables relatively rapid, homogeneous synthesis of THF hydrate and control of the hydrate volume fraction in sediments [Yun *et al.*, 2007; Lee *et al.*, 2007]. No gas phase is present during



hydrate formation, meaning hydrate is not forced to form at or near grain contacts. Instead, it is thought that THF hydrate nucleates on mineral surfaces and grows into the pore space. THF hydrate does not dissociate to a gaseous phase, however, meaning many production-related processes are difficult to study with this analog, though production issues based on THF data are discussed by *Lee et al.* [2009]. Within these limitations, hydrate-bearing sediments prepared with THF hydrate have allowed the study of a wide range of material parameters that provide valuable insight to natural hydrate-bearing sediments [*Lee et al.*, 2007; *Santamarina and Ruppel*, 2008; *Yun et al.*, 2005, 2007; *Lee et al.*, 2008; *Cortes et al.*, 2009].

#### 4. SPATIAL VARIABILITY

[42] Spatial variability affects all Earth processes, including all forms of diffusion, flow, and conduction. In turn, these processes impose spatial variability on the pressures, temperatures, and availability of water and methane that define the local gas hydrate stability field [*Chen and Osadetz*, 2008; *Ginsburg and Soloviev*, 1998; *Judd and Hovland*, 2007; *Wood et al.*, 2002]. Spatially varying hydrate distributions affect the interpretation of measurements used to characterize gas hydrate, the procedures for extracting methane from hydrate as an energy resource, and the analysis of hydrate-related geohazards.

[43] Spatial variability in hydrate-bearing sediments is found from the scale of gas hydrate-bearing reservoirs to the submicron scale (Figure 5). Figure 5a presents a seismic line from the Indian National Gas Hydrate Program (NGHP) drill site NGHP-01-21. The vertical scale in Figure 5a is several hundred meters; thus the smallest observed spatial variability is on the order of tens of meters. The location of the ocean floor, a domed structure and stratolithologic variability of the medium below the ocean floor, locations of subocean floor gas, a significant fault, and a possible debris flow can all be inferred from the profile. The presence of methane hydrate, sustained by the confluence of gas accumulation in the dome-like structure with appropriate pressure and temperature conditions, further alters the system's permeability, stiffness, and thermal and electrical properties.

[44] Figure 5b contains well log and core sample data from hole NGHP-01-10D from the Indian NGHP. Logging provides a degree of "ground truth" quantification of physical property differences between stratigraphic layers inferred from seismic data. The finer resolution of logging relative to shipboard seismic data reveals vertical heterogeneities on the order of meters to centimeters in which properties such as water content and bulk density can vary significantly even within a single stratum.

[45] Figure 5c shows spatial variability of elastic wave velocities on the centimeter scale. Shear and compressional wave velocities ( $V_s$  and  $V_p$ ) of a pressure core, continuously maintained at its in situ pore pressure, were measured approximately every 7 cm using the instrumented pressure testing chamber. The higher seismic velocities 35 cm from

the top suggest increased sediment stiffness, possibly due to the presence of gas hydrate.

[46] Figure 5d demonstrates millimeter-scale variability in density images provided by 3-D X-ray computed tomography (CT) of preserved NGHP core. Additional NGHP CT tomographic images are given by *Clayton et al.* [2008] and *Holland et al.* [2008]. Dark, hydrate-bearing veins are apparent in this fine-grained sediment, demonstrating how hydrate can be inhomogeneously distributed even within a single hydrate-bearing layer. The veins themselves are often a collection of still finer-scale veins [*Priest et al.*, 2008].

[47] X-ray microtomography can reveal submillimeter-scale features, such as in the structure of a frozen sandstone from the Nankai Trough containing hydrate and ice, shown in Figure 5e with a pixel resolution of 5.5  $\mu\text{m}$ . Though at this scale the sample appears somewhat homogeneous, the analysis of possible flow paths through a small portion of the sample shows considerable variability. As Figure 5f demonstrates for a laboratory-made specimen, flow variability can result from the heterogeneous, micron-scale pore space distribution of gas, hydrate, and water.

[48] Each of these measurement scales provides a different perspective on the system. Kilometer-scale measurements are needed to understand large-scale system behavior such as the geologic plumbing and structural traps needed for transporting and concentrating methane. Meter-scale logging and core-based measurements provide system characterizations relevant to methane production applications. Pore-scale observations underlie the conceptual models required for understanding electrical, mechanical, and hydraulic properties of hydrate-bearing sediments.

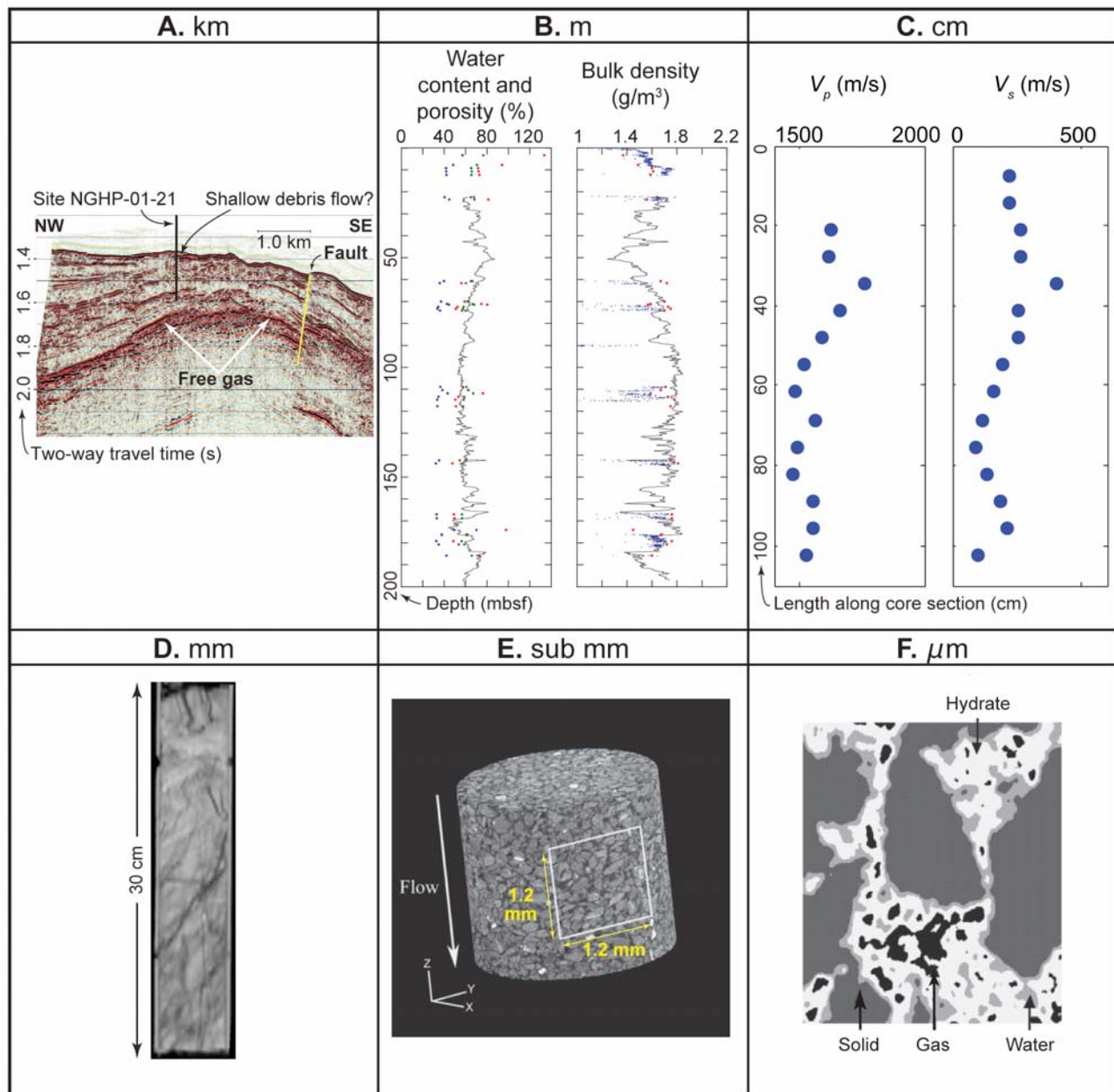
#### 5. SAMPLING AND HANDLING EFFECTS

[49] Geologic sampling inevitably disturbs natural sediments. The presence of hydrate adds further difficulties during sampling and may aggravate sampling disturbance. Sampling effects in hydrate-free and hydrate-bearing sediments are reviewed here.

##### 5.1. Hydrate-Free Sediments

[50] Sampling-induced changes in the mechanical properties of hydrate-free sediments have been recognized and extensively studied in the geotechnical community. Relevant observations include (1) pore pressure decreases from the in situ hydrostatic pressure when samples are extruded from core recovery systems, potentially subjecting the sample to an effective stress comparable to the in situ vertical effective stress [*Kimura and Saitoh*, 1984]; (2) reduced undrained strength due to the stress release [*Hight et al.*, 1992; *Ladd and Lambe*, 1963; *Santagata and Germaine*, 2002; *Skempton and Sowa*, 1963]; (3) more pronounced effects on the loss of effective stress and undrained strength for soils with plasticity index, PI, below 10%–15% [*Kimura and Saitoh*, 1984; *Matsuo and Shogaki*, 1988; *Siddique et al.*, 2000]; (4) decrease in small-strain shear stiffness ( $G_{\text{max}}$ ) in stiff and/or cemented soils, yet an increase in  $G_{\text{max}}$  for very soft sediments (database and





**Figure 5.** Spatial variability over a range of scales. (a) Seismic line crossing drill site NGHP-01-21 (modified from Collett *et al.* [2008]). Deep-seated high-amplitude reflectors indicate the occurrence of free gas as well as a potential shallow debris flow (vertical scale  $\sim 750$  m). (b) Well log (curves) and core data (points) for site NGHP-01-10 showing profiles of water content and bulk density (modified from Collett *et al.* [2008]). (c) Compressional and shear wave velocity measured by the instrumented pressure testing chamber (NGHP specimen 21A-03E) (Yun *et al.*, submitted manuscript, 2009) (modified from Collett *et al.* [2008]). (d) X-ray computed tomography (CT) scan of a core segment from NGHP 21H (T. Kneafsey, unpublished data, 2007). (e) Three-dimensional X-ray CT image of a sand sample retrieved from the Nankai Trough. The white box is 1.2 mm on a side (reproduced from Jin *et al.* [2007]). Flow is inhomogeneous through this seemingly uniform sample because of pore-scale variability, as observed in Figure 5f. (f) X-ray MicroCT imagery showing the distribution of mineral grains (dark gray), gas (black), water (light gray), and hydrate (white) in a laboratory-made sample (reproduced from Jin *et al.* [2006]).

interpretation by Rinaldi and Santamarina [2008]); (5) increased axial strain at peak deviatoric stress with increased disturbance [Siddique *et al.*, 2000]; and (6) friction between the sampler and sediments during sampling, which may produce shear failure and plastic deformation [Arman and McManis, 1977; Hvorslev, 1949; Young *et al.*, 1983].

## 5.2. Hydrate-Bearing Sediments

[51] Additional sample disturbance should be expected if pore fluid depressurization leads to gas coming out of solution [Young *et al.*, 1983] and hydrate dissociation. These changes are often not uniform and can impart additional spatial variability to the sample.

TABLE 3. Index Property Definitions<sup>a</sup>

Sediment Type	Property	Definition
General	soil classification	
	porosity, $\phi^b$	$\phi = V_v/V_T$
	specific gravity of solids, $G_s$	$G_s = \rho_s/\rho_w$
	bulk density, $\rho_b$ ( $\text{kg m}^{-3}$ )	$\rho_b = M_T/V_T$
	water content, $w$	$w = M_w/M_s$
	pore space hydrate saturation, $S_h^b$	$S_h = V_h/V_v$
	mineralogy	
	organic content	
	carbonate content	
	preconsolidation stress (kPa)	
Coarse grained	particle size distribution	$D_{10}, D_{60}, D_{30}$
	particle size distribution	$C_{\text{unif}} = D_{60}/D_{10}$
	particle size distribution	$C_{\text{curv}} = (D_{30})^2/(D_{10}D_{60})$
	particle shape	
Fine grained	pore size distribution	
	extreme void ratio, $e_{\text{min}}, e_{\text{max}}$	$e = V_v/V_s$
	Atterberg limit: liquid limit	LL
	Atterberg limit: plastic limit	PL
	Atterberg limit: plasticity index	PI = LL – PL
	Atterberg limit: liquidity index	LI = (w – PL)/PI
	activity, mineralogy	
Pore fluid	specific surface, $S_s$ ( $\text{m}^2 \text{g}^{-1}$ )	
	salinity	
	pH	

<sup>a</sup>Notation is as follows:  $C_{\text{curv}}$ , coefficient of curvature;  $C_{\text{unif}}$ , coefficient of uniformity;  $D_{10}$ , diameter at which 10% of sample is finer;  $D_{30}$ , diameter at which 30% of sample is finer;  $D_{60}$ , diameter at which 60% of sample is finer;  $e$ , void ratio;  $e_{\text{max}}$ , maximum void ratio (minimum grain packing);  $e_{\text{min}}$ , minimum void ratio (maximum grain packing); LI, liquidity index; LL, liquid limit; PI, plasticity index; PL, plastic limit;  $M_s$ , mass of solids;  $M_T$ , total mass;  $M_w$ , mass of water;  $V_h$ , volume of hydrate;  $V_s$ , volume of solids;  $V_T$ , total volume;  $V_v$ , volume of voids;  $w$ , gravimetric water content based on mass of minerals;  $\rho_s$ , density of solids;  $\rho_w$ , density of water. These properties and the means by which they are measured are discussed further by *Lambe and Whitman* [1969] and *Mitchell and Soga* [2005].

<sup>b</sup>Though porosity,  $\phi$ , and pore space hydrate saturation,  $S_h$ , are often reported as percentages, formulae in which they appear typically require the unitless values defined here in Table 3.

[52] Sampling disturbance in hydrate-bearing sediments can be reduced with pressure coring, in which pore fluid pressure and temperature conditions are maintained within the stability field. Pressure coring was first successfully applied to hydrate-bearing sediment during Ocean Drilling Program Leg 164 [*Dickens et al.*, 1997]. Two pressure coring systems currently in use, the HYACE Rotary Corer and the Fugro Pressure Corer, use a motor driven by mud circulation to rotate the cutting shoe and a water hammer driven percussion to drive the core barrel up to 1 m ahead of the drill bit. The sample is retrieved inside a pressure vessel after closing a valve to preserve the in situ pore fluid pressure.

[53] Pressure coring reduces, but does not eliminate, sample disturbance when recovering hydrate-bearing sediment [*Yun et al.*, 2006]. Current measurement techniques are ineffective at discerning whether observed features reflect in situ conditions or handling and measurement artifacts due to the following:

[54] 1. The loss of effective stress, which eventually decreases nearly to zero in the sediment, results in the sampling effects listed in section 5.1 for sediments without

hydrates. The state of effective stress can be restored after sampling, but the in situ soil fabric and internal structure are not fully recoverable.

[55] 2. Shear along the soil–core liner interface affects the periphery of cores even when conditions are kept within the hydrate stability field for their entire recovery and measurement history, as observed in electrical conductivity profiles obtained with millimeter-scale resolution from the periphery of pressure cores (T. S. Yun et al., Hydrate bearing sediments from Krishna-Godavari Basin: Physical characterization, pressure core testing and scaled production monitoring, submitted to *Marine and Petroleum Geology*, 2009).

[56] 3. Creep and diffusion processes are anticipated to affect hydrate distribution and the physical properties measured after pressure cores have been stored for prolonged periods of time.

## 6. SEDIMENT INDEX PROPERTIES

[57] The properties and behavior of sediments result from complex mechanical, hydraulic, electrical, thermal, and chemical interactions between mineral grains and pore fluids. These interactions are expressed in terms of sediment index properties, which capture grain and pore fluid characteristics that have profound effects on the morphology, extent, and growth characteristics of natural gas hydrate [*Winters et al.*, 1999]. Index properties can be used to anticipate hydrate occurrence, foresee phenomena during production, and estimate engineering properties for design. Salient index properties are listed in Table 3. Note that Tables 3–5 draw a distinction between coarse sediments, with a fines content below 7%, and fine-grained sediment having a fines content exceeding 15% of the sediment by mass. This distinction is drawn because the fines content, meaning the fraction of sediment grains smaller than 0.075 mm, exerts considerable control over the sediment behavior.

### 6.1. Hydrate Saturation and Distribution

[58] Gas hydrates are found in coarse-grained, fine-grained, and fracture-dominated reservoirs [*Collett et al.*, 2008; *Trehu et al.*, 2006]. As shown in Table 4, field studies suggest that correlations can be made between grain size, other sediment characteristics, and the modes of hydrate occurrence [*Booth et al.*, 1996, 1998]. Coarse-grained reservoirs, such as those found in the Mallik permafrost site in Canada and the Nankai Trough offshore Japan, tend to develop gas hydrate as a pore-filling material, occasionally reaching pore saturations of 80% (Table 4) [*Dallimore et al.*, 1999; *Winters et al.*, 1999]. Low volume fractions of hydrate are reported in fine-grained layers at these sites.

[59] Hydrate has been found extensively in fine-grained sediments elsewhere, however. For some cores taken at sites including the Blake Ridge offshore the U.S. east coast, Gulf of Mexico, offshore Taiwan, Hydrate Ridge offshore western Canada, and Indian Ocean, hydrates were found in fine-grained clayey sediments where the mass of fines content is typically over 60% and as high as 90%. Because of their

TABLE 4. Dominant Characteristics of Gas Hydrate-Bearing Reservoirs

Reservoir Type	Sediment Type	Dominant Gas Hydrate Type	Maximum $S_h$ (%)	LL (PI)	Locations	References
Coarse grained	sand, gravel	pore filling	80	–	Mackenzie Delta	<i>Dallimore et al.</i> [1999], <i>Uchida and Takashi</i> [2004], and <i>Winters et al.</i> [1999]
Fine grained	clay, silt	finely disseminated, nodules, layers	typically 10 except in discrete layers of segregated hydrate	0.68–0.99 (0.44–0.64)	Nankai Trough Blake Ridge	<i>Uchida and Takashi</i> [2004] <i>Paull and Matsumoto</i> [2000], <i>Trehu et al.</i> [2004], <i>Winters</i> [2000], and <i>Winters et al.</i> [2007]
				0.51–1.02 (0.28–0.57)	Gulf of Mexico	<i>Francisca et al.</i> [2005] and <i>Yun et al.</i> [2006]
				0.64–0.87 (0.25–0.45)	Hydrate Ridge	<i>Tan et al.</i> [2006]
				0.73–0.75 (0.34–0.36)	offshore India	<i>Yun et al.</i> (submitted manuscript, 2009)
Fractured	clay, silt	complex vertical veins	100 in discrete fractures	unknown	offshore India	<i>Collett et al.</i> [2008] and <i>Winters et al.</i> [2008]

abundance, fine-grained marine sediments collectively contain more gas hydrate than all coarse-grained reservoirs, even though disseminated gas hydrate saturations in the pore space of fine-grained sediments are typically <10%. As indicated in Figures 4 and 5, however, hydrate in fine-grained sediments often forms in localized areas of elevated permeability associated with slightly increased sediment grain size [Ginsburg et al., 2000] or faults [Nimblett and Ruppel, 2003; Wood and Ruppel, 2000]. In these cases, hydrate can form inhomogeneously as discrete nodules, sheets, or lenses [Clennell et al., 1999; Cook et al., 2008; Stern and Kirby, 2008; Trehu et al., 2004].

## 6.2. Phenomena During Production

[60] Index properties can be used to predict sediment behavior during methane production. For example, sand production [Walsh et al., 2009] or flow clogging due to migrating fine-grained material [Goldsztein and Santamarina, 2004; Valdes and Santamarina, 2007] may accompany methane production from coarse-grained hydrate-bearing sediments, while hydraulic fracturing and leaky reservoirs

should be expected when producing methane from fine-grained sediments.

## 6.3. Estimation of Design Parameters

[61] The use of index properties to obtain qualitative or semiquantitative estimates of baseline (hydrate-free) sediment behavior is based on correlations developed for sediments around the world [Lambe and Whitman, 1969; Mayne et al., 1992; Mitchell and Soga, 2005; Santamarina et al., 2001; Terzaghi et al., 1996]. Examples are presented in Table 5.

## 7. THERMAL PROPERTIES

[62] A material's response to the addition or loss of heat is described using the thermal conductivity,  $\lambda$  ( $\text{W m}^{-1} \text{K}^{-1}$ ); specific heat,  $c_p$  ( $\text{J kg}^{-1} \text{K}^{-1}$ ); and thermal diffusivity,  $\kappa$  ( $\text{m}^2 \text{s}^{-1}$ ). Heat flow in materials undergoing a phase change such as hydrates undergoing formation or dissociation is described by the enthalpy of reaction,  $\Delta H$  ( $\text{J mol}^{-1}$ ). The thermal properties of hydrate-bearing sediment components are summarized in Tables 6 and 7.

TABLE 5. Correlations Between Baseline Hydrate-Free Sediment Index Properties<sup>a</sup>

Parameter	Correlation	Reference
Compressibility	$C_c \approx 0.009(\text{LL} - 10)$ $C_c \approx [(\text{PI})G_s]/200$	<i>Terzaghi et al.</i> [1996] <i>Wroth and Wood</i> [1978]
Shear strength	$S_u = \sigma_v'[0.11 + 0.0037(\text{PI})]$	<i>Skempton</i> [1957]
Friction angle (fine)	$\Phi_{cv} = 0.8 - 0.094 \ln(\text{PI})$	<i>Mitchell and Soga</i> [2005]
Friction angle (coarse)	$\Phi_{cv} = 42 - 17R$	<i>Santamarina and Cho</i> [2004]
Hydraulic conductivity (fine)	$K = \frac{1}{S_g} \frac{\theta \gamma_w e^3}{\mu \rho_m^2 (1+e)}$	<i>Perloff and Baron</i> [1976]
Hydraulic conductivity (coarse)	$K = C_H(D_{10})^2$	Hazen's equation [ <i>Holtz and Kovacs</i> , 1981]
$e_{\max}$	$e_{\max} = 0.359 + 0.082R^{-1}$	<i>Santamarina and Cho</i> [2004]
$e_{\min}$	$e_{\min} = 0.554 + 0.154R^{-1}$	<i>Santamarina and Cho</i> [2004]

<sup>a</sup>Notation is as follows:  $C_c$ , compression index;  $C_H$ , Hazen's empirical coefficient,  $\sim 100 \text{ (cm s)}^{-1}$  or  $1 \times 10^4 \text{ (m s)}^{-1}$  [Carrier, 2003];  $D_{10}$ , diameter at which 10% of sample is finer;  $e$ , void ratio;  $e_{\max}$ , maximum void ratio;  $e_{\min}$ , minimum void ratio;  $K$ , hydraulic conductivity; LL, liquid limit; PI, plasticity index;  $R$ , roundness (particle shape);  $S_g$ , specific surface;  $S_u$ , undrained shear strength;  $\gamma_w$ , unit weight of water =  $\rho_w g$ , where  $\rho_w$  is mass density of water and  $g$  is  $9.8 \text{ m s}^{-2}$ ;  $\mu$ , dynamic fluid viscosity;  $\theta$ , shape and tortuosity factor;  $\rho_m$ , mass density of mineral grains;  $\sigma_v'$ , effective overburden stress at failure;  $\Phi_{cv}$ , friction angle during constant volume shear, also known as the critical state friction angle.

**TABLE 6. Thermal Properties of Hydrate-Bearing Sediment Components<sup>a</sup>**

Material	$\lambda$ (W m <sup>-1</sup> K <sup>-1</sup> )	$\kappa$ (m <sup>2</sup> s <sup>-1</sup> )	$c_p$ (J kg <sup>-1</sup> K <sup>-1</sup> )	$\rho$ (kg m <sup>-3</sup> )
Air	0.024 <sup>b</sup> (273 K)	$183 \times 10^{-7c}$	1010 <sup>b</sup> (273 K)	1.298 <sup>d</sup> (272 K)
Water	0.56 <sup>e</sup> (273 K)	$1.33 \times 10^{-7c}$	4218 <sup>e</sup> (273 K)	999.9 <sup>e</sup> (273 K)
Water	0.58 <sup>e</sup> (283 K)	$1.38 \times 10^{-7c}$	4192 <sup>e</sup> (283 K)	999.7 <sup>e</sup> (283 K)
Ice Ih	2.21 <sup>f</sup> (270 K)	$11.7 \times 10^{-7c}$	2052 <sup>g</sup> (270 K)	917 <sup>h</sup> (273 K)
Methane gas	0.0297 <sup>i</sup> (260 K, 1 MPa)	$18.0 \times 10^{-7c}$	2170 <sup>d</sup> (260 K)	7.61 <sup>j</sup> (260 K, 1 MPa)
Methane gas	0.099 <sup>i</sup> (260 K, 40 MPa)	$1.6 \times 10^{-7c}$	2170 <sup>d</sup> (260 K)	286 <sup>j</sup> (260 K, 40 MPa)
Methane hydrate, CH <sub>4</sub> · 6H <sub>2</sub> O	0.57 <sup>k</sup> (263 K)	$3.35 \times 10^{-7l}$	2031 <sup>m</sup> (263 K)	929 <sup>n</sup> (263 K)
THF + water, THF · 17H <sub>2</sub> O	0.47 <sup>f,o</sup> (283 K)	$3.12 \times 10^{-7c}$	4080 <sup>p</sup> (282 K)	982 <sup>q</sup> (283 K)
THF hydrate, THF · 17H <sub>2</sub> O	0.5 <sup>f</sup> (261 K)	$2.55 \times 10^{-7f}$	2020 <sup>f</sup> (261 K)	971 <sup>r</sup> (273 K)
THF hydrate, THF · 17H <sub>2</sub> O	0.5 <sup>f</sup> (261 K)	$2.60 \times 10^{-7c}$	1980 <sup>s</sup> (260 K)	971 <sup>r</sup> (273 K)
Quartz	7.7 to 8.4 <sup>t</sup>	$41 \times 10^{-7c}$	730 <sup>b</sup> (273 K)	2650 <sup>h</sup>

<sup>a</sup>Temperature is in kelvins, and pressure is in megapascals. THF, tetrahydrofuran.

<sup>b</sup>Kaye and Laby (Tables of Physical and Chemical Constants, National Physical Laboratory, 2008, <http://www.kayelaby.npl.co.uk/>).

<sup>c</sup>Calculated from equation (4).

<sup>d</sup>Engineering ToolBox (Material Properties, available at <http://www.engineeringtoolbox.com/>).

<sup>e</sup>Weast [1987].

<sup>f</sup>Waite et al. [2005].

<sup>g</sup>Leaist et al. [1982].

<sup>h</sup>Dvorkin et al. [2000].

<sup>i</sup>Vargaftik et al. [1993].

<sup>j</sup>Sychev et al. [1987].

<sup>k</sup>Huang and Fan [2004].

<sup>l</sup>Turner et al. [2005].

<sup>m</sup>Handa [1986].

<sup>n</sup>Waite et al. [2007].

<sup>o</sup>BASF Corporation [1998].

<sup>p</sup>Tombari et al. [2006].

<sup>q</sup>Smallwood [2002].

<sup>r</sup>Mork et al. [2000].

<sup>s</sup>Handa et al. [1984].

<sup>t</sup>Revil [2000].

## 7.1. Thermal Conductivity, $\lambda$

[63] Thermal conductivity quantifies the efficiency of heat transport. In sediments, this involves transport (1) from grain to grain, (2) from grain to liquid to grain, and (3) through pore-filling liquid [deMartin, 2001; Waite et al., 2002; Yun and Santamarina, 2008]. Rather than calculate the contribution of each heat transport path explicitly, thermal conductivity is often estimated using a two-phase mixing model to combine the thermal conductivities of the sediment grains with the pore fluid. As shown in Tables 6 and 7, the thermal conductivities of methane hydrate and water differ by <10% at the temperatures found in hydrate-bearing sediments [Huang and Fan, 2004; Waite et al., 2007; Weast, 1987]. For this reason, first-order thermal conductivity estimates can neglect the presence of methane hydrate and assume the sediment pore space contains only water [Ruppel, 2000].

[64] The presence of gas complicates the analysis by adding a phase with strongly contrasting thermal properties (Table 6). The pore fluid can no longer be treated simply by

averaging the thermal conductivities of water and gas because as the wetting phase, water migrates to contacts and enhances grain-to-grain conduction. Hence, even low degrees of water saturation have a strong effect on thermal conductivity [Andersland and Ladanyi, 2004; Farouki, 1985; Lu et al., 2007; Singh and Devid, 2000].

[65] As described by Cortes et al. [2009], even in gas-free systems, precise thermal conductivity calculations must account for sediment-altering processes caused by hydrate formation, including porosity changes [Tarnawski et al., 2002] and the associated effective stress changes [Sridhar and Yovanovich, 1996], as well as the improved thermal transport across the sediment grain–hydrate interface compared to the sediment grain–water interface [Swartz and Pohl, 1989].

[66] Despite these shortcomings, simple mixing models provide reasonable bounds for thermal conductivity values. As shown in Table 8 and Figure 6, the parallel model, in which heat travels simultaneously through the pore fill and the sediment grains, and the series model, in which heat

**TABLE 7. Temperature Dependence of Methane Hydrate Thermal Properties<sup>a</sup>**

Temperature Dependence Fit Equations	Temperature Range
$\lambda$ (W m <sup>-1</sup> K <sup>-1</sup> ) = $-(2.78 \pm 0.05) \times 10^{-4}T$ (°C) + (0.624 ± 0.001)	−20°C to 17°C <sup>b</sup>
$\lambda$ (W m <sup>-1</sup> K <sup>-1</sup> ) = $-1.99 \times 10^{-4}T$ (°C) + 0.682	−12°C to 4°C <sup>c</sup>
$\kappa^d$ (m <sup>2</sup> s <sup>-1</sup> ) = $(4.70 \pm 0.02) \times 10^{-5}T$ (K) + $(1.35 \pm 0.03) \times 10^{-7}$	−128°C to 17°C <sup>b</sup> (145 to 290 K)
$c_p$ (J kg <sup>-1</sup> K <sup>-1</sup> ) = $(6.1 \pm 0.3)T$ (°C) + (2160 ± 20)	1°C to 17°C <sup>b</sup>
$c_p$ (J kg <sup>-1</sup> K <sup>-1</sup> ) = 13T (°C) + 2215	−9°C to 3°C <sup>c</sup>

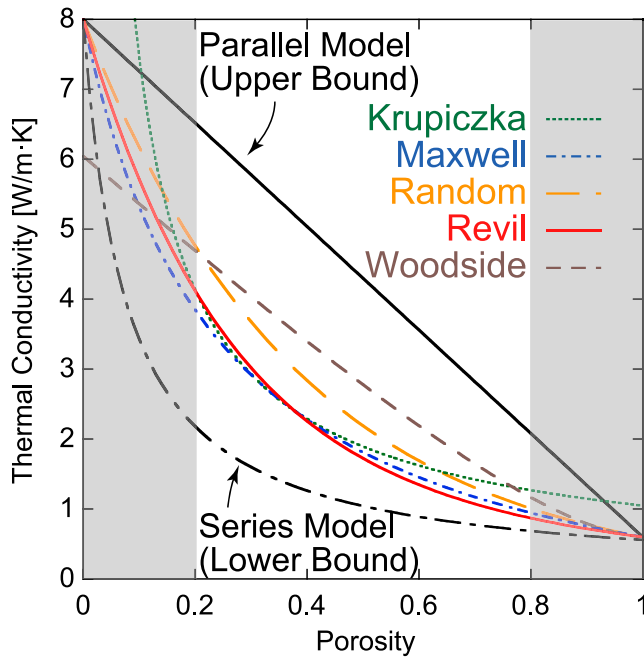
<sup>a</sup>Temperatures in Celsius unless otherwise noted.

<sup>b</sup>Waite et al. [2007], measured at 31.5 MPa.

<sup>c</sup>Rosenbaum et al. [2007], measured between 2.5 and 43.7 MPa.

<sup>d</sup>The  $T^{-1}$  dependence of the  $\kappa$  fit requires input temperatures in kelvins.

<sup>e</sup>Nakagawa et al. [2008], measured at 5 MPa.



**Figure 6.** Model predictions for mixtures of quartz ( $8.0 \text{ W m}^{-1} \text{ K}^{-1}$ ) and water ( $0.6 \text{ W m}^{-1} \text{ K}^{-1}$ ). White region denotes the range of relevant porosities.

alternates between flowing through the pore fill and the sediment, provide the upper and lower bounds, respectively, for thermal conductivity. The models of Krupiczka [1967], Maxwell [1954], and Revil [2000], collected by Revil [2000], yield similar results lying midway between the upper and lower bounds.

## 7.2. Specific Heat, $c_p$

[67] Specific heat measures the heat stored in, or extracted from, a material due to a temperature change. Unlike thermal conductivity, specific heat depends only on the mass fractions of sediment, hydrate, and water rather than on their pore-scale distribution and interfacial effects. Using the subscripts  $m$ ,  $w$ , and  $h$  to refer to the host sediment mineral, pore water, and methane hydrate, respec-

tively, the formation's bulk specific heat,  $c_{p,b}$ , is given for a gas-free system by

$$c_{p,b}\rho_b = c_{p,m}\rho_m(1 - \phi) + c_{p,w}\rho_w(1 - S_h)\phi + c_{p,h}\rho_h S_h\phi, \quad (2)$$

where  $\rho_b$  is given by the mass fractions of the sediment grains, water, and hydrate,

$$\rho_b = \rho_m(1 - \phi) + \rho_w(1 - S_h)\phi + \rho_h S_h\phi. \quad (3)$$

Here the porosity,  $\phi$ , and hydrate saturation,  $S_h$ , must be considered in decimal notation rather than in units of percent.

[68] Because the specific heat of methane hydrate is less than half that of water, hydrate formation can significantly lower the specific heat of hydrate-bearing sediments [Waite et al., 2007]. Hydrate-bearing layers with potentially economic hydrate saturations for production, such as the Mallik 5L-38 permafrost hydrate well with porosity,  $\phi$ , of  $\sim 35\%$  and methane hydrate saturation,  $S_h$ , of  $\sim 80\%$  [Collett et al., 2005], are particularly affected by the presence of hydrate [Kurihara et al., 2005; Moridis et al., 2005]. Depending on sediment porosity, even in sediments with moderate hydrate saturations of 20%–40%, the specific heat is reduced by  $\sim 10\%$  relative to hydrate-free sediment [Waite et al., 2007].

## 7.3. Thermal Diffusivity, $\kappa$

[69] Thermal diffusivity is a measure of the rate at which a body changes temperature when subjected to an external heat flux. In the absence of systematic studies of thermal diffusivity, we quantify the effect of hydrate on the properties of hydrate-bearing sediment by combining the thermal conductivity,  $\lambda$ ; specific heat,  $c_p$ ; and density,  $\rho$ , results discussed in sections 7.1 and 7.2 with the definition of thermal diffusivity,  $\kappa$ ,

$$\kappa = \frac{\lambda}{\rho c_p}. \quad (4)$$

[70] The thermal diffusivity of methane hydrate is more than twice that of water; therefore, hydrate-bearing sedi-

**TABLE 8. Common Thermal Conductivity Mixing Models<sup>a</sup>**

Model	Equation for the Estimation of $\lambda_{\text{effective}}$
Parallel (upper bound) [Huang and Fan, 2005]	$\phi \lambda_f + (1 - \phi) \lambda_s$
Series (lower bound) [Huang and Fan, 2005]	$\frac{\lambda_f \lambda_s}{\phi \lambda_s + (1 - \phi) \lambda_f}$
Krupiczka [1967]	$\lambda_f \left( \frac{\lambda_s}{\lambda_f} \right)^{A+B \log_{10} \left( \frac{\lambda_s}{\lambda_f} \right)}, A = 0.280 - 0.757 \log_{10}(\phi), B = -0.057$
Maxwell [1954]	$\lambda_f \frac{2\phi \lambda_f + (3 - 2\phi) \lambda_s}{(3 - \phi) \lambda_f + \phi \lambda_s}$
Random [Huang and Fan, 2005]	$\lambda_f^\phi \lambda_s^{(1 - \phi)}$
Revil [2000]	$\frac{\lambda_f}{\xi} \left[ \xi \Theta + \frac{1}{2} (1 - \Theta) \left( 1 - \Theta + \sqrt{(1 - \Theta)^2 + 4\xi \Theta} \right) \right], \Theta = \frac{\lambda_s}{\lambda_f}, \xi = \phi \left( \frac{m}{1 - m} \right)$
Woodside and Messmer [1961]	$A \lambda_f + \frac{B \lambda_s \lambda_f}{\lambda_s (1 - C) + C \lambda_f}, A = \phi - 0.03, B = 1 - A, C = (1 - \phi)/B$

<sup>a</sup>See Figure 6 for an illustration of their behavior in a quartz sediment and water system.

ments can change temperature more rapidly than hydrate-free sediments [Waite et al., 2007]. In sediment with porosity  $\phi = 35\%$ , a hydrate saturation  $S_h = 35\%$  increases heating rates by more than 10% relative to those in the absence of hydrate. This effect is magnified in high-porosity formations, such as the 74% porosity, near-surface sediments on the Congo continental slope [Sultan et al., 2004b]. In this environment, hydrate saturations of only 19%–22% reduce heating times relative to hydrate-free sediment by more than 10%. Hydrate should therefore be accounted for in transient heat flow applications such as safety assessments for drilling into or through hydrate-bearing sediment [Briaud and Chaouch, 1997; Hadley et al., 2008; Ji et al., 2003; Pooladi-Darvish, 2004].

#### 7.4. Enthalpy of Reaction, $\Delta H$

[71] The organized hydrate structure has less internal energy than a freely moving, disordered combination of methane and water, so energy must be released for hydrate to form and reabsorbed for hydrate to dissociate [Rydzy et al., 2007]. This energy change is defined as the enthalpy of reaction,  $\Delta H$ .

[72] Calorimetry can provide measurements of  $\Delta H$ , but only a limited number of studies are available. Enthalpies can also be estimated from phase equilibrium and thermodynamic data using the Clausius-Clapeyron equation to relate pressure,  $P$ ; temperature,  $T$ ; enthalpy,  $\Delta H$ ; and compressibility,  $Z$ :

$$\frac{d \ln P}{d \left( \frac{1}{T} \right)} = \frac{-\Delta H}{ZR}, \quad (5)$$

where  $R$  is the ideal gas constant. The validity of this method is contingent upon negligible changes in compressibility. There is good agreement between experimental results and indirectly derived enthalpies from the Clausius-Clapeyron method.

[73] The ice-water enthalpy of melting is  $\sim 6 \text{ kJ mol}^{-1}$  [Handa, 1986; Kumano et al., 2007]. Per mole of guest molecule, the enthalpy of dissociation of structure I methane hydrate into methane gas and liquid water is  $\Delta H = 52.7\text{--}56.9 \text{ kJ mol}^{-1}$  at  $T \sim 0^\circ\text{C}$  [De Roo et al., 1983; Deaton and Frost, 1946; Handa, 1986; Kang et al., 2001; Kuuskraa et al., 1983; Lee et al., 2005; Lievois et al., 1990; Rueff et al., 1988; Sloan and Fleyfel, 1992; Voronov et al., 2008].  $\Delta H$  is insensitive to pressure and temperature for conditions typical in terrestrial applications, remaining in the range  $54.44 \pm 1.46 \text{ kJ mol}^{-1}$  between 5.5 and 19.3 MPa and  $7.5^\circ\text{C}\text{--}18.5^\circ\text{C}$  [Gupta et al., 2008].

[74] Replacing just 1% of the hydrate methane with ethane, however, increases  $\Delta H$  by  $\sim 30\%$  to  $68.7 \text{ kJ mol}^{-1}$  [Rydzy et al., 2007], and a structure II propane hydrate has a  $\Delta H$  of  $129.2 \text{ kJ mol}^{-1}$  [Handa, 1986]. This illustrates that  $\Delta H$  depends on the guest molecule but is primarily controlled by the number of hydrogen-bonded water molecules. Typically, there are  $\sim 6$  water molecules per guest molecule

in structure I hydrate [Circone et al., 2005, 2006] but  $\sim 17$  per guest in structure II hydrate [Davidson, 1973].

[75] The heat of reaction can be significant when generating hydrate for storing large volumes of gases. When dissociating hydrate to produce methane from permafrost regions or beneath the ocean floor, the heat absorbed during hydrate dissociation can cool the surroundings, resulting in secondary hydrate or ice formation, both of which reduce the permeability of the producing formation [Moridis et al., 2008]. Moreover, the enthalpy variation with guest occupant means the heat of reaction for dissociation may not be constant throughout a formation, nor over the lifetime of a production well, complicating production rate predictions.

### 8. PERMEABILITY AND FLUID MIGRATION

[76] Permeability controls fluid migration through sedimentary systems and plays an important role in heat and chemical transfer occurring via fluid migration. In hydrate-bearing sediments, permeability affects dissolved gas and free gas transport as well as the accumulation, distribution, and concentration of hydrate [Bhatnagar et al., 2007; Garg et al., 2008; Liu and Flemings, 2007; Nimblett and Ruppel, 2003]; the ability to produce gas from hydrate reservoirs [Moridis, 2003; Moridis et al., 2004, 2007]; local perturbations of the hydrate stability field [Wood et al., 2002]; and methane flux to the ocean [Moridis and Reagan, 2007a, 2007b; Reagan and Moridis, 2007]. In spite of the importance of flow through hydrate-bearing systems [Gbaruko et al., 2007; Haacke et al., 2007; Hensen and Wallmann, 2005; Shankar et al., 2006], few reliable permeability measurements are available [Minagawa et al., 2005, 2008; Nadem et al., 1988].

[77] Macroscale analyses of single-phase and multiphase flow in sediments generally assume the sediments can be represented by an equivalent homogeneous porous medium; however, a proper understanding of conduction properties requires the pore-scale assessment of the multiple coexisting phases and of all relevant flow pathways.

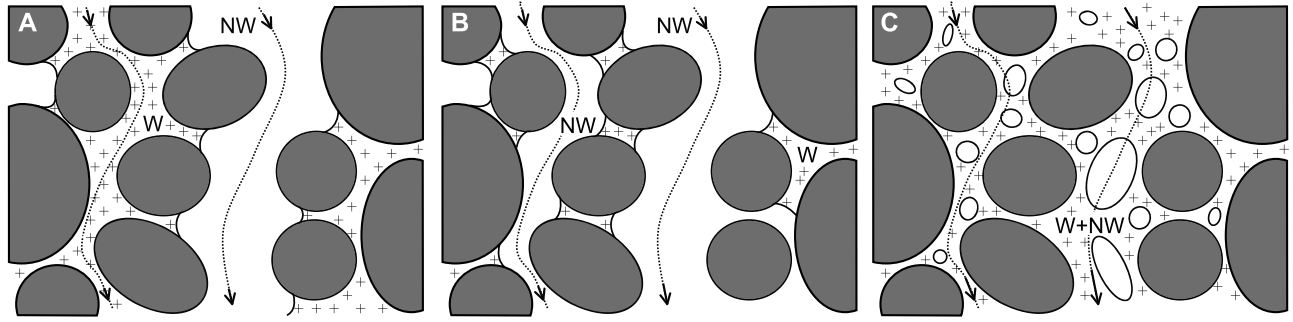
#### 8.1. Single-Phase Fluid Flow

[78] Single-phase flow rate,  $q$  ( $\text{m}^3 \text{ s}^{-1}$ ), through a porous medium under laminar conditions is described by Darcy's law,

$$q = \frac{-k \rho_f g}{\mu_f} \frac{d \left( \frac{P}{\rho_f g} + z \right)}{dl} A, \quad (6)$$

where  $A$  ( $\text{m}^2$ ) is the cross-sectional area,  $z$  (m) is the elevation above a reference datum,  $P$  (Pa) is the pressure at elevation  $z$ ,  $\mu_f$  (Pa s) is the dynamic fluid viscosity,  $l$  (m) is the length over which the flow-driving change ( $P/\rho_f g + z$ ) is measured,  $k$  ( $\text{m}^2$ ) is the intrinsic permeability of the porous medium,  $\rho_f$  ( $\text{kg m}^{-3}$ ) is the mass density of the fluid, and  $g = 9.8 \text{ m s}^{-2}$  is the acceleration due to gravity.

[79] The intrinsic permeability is a measure of fluid flowability through a porous medium, and it is determined



**Figure 7.** Illustrations showing end-member multiphase fluid saturations and complexity of multiphase flow. (a and b) Stable fluid interfaces and (c) unstable conditions. In Figure 7a, phases occupy different channels according to wettability properties: nonwetting phase (NW) occupies larger pores, and wetting phase (W) occupies smaller pores. In Figure 7b, wetting phase is discontinuous and isolated to small pore throats. The wetting phase irreducible saturation has been reached in Figure 7b, and only the nonwetting fluid flows. In Figure 7c, both phases flow together, one dispersed in the other.

by the interconnectivity and size of voids within the medium. The tortuosity,  $\theta$ , defined as the ratio  $(l/l_E)^2$  accounts for the effective flow path,  $l_E$ , being longer than the sample length,  $l$ . Typical values for  $\theta$  range from 0.4 to 0.8 [Bear, 1972]. Physically, the dependence on void size, which can also be expressed as a specific surface area,  $S_s$  ( $m^2$ ), represents the frictional drag between the flowing fluid and the sediment grain surfaces.

[80] The Kozeny-Carman model captures the permeability's strong dependence on sediment specific surface area,  $S_s$ ; the role of tortuosity,  $\theta$ ; and the lesser effect of void ratio,  $e$  (form adapted from Perloff and Baron [1976]):

$$k = \left( \frac{\theta}{\rho_m^2 S_s^2} \right) \left( \frac{e^3}{1+e} \right), \quad (7)$$

where the grain mineral density,  $\rho_m$ , relates the gravimetric specific surface to the volumetric nature of permeability (see other models in Table 5). The intrinsic permeability of a sediment given in equation (7) can be converted to the hydraulic conductivity for a given fluid (Table 5) by taking into consideration the fluid dynamic viscosity,  $\mu_f$ , and unit weight,  $\rho_f g$ , through a multiplicative factor,  $\rho_f g / \mu_f$ .

[81] The correlation between specific surface area and permeability is readily established with clays (Table 5 [Carrier, 2003]), but it can be useful to relate permeability to sediment size rather than specific surface area. To convert from specific surface area to grain size, consider that a particle's surface area is determined by its smallest dimension, which corresponds to the diameter of rotund sandy grains or the thickness of platy clay particles. When this observation is extended to the entire sediment mass, it follows that the specific surface of sediments is governed by the specific surface of the finest fraction. Hence,  $k$  correlates well with the size of the finer grains in sandy sediments,  $D_{10}$ , as in Hazen's equation (Table 5).

[82] Given the wide range in particle sizes, permeability varies over 10 orders of magnitude between clay and clean

sand sediments [Dullien, 1992]. In general, expressions based on sediment index properties such as  $S_s$  and  $D_{10}$  provide order-of-magnitude permeability estimates only. In addition, other local geologic features such as grain orientation anisotropy, lithology, fractures, stratigraphic variability, or hydrate presence can all produce dramatic changes in the permeability field, and empirical relations should be used with care.

[83] Laboratory measurements show that permeability is scale-dependent [Tidwell and Wilson, 1997] as all natural media have some degree of spatial variability (Figures 4 and 5). Thus, permeability measured on the core scale will differ from permeability inferred from field-scale flow measurements. Complementary core-scale information gathered using X-ray CT imaging [Jin et al., 2007], electrical measurements (section 9), and NMR [Kleinberg et al., 2005; Kleinberg et al., 2003] helps develop robust conceptual models that can then be upscaled based on seismic imagery to handle field-scale spatial variability in simulations of flow in hydrate-bearing sediments.

## 8.2. Multiphase Fluid Flow

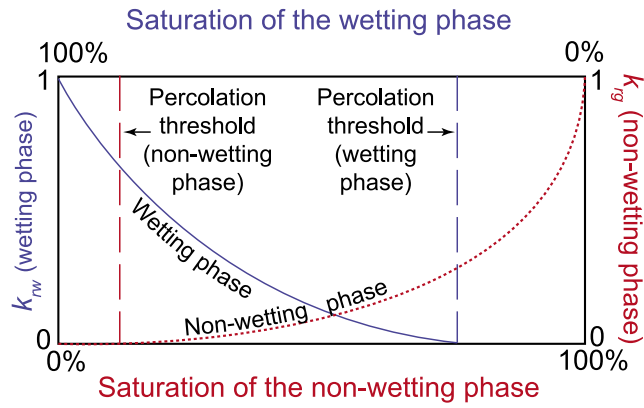
[84] Steady state immiscible flow in multiphase systems, such as gas and water flow in hydrate systems, can be modeled as Darcian flow by incorporating relative permeabilities for water,  $k_{rw}$ , and gas,  $k_{rg}$ ,

$$q_w = -k_{rw} \frac{k \rho_w g}{\mu_w} \frac{d \left( \frac{P_w}{\rho_w g} + z \right)}{dl} A \quad (8)$$

$$q_g = -k_{rg} \frac{k \rho_g g}{\mu_g} \frac{d \left( \frac{P_g}{\rho_g g} + z \right)}{dl} A. \quad (9)$$

[85] The dimensionless relative permeabilities  $k_{rw}$  and  $k_{rg}$  vary from 0 to 1 and are functions of phase saturations, the





**Figure 8.** Relative permeability curves for a two-phase flow system. Interfacial tension causes the nonlinearity in the relative permeability curves for water,  $k_{rw}$ , and gas,  $k_{rg}$ , and imposes percolation thresholds marking the lower saturation limit required for conventional fluid flow. While the two phases interfere with each other's flow,  $k_{rw} + k_{rg} < 1$ . Shown are the typical curve shapes for water and gas. For water or gas saturations below their respective percolation limits, water can flow as a film or vapor phase, and gas can flow as a dissolved phase. These types of flow are limited and hence do not contribute to the relative permeabilities plotted in Figure 8.

spatial distribution of the phases, mineral wettability, and pore space geometry (Figure 7). Relative permeabilities  $k_{rw}$  and  $k_{rg}$  vary with water and gas saturations as shown in Figure 8 (see *Dong and Dullien* [2006] for numerical examples). Note that relative permeabilities typically add up to  $< 1$  because of fluid-to-fluid interactions. For example, water wets mineral surfaces in most sediments; this preferential wetting means that gas or oil will tend to occupy larger pore spaces and significantly reduce water flow.

[86] Water saturation,  $S_w$ , is determined by the pressure difference between fluid and gas, or capillary pressure,  $\Delta P = P_g - P_w$ , which depends on the pore size distribution in the sediment (see section 2.2). A common model used to capture this dependency follows the formulations of *van Genuchten* [1980], shown here in the form from *Parker et al.* [1987],

$$S_{w, \text{eff}} = \left[ 1 + \alpha^n \left( \frac{\Delta P}{g \rho_w} \right)^n \right]^{-m} = \frac{S_w - S_{w, \text{irr}}}{1 - S_{w, \text{irr}}}, \quad (10)$$

where  $m = (n - 1)/n$ . Note that the expression is in terms of the effective water saturation,  $S_{w, \text{eff}}$ , which is the actual water saturation,  $S_w$ , corrected for the sediment irreducible water saturation,  $S_{w, \text{irr}}$ . The fitting parameter  $\alpha$  is related to the modal pore size, while  $n$  is a function of the spread of the pore size distribution. For example,  $\alpha$  is  $4.57 \text{ m}^{-1}$  and  $n$  is 7.43 for a volcanic sand,  $\alpha$  is  $1.94 \text{ m}^{-1}$  and  $n$  is 9.06 for Berea Sandstone, and  $\alpha$  is  $0.15 \text{ m}^{-1}$  and  $n$  is 1.17 for Biet Netofa clay (values for additional materials are compiled by *Carsel and Parrish* [1988] and by *Ghezzehei et al.* [2007]).

[87] In terms of the effective water saturation, the relative permeabilities of water and gas are given by [*Parker et al.*, 1987]

$$k_{rw} = S_{w, \text{eff}}^{1/2} \left[ 1 - \left( 1 - S_{w, \text{eff}}^{1/m} \right)^m \right]^2 \quad (11)$$

$$k_{rg} = C(1 - S_{w, \text{eff}})^{1/2} \left( 1 - S_{w, \text{eff}}^{1/m} \right)^{2m}, \quad (12)$$

where  $C$  is a “gas slippage” correction that approaches 1 as the grain size increases. Other models include the Brooks and Corey model [*Honarpour et al.*, 1986; *Pruess and Moridis*, 1999] and the Stone power model [*Rutqvist and Moridis*, 2007].

### 8.3. Fluid Flow in Hydrate-Bearing Systems

[88] The presence of hydrate adds additional complications because hydrate can alter flow and affect permeability by reducing the pore size and changing the pore shape. Pore-filling hydrate reduces the permeability more significantly than mineral-coating hydrate [*Liu and Flemings*, 2007]; however, hydrate at grain contacts can readily block pore throats, causing a more pronounced reduction in permeability. Based on the limited data available for gas-free, hydrate-bearing systems [*Minagawa et al.*, 2008], pore-filling hydrate models provide the best estimates of permeability [*Kleinberg et al.*, 2003; *Lee*, 2008].

[89] Water-saturated systems evolve into multiphase gas and water systems if gas invades the hydrate stability field [*Flemings et al.*, 2003; *Liu and Flemings*, 2006, 2007] or if hydrate begins dissociating [*Tryon et al.*, 2002]. The van Genuchten model described in section 8.2 has been adapted to the simulation of dissociation in hydrate-bearing sediments [*Hong and Pooladi-Darvish*, 2005; *Moridis et al.*, 2005]. However, the evolution of water saturation and capillary pressure during dissociation differs from imbibition processes typically used to determine the water retention curve and relative permeability values for sediment.

[90] There are also additional particle-scale mechanisms that impact relative permeability. For example, where hydrate supports the frame of the medium, permeability may increase as hydrate is removed from the system but then decrease as the granular skeleton collapses. Hence, further research is still required to better quantify relative gas and water permeabilities in hydrate-bearing sediment and their evolution during dissociation.

## 9. ELECTROMAGNETIC PROPERTIES

[91] Three electromagnetic phenomena have direct applications to the study of hydrate-bearing sediments: steady state charge migration under an applied constant electric field (conduction), frequency-dependent polarization (permittivity), and magnetization (permeability). Inertial and viscous forces oppose charge displacement and rotations, meaning that permittivity and magnetic permeability are

frequency-dependent, and their response is partially out of phase with the electrical excitation. Permittivity and magnetic permeability are therefore expressed as complex numbers to capture both the magnitude of each parameter and its phase relative to the excitation. Symbolically, these three electromagnetic parameters are electrical conductivity,  $\sigma$ ; complex permittivity (relative to “free space”  $\epsilon_0$ ),  $\kappa^* = \kappa' - j\kappa''$ ; and complex permeability (relative to “free space”  $\mu_0$ ),  $\mu^* = \mu' - j\mu''$ .

[92] Components of hydrate-bearing sediments are generally nonferromagnetic, and the magnetic permeability is assumed to be  $\mu^* \approx 1$ . This section therefore focuses on the conductivity and permittivity of hydrate-bearing sediments. Both properties reflect characteristics of the sediment components, their volume fraction, and their spatial arrangement. Detailed reviews and estimation guidelines for these parameters are given by *Santamarina et al.* [2001, 2005]; a comprehensive database of permittivity and conductivity measurements for hydrate-bearing clay, silt, and sand at different effective stress and hydrate saturation levels is documented by *Lee* [2007] and J. Y. Lee et al. (Parametric study of the physical properties of hydrate-bearing sand, silt, and clay sediments. Part I: Electromagnetic properties, submitted to *Journal of Geophysical Research*, 2009).

### 9.1. Electrical Conductivity of Hydrate-Bearing Sediments

[93] Electrical conduction in sediments consists of the movement of hydrated ions in the pore fluid and in electrical double layers around mineral surfaces. The electrical conductivity of the pore water,  $\sigma_w$ , is proportional to the concentration,  $c$ , of mobile hydrated ions,  $\sigma_w = \zeta c$ . The molar conductivity,  $\zeta$ , describes the ionic mobility, a characteristic parameter for each ion, which decreases as the ion's concentration approaches saturation. The following empirical approximation is valid for seawater [*Annan*, 1992]:

$$\sigma_w = 0.15(\text{TDS}), \quad (13)$$

where  $\sigma_w$  is in  $\text{mS m}^{-1}$  and the total dissolved solids (TDS) are in  $\text{mg L}^{-1}$ . A nominal value for seawater conductivity is  $3 \text{ S m}^{-1}$ .

[94] Hydrated counterions are always present in the vicinity of minerals to neutralize their surface charge. These counterions also move when an electric field is imposed, contributing surface conduction,  $\lambda_{ddl}$ , to the bulk conduction. Mineral surface conduction becomes significant in sediments with a high specific surface area,  $S_s$ , such as clayey sediments; when the porosity is low, meaning that there is more mineral surface area per volume; and when the conductivity of the pore fluid is low, such as after hydrate dissociation and subsequent pore water freshening.

[95] The electrical conductivity of hydrate-bearing sediments is dominated by the electrical conductivity of the pore fluid,  $\sigma_f$ , scaled by the volume fraction of liquid in pores,  $\phi(1 - S_h - S_g)$ . However, surface conduction must also be considered in high surface area sediments. A first-order

approximation to the conductivity of hydrate-bearing sediments is [*Klein and Santamarina*, 2003]

$$\sigma_b = \sigma_f \phi(1 - S_h - S_g) + \frac{2}{2+e} \lambda_{ddl} \rho_m S_s, \quad (14)$$

where  $e$  is the void ratio and the hydrate, gas, and water saturations are defined in terms of  $V_v$ , the pore volume in the mineral skeleton:  $S_h = V_h/V_v$ ,  $S_g = V_g/V_v$ , and  $S_w = V_w/V_v$  so that  $1 = S_g + S_h + S_w$ .

[96] Equation (14) does not account for the relative spatial arrangement of the mineral grains; fluid, hydrate, and gas phases; nor their interconnectedness [*Spangenberg*, 2001; *Spangenberg and Kulenkampff*, 2006]. Archie's semi-empirical expression is often used to add degrees of freedom to the expression in order to describe these interactions but fails to capture surface conduction accounted for in equation (14) [*Archie*, 1942]. In terms of resistivities,  $\rho = 1/\sigma$ ,

$$(1 - S_h - S_g) = \left( \alpha \frac{\rho_f}{\rho_b} \phi^\beta \right)^{\frac{1}{\chi}}, \quad (15)$$

where  $\alpha$ ,  $\beta$ , and  $\chi$  are empirically determined parameters. This equation is extensively applied in hydrate studies, as summarized in Table 9 (see typical field data given by *Jin et al.* [2002]). Because Archie-type equations fail to properly capture the additive contribution of surface conduction, the reliability of Archie parameters (Table 9) in applications such as production monitoring studies requires careful reassessment [*Lee et al.*, 2008; *Santamarina and Ruppel*, 2008].

### 9.2. Permittivity of Hydrate-Bearing Sediments

[97] To avoid electrode polarization, conductivity is determined by imposing an AC field of frequency  $\omega$ . As a result, the measured conductivity,  $\sigma_{AC}$ , contains Ohmic effects,  $\sigma_{DC}$ , as well as a contribution from the polarization losses,  $\kappa''$ ; the measured value is  $\sigma_{AC} = \sigma_{DC} + \kappa'' \epsilon_0 \omega$ . The contribution due to polarization losses is typically small when the operating frequencies are in the Hz to kHz range, so here we focus on  $\kappa'$ , the real component of the complex permittivity.

[98] Nominal permittivity values for components of hydrate-bearing sediments in the microwave frequency range are as follows: unfrozen water,  $\kappa_w' = 86$  (at  $4^\circ\text{C}$ ); gas/air,  $\kappa_g' \approx 1$ ; oil,  $\kappa_{oil}' = 3-5$ ; most minerals,  $\kappa_m' = 4-9$ ; and methane hydrate,  $\kappa_h' = 2.5$ . The polarization of unfrozen water dominates the permittivity of hydrate-bearing sediments, though the permittivity of hydrate may be significantly higher at lower frequencies. A first approximation to the high-frequency permittivity of hydrate-bearing sediments,  $\kappa_b'$ , is a volumetric linear combination,

$$\kappa_b' = (1 - \phi) \kappa_m' + \phi \left( \kappa_g' S_g + \kappa_h' S_h + \kappa_w' S_w \right). \quad (16)$$

[99] Geometric and spatial effects alter the permittivity of the mixture. Averaging by traveltime resembles the complex

TABLE 9. Applications of Archie's Law<sup>a</sup>

Site	Equation	$\alpha$	$\beta$	$\chi$	Reference
Blake Ridge (ODP Leg 164)	$S_h = 1 - (\rho_{sed}/\rho_b)^{\frac{1}{\beta}}$ . The background resistivity of the fully water saturated sediment without hydrate is $\rho_{sed} = 0.8495 + (2.986 \times 10^{-4})z$ (m) for the Blake Ridge.	$\phi^{\beta}$ , $\alpha$ , and $\rho_f$ cancel when $\rho_{sed}/\rho_b$ is computed	$\phi^{\beta}$ , $\alpha$ , and $\rho_f$ cancel when $\rho_{sed}/\rho_b$ is computed	1.9386	Lu and McMechan [2002]
Hydrate Ridge (ODP Leg 204)	$\rho_f = 0.33 \Omega \text{ m}$ , $\phi = 0.65$ for GHSZ (CSEM, 5 and 15 Hz) $\rho_b = \alpha \rho_f \phi^{\beta} = 0.55 \phi^{\beta}$ >20 mbsf shallow	1.05 1	-2.56 -2.8	1.9386 1.9	Collett and Ladd [2000] Weitemeyer et al. [2006]
Mallik	$\rho_f = 0.56$ ( $z = 738.23$ m), $\rho_f = 0.27$ ( $z = 1141.02$ m)	— 0.967 1.35 0.62	-1.3 -2.81 -1.76 -2.15	1.9386 1.96 1.96 1.9386	Lee and Collett [2006] Riedel et al. [2006] Riedel et al. [2006] Lee and Collett [2005], Guerin and Goldberg [2002], and Reister [2003]
Cascadia margin/ Makran region	$\rho_f = 1/(3 + T (^{\circ}\text{C})/10)$	1	-2.8	1.9	Ghosh et al. [2006]
Vancouver island	$\rho_f = (C_{sw}/C_f)\rho_{sw}$ , where $C_{sw}$ is salinity of the seawater reference and $C_f$ is salinity of the in situ fluid	1.4	-1.76	1.76	Hyndman et al. [1999]
Milne Point, North Slope of Alaska	$\alpha \rho_f = 1 \Omega \text{ m}$ $\rho_f = 3 \Omega \text{ m}$ , $0.5 < \alpha < 2.5$ , $-3 < \beta < -1.5$	— 1	-2.15 -2	1.9386 2	Lee [2005] Edwards [1997]

<sup>a</sup>General form for no gas phase  $S_g = 0$ :  $S_w = [\alpha(\rho_f/\rho_b)\phi^{\beta}]^{\frac{1}{1-\beta}}$  or  $S_h = (1 - S_w) = 1 - [\alpha(\rho_f/\rho_b)\phi^{\beta}]^{\frac{1}{1-\beta}}$ .  $S_h = V_h/V_v$ ,  $S_g = V_g/V_v$ ,  $S_f = V_f/V_v$ , and  $1 = S_g + S_h + S_f$ . GHSZ, gas hydrate stability zone; ODP, Ocean Drilling Program. The cautious use of these parameters is suggested by Santamarina and Ruppel [2008].

refraction index mixing model albeit assuming lossless media. In the case of hydrate-bearing sediments, this frequently adopted model becomes

$$\kappa'_b = \left[ (1 - \phi) \sqrt{\kappa'_m} + \phi \left( S_g \sqrt{\kappa'_g} + S_h \sqrt{\kappa'_h} + S_w \sqrt{\kappa'_w} \right) \right]^2. \quad (17)$$

Equation (17) and similar formulations have been applied to Gulf of Mexico sediments [Francisca et al., 2005], Mallik permafrost hydrate field measurements [Lee and Collett, 2005; Sun and Goldberg, 2005], and laboratory measurements [Lee et al., 2008]. Polynomial expressions are also used [Kliner and Grozic, 2006], and semiempirical equations developed for unsaturated soils can be adapted to hydrate-bearing sediments with free gas [Topp et al., 1980; Wensink, 1993].

### 9.3. Field-Based Characterization of Hydrate-Bearing Sediments: Limitations

[100] Either resistivity or permittivity measurements can be used to distinguish between water and hydrate or other pore fillers such as gas or ice. Because ionic concentration has a second-order effect on permittivity but a primary effect on resistivity, permittivity is a more reliable parameter to estimate water saturation. For either measurement, hydrate saturation is extracted from the volumetric sum  $1 = S_h + S_w + S_g + S_{ice}$ . The common replacement  $S_h = 1 - S_w$  presumes that  $S_g = 0$ , which is not true in water-limited systems or during gas production, and that  $S_{ice} = 0$ , which is not true in permafrost hydrate or during fast pressurization that results in secondary ice formation.

[101] At the field scale, resistivity-based measurements, such as the profiles measured by Weitemeyer et al. [2006], have been used to estimate in situ hydrate saturation. More commonly, though, electrical measurements are paired with well log data to provide a more reliable hydrate saturation

estimate, which compliments information gathered from seismic data (section 10). Examples are provided by Coren et al. [2001], Guerin and Goldberg [2002], Lee [2002, 2005], Lee and Collett [2006], Ghosh et al. [2006], and Ellis et al. [2008], among others.

[102] The connection between electrical properties and hydrate saturation is generally based on Archie's equation (equation (15)). As noted in section 9.1 and Table 9, Archie parameters must be chosen with care. Several pore-scale characteristics, such as surface conduction and the nature of the sediment fabric in fine-grained sediments, are either disregarded or hidden in the Archie parameters [Santamarina and Ruppel, 2008; Spangenberg, 2001].

[103] Anisotropy and spatial heterogeneity, such as in sediments traversed by networks of hydrate lenses (section 4), add additional difficulty to data interpretation and the selection of proper models. Consider an example by Lee and Collett [2009], based on the NGHP-01 study of fine-grained sediments offshore India [Collett et al., 2008]: Archie equation-based hydrate saturation estimates using parameters relevant for homogeneous sediment ranged from 50% to 80% at depths for which pressure cores taken in nearby wells indicate hydrate saturations are <26% [Lee and Collett, 2009].

## 10. SEISMIC WAVE VELOCITY, ATTENUATION, AND SMALL-STRAIN STIFFNESS

[104] Compressional  $P$  waves and shear  $S$  waves are extensively used for mapping hydrate occurrences and estimating the hydrate saturation within those occurrences. Acoustic remote sensing is possible because the presence of hydrate stiffens the host sediment, increasing the  $P$  and  $S$  wave velocities. This has been comprehensively demonstrated in hydrate-bearing clay, silt, and sand at different

TABLE 10. Elastic Constants of Selected Sediment Components<sup>a</sup>

Material	$V_p$ (km s <sup>-1</sup> )	$V_s$ (km s <sup>-1</sup> )	$K$ (GPa)	$G$ (GPa)	$\rho$ (kg m <sup>-3</sup> )
Methane gas (10 MPa, 273 K)	0.412 <sup>b</sup>	0	0.015 <sup>c</sup>	0	90 <sup>d</sup>
Water	1.5 <sup>e,f</sup>	0	2250 <sup>e</sup>	0	1000 <sup>e</sup>
Ice Ih <sup>g</sup> (5 MPa, 273 K)	3.87	1.94	9.09	3.46	917
Methane hydrate <sup>g</sup> (5 MPa, 273 K)	3.77	1.96	8.41	3.54	925
Clay	3.41 <sup>c</sup>	1.63 <sup>c</sup>	20.9 <sup>h</sup>	6.85 <sup>h</sup>	2580 <sup>h</sup>
Quartz	6.04 <sup>c</sup>	4.12 <sup>c</sup>	36.6 <sup>h</sup>	45.0 <sup>h</sup>	2650 <sup>i</sup>

<sup>a</sup>Notation is as follows:  $V_p$ , compressional wave velocity;  $V_s$ , shear wave velocity;  $K$ , bulk modulus;  $G$ , shear modulus; and  $\rho$ , density.

<sup>b</sup>Estela-Urribi et al. [2006].

<sup>c</sup>Calculated from equation (18).

<sup>d</sup>Sychev et al. [1987].

<sup>e</sup>Lee et al. [1996].

<sup>f</sup>See Mavko et al. [1998, section 6.15] for variations with pressure, temperature, and salinity.

<sup>g</sup>Helgerud et al. [2009].

<sup>h</sup>Helgerud et al. [1999].

<sup>i</sup>Dvorkin et al. [2000].

effective stress and hydrate saturation levels by Lee [2007] and J. Y. Lee et al. (Parametric study of the physical properties of hydrate-bearing sand, silt, and clay sediments. Part II: Small-strain mechanical properties, submitted to *Journal of Geophysical Research*, 2009). This section relates wave velocity and stiffness properties to pore space hydrate saturation and discusses how seismic data can be used to characterize hydrate-bearing sediments.

### 10.1. Wave Velocities

[105] The propagation of  $P$  waves produces longitudinal strains with particle motion in the direction of wave propagation. In contrast,  $S$  waves cause shear strain with particle motion perpendicular to the direction of wave propagation. Their propagation speeds are controlled by the sediment's small-strain bulk modulus,  $K_b$ , and shear modulus,  $G$ , according to

$$\begin{aligned} V_p &= \sqrt{\frac{K_b + \frac{4}{3}G}{\rho_b}}, \\ V_s &= \sqrt{\frac{G}{\rho_b}}, \end{aligned} \quad (18)$$

where  $\rho_b$  is the bulk sediment density and  $V_p$  and  $V_s$  are the magnitudes of the compressional and shear wave velocities. Differences in their propagation modes mean that  $P$  and  $S$  waves are sensitive to different properties of the sediment: the bulk modulus,  $K_b$ , is determined by both the grains and pore fluid properties, but the shear modulus,  $G$ , is controlled by the shear stiffness of the granular skeleton.

[106] To relate  $V_p$  and  $V_s$  to hydrate saturations, moduli and density in equation (18) must be expressed as functions of mineral, sediment, pore fluid, and hydrate properties. The mass density of hydrate-bearing sediments,  $\rho_b$ , in equation (18) is given simply as a volume average of the individual densities, as a function of porosity,  $\phi$ , and phase saturations,  $S$ ,

$$\rho_b = \phi(\rho_w S_w + \rho_h S_h + \rho_g S_g + \rho_{ice} S_{ice}) + (1 - \phi)\rho_m, \quad (19)$$

where the subscripts  $w$ ,  $g$ ,  $h$ , ice, and  $m$  signify the liquid, gas, hydrate, ice, and mineral phases, respectively.

[107] There are several ways to calculate the moduli. Empirical models have been based, for instance, on seismic traveltimes through layered sediments [Wood et al., 1994] or on weighted combinations of traveltime estimates and stiffness predictions for fluid-saturated sediments [Lee and Collett, 1999] or follow the form of equations governing cemented soils [Santamarina and Ruppel, 2008]. Hydrate-bearing sediments have also been modeled as an effective medium [Jakobsen et al., 2000] or as a combination of three distinct frameworks: a sediment framework, a hydrate framework, and pore fluid occupying the remaining volume [Carcione and Gei, 2004; Carcione and Tinivella, 2000; Lee and Waite, 2008]. To provide physical insight into the relationship between hydrate and the wave velocity in hydrate-bearing sediments, we summarize key equations in sections 10.1.1–10.1.3.

#### 10.1.1. Bulk Stiffness

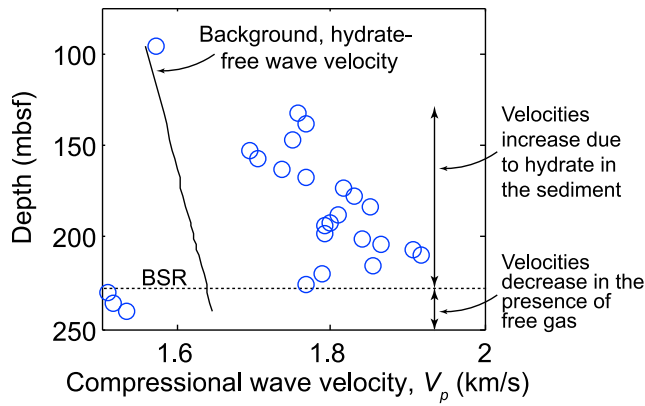
[108] The bulk stiffness or modulus,  $K_b$ , can be estimated from component properties using Gassmann's [1951] equation,

$$K_b = K_{sk} + \frac{\left(1 - \frac{K_{sk}}{K_m}\right)^2}{\phi \left(\frac{S_w}{K_w} + \frac{S_g}{K_g} + \frac{S_h}{K_h} + \frac{S_{ice}}{K_{ice}}\right) + \frac{1 - \phi}{K_m} - \frac{K_{sk}}{K_m^2}}, \quad (20)$$

where  $\phi$  is the porosity and the subscripts  $b$ ,  $w$ ,  $g$ ,  $h$ , ice,  $m$ , and  $sk$  stand for bulk hydrate-bearing sediment, water, gas, hydrate, ice, mineral, and sediment skeleton, respectively. Properties for the clay and quartz minerals are given in Table 10, along with the properties of methane hydrate, methane gas, water, and ice. The bulk stiffness of the skeleton,  $K_{sk}$ , is computed from the shear modulus,  $G = G_{sk}$ , using the standard theory of elasticity relation,

$$K_{sk} = \frac{2(1 + \nu_{sk})}{3(1 - 2\nu_{sk})} G. \quad (21)$$

For this computation, one must use the Poisson ratio for the skeleton,  $\nu_{sk}$ , which is typically  $\sim 0.15 \pm 0.05$  in sediments



**Figure 9.** Effect of gas hydrate and free gas on measured in situ wave velocities for Ocean Drilling Program Site 889 in the Cascadian subduction zone offshore Vancouver, Canada (adapted from *Yuan et al.* [1996]). Relative to the regional “hydrate-free” velocity profile with depth (solid curve [from *Yuan et al.*, 1996]), VSP interval wave velocities [MacKay et al., 1995] are elevated in the presence of hydrate. Below the bottom simulating reflector (BSR), where free gas is present rather than hydrate, the wave velocity falls below the water-saturated sediment wave velocity trend.

with hydrate saturations  $S_h < 40\%$  and may increase to  $\nu_{sk} \sim 0.3$  for sediments with  $S_h > 60\%$ .

[109] It follows from equation (20) that the presence of free gas ( $K_g \ll K_w, K_h$ , and  $K_m$ ) has a pronounced effect in decreasing the bulk stiffness,  $K_b$ , and the longitudinal wave velocity,  $V_p$  (Figure 9). The decrease in bulk density is minor in comparison. Even at very low gas saturations, the presence of gas causes  $V_p$  to rapidly approach  $\sim 1.5V_s$ .

#### 10.1.2. Shear Stiffness Dependence on Hydrate Habit in Pore Space

[110] The presence of hydrate can alter the stiffness of both the pore fluid and sediment skeleton. The pore fluid stiffening impacts only the bulk modulus and is accounted for by the second term in equation (20). Skeletal stiffening increases the shear modulus, which, in turn, increases the skeletal bulk modulus as shown in equation (21). In hydrate-free sediment, shear stiffness is controlled by the mean effective stress,  $\sigma'$  (kPa),

$$G = \alpha \left( \frac{\sigma'}{1 \text{ kPa}} \right)^\beta, \quad (22)$$

where  $\alpha$  is the shear stiffness when  $\sigma' = 1$  kPa and  $\beta$  represents the sensitivity of  $G$  to effective stress. Parameters  $\alpha$  and  $\beta$  depend on the sediment’s granular packing and fabric properties, as well as the nature of the intergranular contacts [Santamarina et al., 2001].

[111] In the presence of hydrate, the estimation of shear stiffness must also take into consideration pore space hydrate saturation,  $S_h$ , and where hydrate forms in the pore space.

##### 10.1.2.1. Pore Filling

[112] The presence of hydrate does not affect the shear stiffness, which remains controlled by effective stress

(equation (22)). Hydrate formers dissolved in water tend to promote pore-filling hydrate growth at low  $S_h$  that becomes load-bearing hydrate as  $S_h$  exceeds 25%–40% [Berge et al., 1999; Yun et al., 2005, 2007].

##### 10.1.2.2. Load Bearing

[113] Load-bearing hydrate increases shear stiffness, but grain contact stiffness continues to reflect the state of effective stress (equation (22)). The relevance of effective stress decreases as hydrate saturation increases.

##### 10.1.2.3. Cementation

[114] Hydrate formation at grain contacts readily takes over from effective stress as the primary control of the skeletal stiffness [Dvorkin et al., 1999, 2000; Fernandez and Santamarina, 2001; Guerin et al., 1999; Xu et al., 2004].

#### 10.1.3. Predicting Hydrate Saturations From Wave Velocities

[115] The dependence of skeletal stiffness  $G = G_{sk}$  and  $K_{sk}$ , and hence wave velocity, on the pore space location of hydrate causes ambiguity when trying to infer hydrate saturations from measured wave velocities: the anomalously high interval wave velocity in Figure 9 could be due to a small amount of hydrate cementing sediment grains, a medium amount of hydrate supporting a portion of the sediment load, a large volume of hydrate floating in the pore space (see Figure 10), or some combination thereof.

[116] The combined interpretation of compressional and shear wave velocity data, together with directional resistivity measurements to characterize the anisotropy in fracture-dominated systems (see sections 4 and 9.3), can help reduce this ambiguity. Field measurements of shear wave velocity remain difficult, however, and even well log measurements of shear wave velocity can be untrustworthy [Dai et al., 2008a; Lee and Waite, 2008].

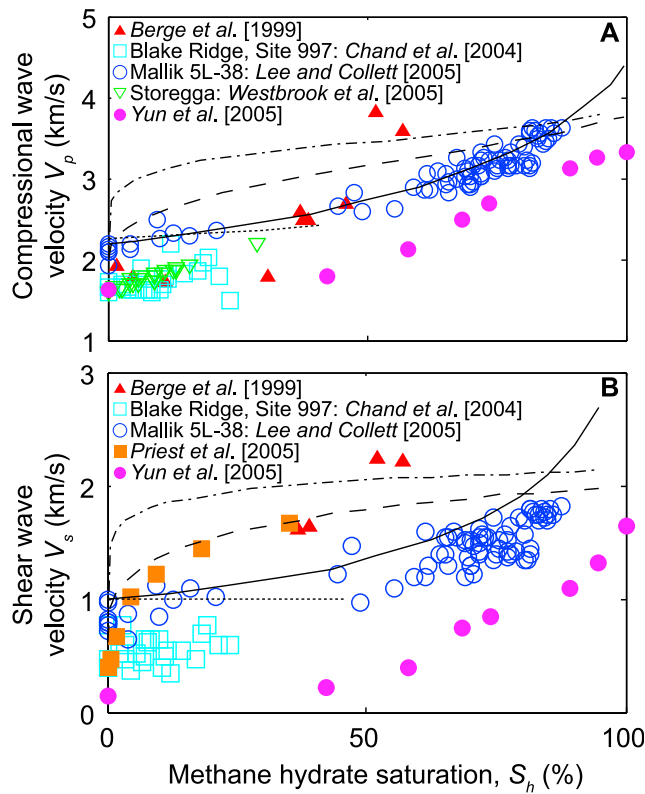
[117] Seafloor compliance measurements, which provide a direct measure of the elastic deformation of the seafloor in response to passing waves on the ocean surface [Willoughby et al., 2008], and controlled source electromagnetic surveys which measure electrical resistivity in sediment via detectors towed along the sediment surface [Ellis et al., 2008; Weitemeyer et al., 2006; Yuan and Edwards, 2000] can also provide independent elastic and electrical measures for the estimation of the in situ hydrate volumes.

[118] An independent estimate of in situ elastic properties at a given location can anchor, and thereby improve, the accuracy of seismic inversions in which elastic properties and hydrate saturations are estimated over broad regions [Inks et al., 2008; Jones et al., 2008]. The inversion, described in detail by Xu et al. [2004] and Dai et al. [2008b], seeks to build a model of the local geology such that synthetic seismic waveforms sent through the model space mimic the seismic waveforms measured in the field. The map of physical properties provided by the inversion is converted to a map of hydrate saturation by assuming a pore space hydrate configuration.

#### 10.2. Attenuation

[119] Attenuation is a measure of energy loss as waves travel from a source to a sensor and is affected by hydrate





**Figure 10.** Comparison between field (open symbols), laboratory (solid symbols), and modeling results (solid and dashed curves) for (a) compressional and (b) shear wave velocities in hydrate-bearing sediments. Modeling results are from Kleinberg and Dai [2005]. Dot-dashed curves represent wave velocities for hydrate forming as cement at grain contacts. Particularly for low hydrate saturations, this distribution most significantly increases the wave velocity. Dashed curves predict wave velocities for hydrate that coats and cements sediment grains. Solid curves represent load-bearing hydrate, and dotted curves show the impact of pore-filling hydrate. Pore-filling distributions begin bridging sediment grains and behaving as load-bearing distributions for  $S_h > \sim 25\%$ – $40\%$ .

saturation [Chand and Minshull, 2004; Dvorkin and Uden, 2004; Guerin and Goldberg, 2005; Guerin et al., 2005]. Unfortunately, measuring the “intrinsic attenuation” of hydrate-bearing sediment is hindered by the prevailing effects of geometric spreading and impedance mismatches in spatially heterogeneous media [Huang et al., 2009]. For example, acoustic energy from borehole sources can reflect off the borehole wall due to the high stiffness of hydrate-bearing sediments and not propagate through the hydrate-bearing sediment at all [Lee and Waite, 2007]. Even if the intrinsic attenuation in sediment could be properly estimated in the field, its interpretation is made more difficult by the multiple coexisting energy loss mechanisms in sediments [Wang and Santamarina, 2007] which are further altered by the presence of hydrates in the pore space [Lee, 2006; Matsushima, 2006].

[120] Attenuation and wave velocity dispersion are causally related, as indicated by the Kramers-Kronig relations [e.g., Toll, 1956; Wang and Santamarina, 2007]. As dis-

cussed by Lee [2006], however, with the exception of the Guerin and Goldberg [2005] model, published attenuation models tend to treat attenuation and wave velocities independently, which can lead to predictions of unphysical behavior. These challenges have limited the reliability of attenuation as a tool for estimating in situ hydrate saturations.

## 11. STRENGTH AND DEFORMATION

[121] Sediment strength and the extent to which sediment deforms under a load are critical inputs for the analysis of potential failures around wells [Masui et al., 2008; Rutqvist and Moridis, 2007] and for evaluating seafloor stability over larger length scales [Nixon and Grozic, 2007; Sultan et al., 2004a].

### 11.1. Definition of Strength and Deformation Parameters

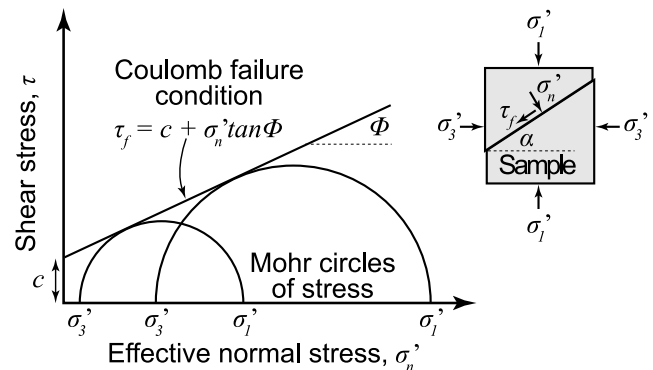
[122] Sediment strength is a combination of the cohesive resistance,  $c$ , and effective stress-dependent frictional resistance described by the friction angle,  $\Phi$ , which includes resistance to sliding between particles, particle rearrangement, and particle crushing. The two contributions to shear strength are captured in the Coulomb failure criterion which relates the shear stress at failure,  $\tau_f$ , to the normal effective stress,  $\sigma_n'$ , acting on the failure plane,

$$\tau_f = c + \sigma_n' \tan \Phi. \quad (23)$$

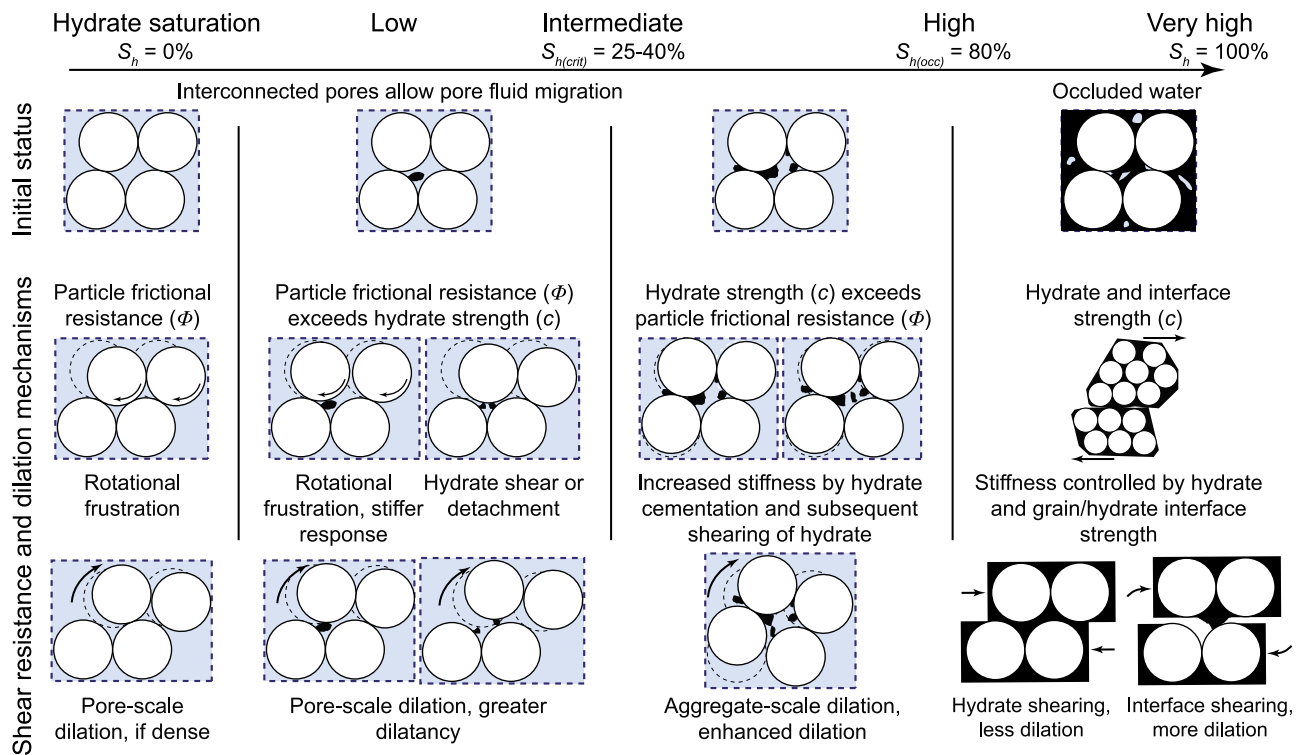
This failure criterion plots as a straight line in  $\tau - \sigma_n'$  space. The state of stress at a point in equilibrium within the test sample plots as a circle in  $\tau - \sigma_n'$  space called the Mohr circle of stress. The sediment reaches failure when the Mohr circle becomes tangent to the Coulomb failure envelope (Figure 11).

### 11.2. Laboratory Measurements

[123] The strength parameters  $c$  and  $\Phi$  can be measured in the laboratory using triaxial compression tests [ASTM



**Figure 11.** Mohr-Coulomb failure diagram. Within a sample subjected to the principal effective stresses  $\sigma_1'$  and  $\sigma_3'$ , the state of stress falls on a Mohr circle in  $\tau - \sigma_n'$  space. Shear failure occurs when the Mohr circle becomes tangent to the Coulomb failure line, meaning that the shear stress along the failure plane,  $\tau_f$ , exceeds the combined resistance of cohesion,  $c$ , and friction,  $\sigma_n' \tan \Phi$ . The friction angle,  $\Phi$ , and failure plane angle,  $\alpha$ , are related by  $\alpha = 45^\circ + \Phi/2$ .



**Figure 12.** Mechanisms controlling the shear strength of hydrate-bearing sediments. Sediment grains are white circles, hydrate is black, and water is blue (modified from *Yun et al.* [2007]). Effective stress measurements are preferred when interpreting shear behavior, but at high hydrate saturations for which pressure in the occluded pores cannot be measured, interpretations must be based on total stress measurements.

*Standard*, 2004, 2006] in which a cylindrical specimen is subjected to an effective confining stress  $\sigma_3' = \sigma_3 - P_p$  and then brought to failure by increasing the axial effective stress  $\sigma_1' = \sigma_1 - P_p$  (Figure 11, inset). Triaxial test data obtained at different effective confining stress levels are combined to define the linear Coulomb failure envelope from which  $c$  and  $\Phi$  are derived. Tests are generally run in either a drained mode, in which the pore pressure is maintained independently from the applied stress, or in an undrained mode, in which drainage of neither gas nor liquid pore fluid from the specimen is allowed and hence the pore pressure changes as the sample deforms. The specimen volume is assumed constant during undrained tests in water-saturated soft sediments, though this will not be the case in hydrate-bearing sediments if free gas forms during the test.

[124] Triaxial tests also provide prefailure information that can be used to determine Young's modulus,  $E$ ; Poisson's ratio,  $\nu$ ; and dilatancy angle,  $\psi$ . Values of  $E$  and  $\nu$  are often reported at 50% of the failure load,  $E_{50}$  and  $\nu_{50}$ . The dilatancy angle measures the rate of volume increase with increasing shear strain. Dilative sediment subjected to undrained shear will experience a decrease in pore fluid pressure, thereby increasing the normal effective stress and sediment strength (equation (23)); the decrease in fluid pressure may cause gas dissolution and hydrate dissociation.

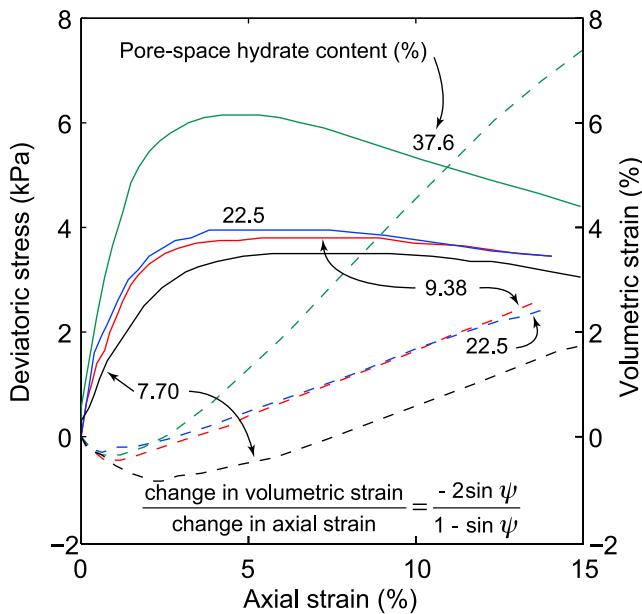
[125] When pores are interconnected, pore fluid pressure can be monitored or controlled independently of the con-

fining stress in drained tests, and data are best interpreted within the framework of effective stresses, for which the pore pressure is subtracted from the applied stresses. The effective stress can be increased by either increasing the total stress under constant pore pressure or decreasing the pore pressure under constant total stress. Both should result in the same volume change for a given change in effective stress; however, decreasing the pore fluid pressure may lead to hydrate dissociation if reduced below the stability pressure at the test temperature. Once pores are occluded and therefore isolated from the external pore fluid reservoir, the local pore pressure evolves in response to the applied total stress and is not measurable using sensors outside the sample. Only the total stresses are known, restricting data analysis to a total stress framework.

### 11.3. General Trends

[126] The presence of methane hydrate increases stiffness, enhances prefailure dilation, and leads to higher strength. Figure 12 illustrates shear resistance and dilation mechanisms occurring at different levels of hydrate saturation in the pore space. Hydrate saturation is considered low for the purposes of shear strength when  $S_h < \sim 30\%$  and high when  $S_h > 40\%$ . Conditions above  $S_h = 70\% - 80\%$  are unusual and involve occluded pores inside the sediment. Specific results for coarse-grained sediment are given in sections 11.3.1 and 11.3.2, and fine-grained sediments are discussed in section 11.3.3. Further details are given by *Soga et al.* [2006].





**Figure 13.** Dependence of stress (solid curves) and volumetric strain (dashed curves) on axial strain for four methane hydrate-bearing sands [Masui et al., 2006]. The dilation angle,  $\psi$ , can be calculated from the slope of the volumetric strain as shown.

### 11.3.1. Coarse-Grained Soils: Drained Tests

[127] The measured stress-strain responses of natural hydrate-bearing sandy sediments retrieved from the Nankai Trough are shown in Figure 13 as a function of pore space hydrate saturation [Masui et al., 2006]. In agreement with previous observations (Figure 12), the peak strength,  $E_{50}$ , and dilation generally increase with hydrate saturation [see also Hyodo et al., 2007]. The Poisson's ratio,  $\nu_{50}$ , varies between 0.10 and 0.19, with no apparent relationship to hydrate saturation.

[128] Effective stress strength parameters can depend strongly on the hydrate formation history (refer to section 3). There is a pronounced increase in strength and stiffness (Figure 14) as well as dilation angle (Figure 15b) when even a small amount of hydrate forms at interparticle contacts and cements particles together. In contrast, pore-filling hydrate begins to have a measurable effect on these parameters only when the hydrate saturation exceeds about  $S_h \sim 30\%$ . However, neither the friction angle nor the cohesion depend strongly on the mode of hydrate occurrence, and friction angle is nearly independent of hydrate saturation as well. It should be noted that the data were gathered from tests run at 1 MPa effective confining pressure; lower dilation is expected at higher confining pressures.

### 11.3.2. Coarse-Grained Soils: Undrained Tests

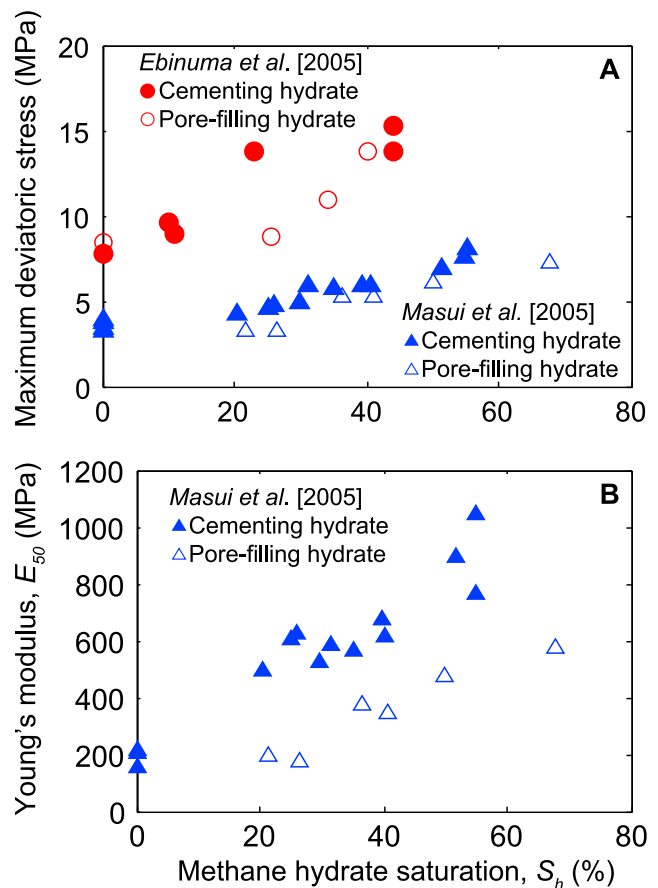
[129] Undrained triaxial test data show congruent trends to those gathered in drained tests. Gas hydrate-bearing sands from the Mackenzie Bay (Mallik 2L-38 between depths of 898 and 913 m, under 640 m of permafrost) exhibit a higher dilative tendency than the same sediments without hydrates (Figure 16) and are correspondingly stronger and stiffer. Similar conclusions are reached in undrained

triaxial tests run on THF hydrate-bearing sands and silts at different stress levels and hydrate saturations [Yun et al., 2007]; this study reached  $S_h = 100\%$  and found that stiffness and undrained strength are determined by the hydrate phase in high hydrate saturation sediments rather than by the initial effective confining stress.

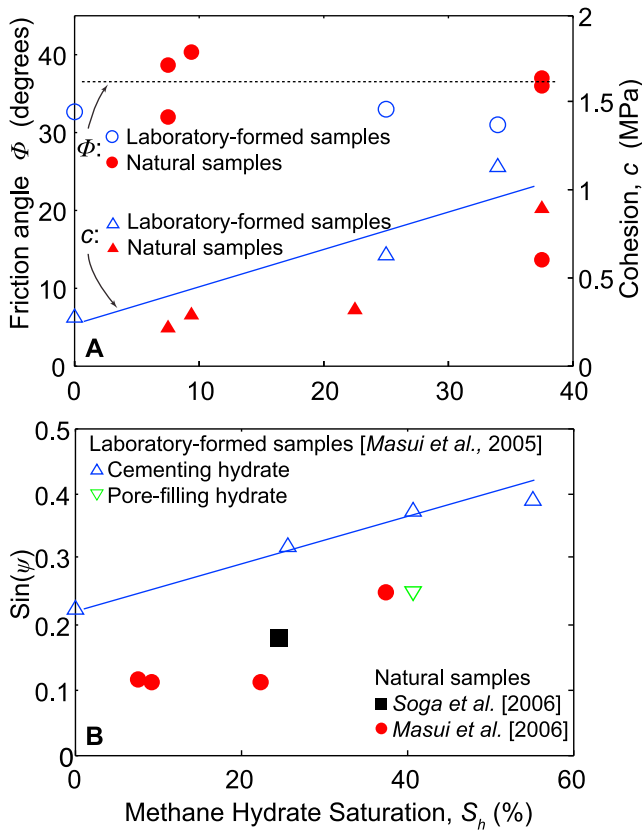
[130] In summary, available data show that (1) stiffness, cohesion, and dilation increase and friction angle remains constant as hydrate concentration increases; (2) at hydrate saturation  $S_h < 30\%$ , cementing hydrate has a more pronounced effect than pore-filling hydrate on mechanical properties; (3) formation history effects gradually diminish at high hydrate saturation; and (4) the initial effective stress loses relevance at very high hydrate concentrations, in which case the hydrate phase controls the strength and deformation characteristics.

### 11.3.3. Fine-Grained Soils

[131] Hydrate-bearing fine-grained soils have not been extensively studied due to a lesser interest from a resource potential perspective, coupled with difficulties in hydrate



**Figure 14.** (a) Peak strength and (b) Young's modulus at 50% of the stress at failure,  $E_{50}$ , versus methane hydrate saturation. Cementing hydrate samples show significant impact of hydrate at low hydrate saturations,  $S_h$ . Pore-filling hydrate does not significantly impact peak strength or  $E_{50}$  until  $S_h$  exceeds 25%. The offset between the two studies is due to the 3 MPa confining pressure used by Ebinuma et al. [2005] compared to the 1 MPa confining pressure used by Masui et al. [2005].



**Figure 15.** (a) Cohesion and friction angle and (b) dilation angle versus hydrate saturation in natural methane hydrate samples (solid symbols) [Masui et al., 2006; Soga et al., 2006] and laboratory-formed cemented methane hydrate samples (open symbols) [Masui et al., 2005]. Though cohesion and dilation angle increase with increasing hydrate saturation (solid trend lines through the cementing hydrate data), friction angle is largely independent of hydrate saturation (dotted trend line).

formation and in mechanical testing. Therefore, limited data are available, and further work is needed to understand the mechanical behavior of hydrated bearing fine-grained sediments.

[132] Undrained, triaxial test data gathered for THF hydrate disseminated in Kaolinite clay and precipitated silt in which each silt grain is an agglomerate are summarized in Figure 17 [Yun et al., 2007]. Specimens without hydrate exhibit a frictional, linear increase in undrained shear strength as the initial effective confining stress increases. In high hydrate saturation sediments, however, the undrained shear strength is insensitive to effective confining stress. The undrained modulus  $E_{50}$  follows a similar trend.

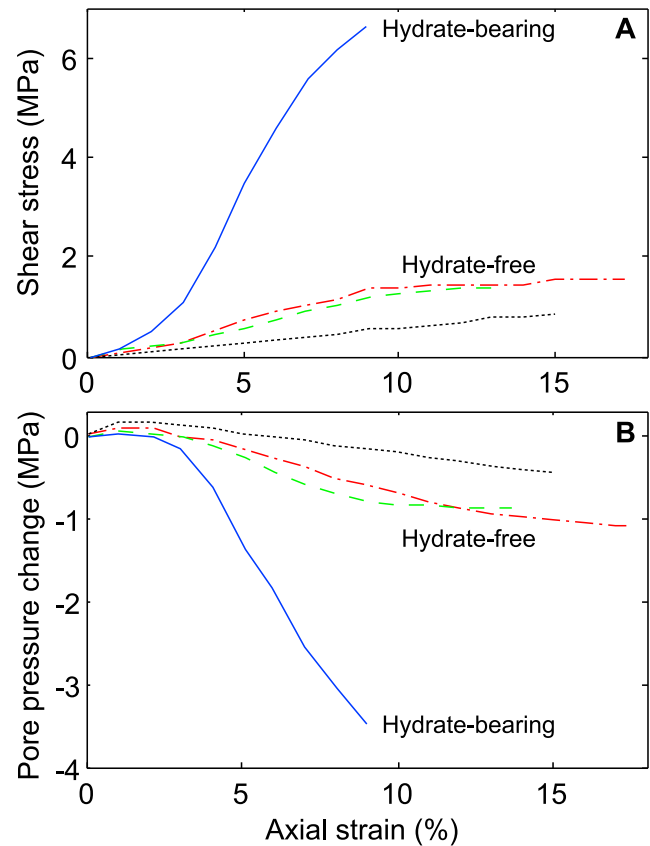
[133] Undrained shear strengths of natural fine-grained sediments with hydrate have been measured using a small cone-shaped penetrometer in pressure cores recovered in the Gulf of Mexico [Yun et al., 2006]. These specimens were maintained at the in situ fluid pressure but with virtually no effective stress. The measured undrained strength therefore indicates only the in situ effects of hydrate and the granular porosity of these fine-grained sediments rather than the combined impact of hydrate, porosity, and effective stress.

In all cases, undrained strength was higher in the hydrate-bearing sediments than in sediments without hydrates at the same burial depth [Yun et al., 2006]. In situ cone resistance and friction during piezocone deployments offshore Nigeria also show an increased strength in the presence of hydrate [Sultan et al., 2007]. These measurements are limited to shallow sediments (less than  $\sim 30$  mbsf), however.

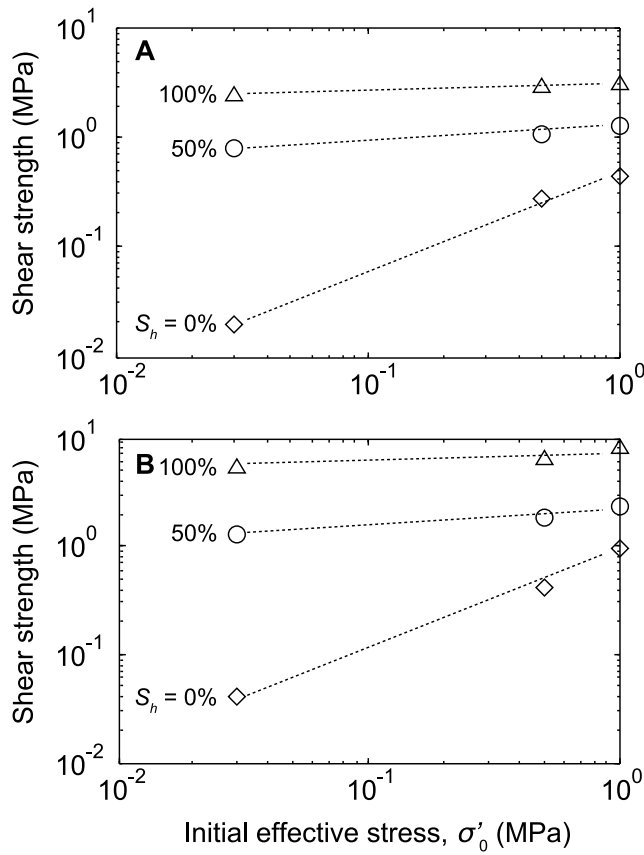
## 12. VOLUME CHANGE UPON DISSOCIATION

[134] Hydrate dissociation reduces the solid hydrate volume, produces gas and water, and decreases the water salinity. Depending on boundary conditions, these changes produce one or both of the following: (1) variations in the pore fluid pressure and effective stress and (2) changes in the volume occupied by the sediment.

[135] In natural settings, volume contraction typically follows hydrate dissociation once the initial pressure increase due to gas produced during dissociation dissipates. The magnitude of contraction depends on the soil type, the current in situ state of stress and the stress state when hydrate formed, the distribution of hydrate within the sediment, and the current mineral porosity defined in terms



**Figure 16.** Dependence of (a) peak shear stress and (b) pore pressure change on pore content and axial strain in coarse sands recovered from the Mallik 2L-38 permafrost research well. Hydrate-free samples (broken curves) were sheared after the gas hydrate dissociated, and the hydrate-bearing sample (solid curve) was sheared with hydrate but no ice present [after Winters et al., 2002].



**Figure 17.** Undrained shear strength versus initial effective confining stress at different hydrate saturations for different soils: (a) Kaolinite and (b) precipitated silt [after Yun *et al.*, 2007]. With increasing tetrahydrofuran hydrate saturation, the dependence of shear strength on effective stress diminishes (dotted trend lines).

of  $(V_T - V_m)/V_T$ , where  $V_m$  is the volume of minerals and  $V_T$  is the total volume.

[136] Very limited data have been gathered for volume changes upon dissociation of hydrate-bearing sediments. However, there are data for similar processes that can provide useful insight to help constrain design parameters, such as the literature on cold regions engineering, which contains a wealth of data on material characterization and the effect of freeze-thaw cycles [Gatto *et al.*, 2001]. In particular, frozen ground characterization schemes can prove helpful in assessing hydrate-bearing sediments that are most susceptible to volume change.

[137] Several volume loss mechanisms are identified in the context of hydrate dissociation in sediments [Lee *et al.*, 2009]: (1) bulk hydrate dissociation, (2) sediment skeleton alteration, (3) consolidation, and (4) sand production. These mechanisms are briefly described in sections 12.1–12.4.

### 12.1. Contraction due to Bulk Hydrate Dissociation

[138] Segregated bulk hydrate exists in sediments in the form of lenses, veins, or nodules that are much larger than the pore size (e.g., Figure 4). The dissociation of bulk

hydrate creates a void volume,  $V_v$ , equal to the hydrate volume,  $V_h$ . The upper bound estimate of the macroscale volumetric strain,  $\varepsilon_{vol}$ , is equal to the void volume,  $V_v = V_h$ , divided by the initial total volume of the sediment,  $V_T$ ; therefore,  $\varepsilon_{vol} \leq (V_h/V_T)$ .

[139] Secondary mechanisms such as arching, in which the stress is transferred away from yielding sediment, or raveling, in which sediment collapses into void spaces, reduce the impact of void formation on volume change. In such cases, a reduction factor  $0 \leq \beta \leq 1.0$  can be used to decrease the estimated upper bound volumetric strain,

$$\varepsilon_{vol} = \beta \frac{V_h}{V_T}. \quad (24)$$

The value of  $\beta$  is a function of the amount, size, and geometry of the bulk hydrate, along with the soil stiffness, strength, and state of stress. Though  $\beta$  could exceed 1.0 in very loose sediments when hydrate dissociation leads to volume collapse in the neighboring sediment, it is within the 0.2–0.4 range for most hydrate-bearing sediments.

### 12.2. Contraction due to Disseminated Hydrate Dissociation

[140] Disseminated hydrate within the intergranular pore space of the sediment can contribute to stiffening of the granular structure and can even carry part of the load (see sections 3, 10, and 11). Hydrate dissociation causes fabric changes such that the granular skeleton continues sustaining the applied effective stresses state. The consequence of this fabric alteration is either volume contraction or stress relaxation, depending on boundary conditions.

[141] The volumetric strain at constant boundary stresses is a function of the degree of hydrate saturation and distribution within the pore space, the soil compressibility, and the in situ state of stress. A comprehensive study conducted with various sediments, stress levels, and both 50% and 100% THF hydrate saturation is reported by Lee [2007] and Lee *et al.* [2007]; complementary data gathered with Gulf of Mexico sediments are given by Lee *et al.* [2008]. Results indicate the volumetric strain due to hydrate dissociation decreases as the effective stress increases, meaning less contraction should be expected in deeper sediments.

### 12.3. Contraction due to Increased Effective Stress: Depressurization

[142] Methane can be produced from hydrate-bearing sediments by reducing the pore fluid pressure by an amount  $\Delta P$  that brings the system to the boundary of hydrate stability. There is a corresponding increase in effective stress state, and sediment compaction follows. In a one-dimensional system, the vertical strain,  $\varepsilon_z$ , is equal to the volumetric strain,  $\varepsilon_{vol}$ , and can be computed as

$$\varepsilon_z = \varepsilon_{vol} = \frac{C_c}{1 + e_0} \log \left( \frac{\sigma'_{z0} + \Delta P}{\sigma'_{z0}} \right), \quad (25)$$

where  $C_c$  is the sediment compressibility,  $e_0$  is the initial void ratio, and  $\sigma_{z0}'$  is the initial vertical effective stress. The parameter  $C_c$  can be estimated from sediment properties (Table 5).

[143] Case histories for subsidence due to the depressurization of aquifers during water or hydrocarbon removal show that surface subsidence estimates must account for three processes: (1) the reservoir response, which is generally nonlinear, time-dependent, and spatially variable; (2) the behavior of the upper layers, including sediment stiffness, shear-induced volume changes, and time-dependent deformation processes; and (3) geometric-mechanical interaction effects, including reservoir thickness, thickness of the overlying sediment column, spatial extent of production, and production history [Atkinson and Pedersen, 1998; Chan, 2005; Geertsma, 1973; Siriwardane, 1992; Sorey et al., 1993; Sylte et al., 1999; Xu et al., 2001; Yerkes and Castle, 1970].

#### 12.4. Contraction due to Mineral Migration and Removal

[144] Volume loss associated with the transport of mineral particles out of the sediment and into the well can be an important volume contraction mechanism, particularly in sandy sediments. Sand production is facilitated by hydrate dissociation and mixed fluid flow conditions. The potential volume loss depends on flow rates, the geometry of the layer, and soil type.

#### 12.5. Additional Consequences of Volume Contraction

[145] Compaction is not the only effect associated with hydrate dissociation. There is evidence that the horizontal effective stress also decreases during dissociation and that the sediment can reach internal shear failure conditions [Shin and Santamarina, 2009]. In geomechanical terms, the stress ratio at rest,  $k_o$ , decreases toward Rankine's active Earth pressure coefficient,  $k_a$ , defined as the minimum lateral effective stress for soils at their extensional failure condition. In strain-softening sediments, this situation may lead to the formation of shear planes within the sediment [Shin et al., 2008].

### 13. FUTURE RESEARCH DIRECTIONS IN THE CHARACTERIZATION OF HYDRATE-BEARING SEDIMENTS

[146] Particle and pore-scale interactions between hydrate and its host sediment lead to a richly complex system of interdependent macroscale physical properties that govern the evolution of hydrate-bearing sediments. Understanding these interdependencies can provide a framework for understanding hydrate-bearing sediments as well as providing a robust basis for preliminary evaluations of gas production strategies and instability conditions, such as slope and borehole failures.

[147] The three most relevant properties for predicting the behavior of hydrate-bearing sediments are the pore space

hydrate saturation, effective stress, and sediment grain size, particularly the content of fine-grained silts and clays. These parameters must be explicitly assessed and reported in all future studies.

[148] Above 25%–40% pore space hydrate saturation, hydrate behaves as a load-bearing member of the sediment, decreasing the permeability while increasing sediment stiffness and strength. As the hydrate saturation decreases, effective stress becomes the primary control on sediment stiffness and strength. The influence of hydrate on the host sediment properties can be subtle at low saturations, and fewer measurements have been made on these systems relative to the highly hydrate-saturated sands. The low-saturation case must nevertheless be examined because, for instance, the dissociation of small quantities of hydrate can still have pronounced effects on pore fluid pressure, effective stress, and stability conditions.

[149] The host sediment's silt and clay content, the fines, determines the mode of hydrate occurrence. In coarse-grained systems with a fines content below  $\sim 7\%$ , hydrate generally occurs in the pore space between grains. When the fines content exceeds  $\sim 15\%$ , hydrate is found disseminated in the sediment and forming veins and nodules that displace sediment grains. As a result, pronounced spatial variability is common in the fine-grained sediments that host the majority of the Earth's hydrate. Fines content also determines fluid permeability and plays a critical role in sediment evolution after hydrate dissociation. Future studies should further explore the effect of the amount of fines, their mineralogy, and specific surface area on the characteristics of hydrate-bearing sediments.

[150] The structure of hydrate-bearing sediments comprises the sediment fabric and the hydrate distribution at the pore scale. Both structural characteristics can be modified by changes in effective stress, fluid pressure, and/or temperature. Sampling and core extraction inherently modify the effective stress and physical state of sediments and may also cause hydrate dissociation. Therefore, emphasis must be placed on further developing comprehensive in situ sediment characterization through borehole logging tools that incorporate the simultaneous measurements of multiple properties from the minimally disturbed material surrounding the probe. For measurements that cannot be made in a borehole, the advent of routine pressure coring and the testing of such cores at their in situ pore pressure is invaluable. A key advance would be to maintain or quickly reinstate the in situ effective stresses.

[151] Laboratory studies using synthetic specimens attempt to emulate field conditions while avoiding core disturbance problems. The importance of emulating the noncementing methane hydrate observed in most marine field studies highlights the need to develop reproducible hydrate formation techniques, likely involving dissolved phase methane, that avoid the cementing nature of methane hydrate formed in the presence of free gas.

[152] Field and laboratory specimens tend to exhibit marked heterogeneity. Future experimental studies should routinely image specimens to visualize hydrate distribution

so that proper data inversion procedures can be implemented in the interpretation of measured properties.

## NOTATION

The following subscripts, used throughout the paper, refer a parameter to a particular material or condition:

$b$	bulk material, including all constituents.
$f$	pore fluid.
$g$	gas.
$h$	hydrate.
$m$	sediment grain mineral.
max	maximum value.
min	minimum value.
$s$	solid sediment constituents.
$T$	total value, including all constituents.
$v$	void space or pore space.
$w$	water.

Parameters given below are listed in SI units. When applicable, common usage units are given in the main text.

### Section 2: solubility

$a_i^j$	activity of species $i$ in phase $j$ (unitless).
$f_i^j$	fugacity of species $i$ in phase $j$ (Pa).
$f_i^0$	fugacity of species $i$ in a convenient reference state (Pa).
$G$	Gibbs free energy (J).
$H$	superscript referring to the hydrate phase.
$L$	superscript referring to the liquid phase.
$m$	molality (moles of solute per kilogram of solvent).
$M$	molarity (moles of solute per liter of solution).
$n_i^j$	number of moles of species $i$ in phase $j$ (mol).
$P_i$	pressure in species $i$ (Pa).
$r$	interfacial radius of curvature (m).
$R$	universal gas constant ( $8.314 \text{ J (mol K)}^{-1}$ ).
$T$	temperature (K).
$x_i^j$	concentration of species $i$ in phase $j$ (mole fraction).
$\beta$	superscript referring to hypothetical empty hydrate phase with no guest molecules.
$\gamma_{i,w}$	interfacial tension between species $i$ and water ( $\text{N m}^{-1}$ ).
$\Delta P$	capillary pressure (Pa).
$\mu_i^j$	chemical potential of species $i$ in phase $j$ ( $\text{J mol}^{-1}$ ).
$\mu_i^0$	chemical potential of species $i$ in a convenient reference state ( $\text{J mol}^{-1}$ ).
$\nu_i^j$	activity coefficient of species $i$ in phase $j$ (unitless).

### Section 3: formation history

$S_h$	hydrate saturation in the pore space (% or unitless).
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### Section 4: spatial variability

$V_p$	compressional wave velocity ( $\text{m s}^{-1}$ ).
$V_s$	shear wave velocity ( $\text{m s}^{-1}$ ).

### Section 5: sampling and handling effects

$G_{\max}$	small-strain shear stiffness (Pa).
PI	plasticity index (% or unitless).

### Section 6: index properties

$C_c$	coefficient of compressibility (unitless).
$C_{\text{curv}}$	coefficient of curvature (unitless).
$C_H$	Hazen's empirical coefficient ( $\sim 1 \times 10^4 \text{ (m s)}^{-1}$ ) [Carrier, 2003].
$C_{\text{unif}}$	coefficient of uniformity (unitless).
$D_X$	grain diameter at which $X\%$ of the sample is finer (m).
$e$	void ratio (unitless).
$G_s$	specific gravity (unitless).
$K$	hydraulic conductivity ( $\text{m s}^{-1}$ ).
LI	liquidity index (% or unitless).
LL	liquid limit (% or unitless).
$M$	mass (kg).
PI	plasticity index (% or unitless).
PL	plastic limit (% or unitless).
$R$	particle roundness (unitless).
$S_h$	hydrate saturation in the pore space (% or unitless).
$S_s$	specific surface ( $\text{m}^2 \text{ kg}^{-1}$ ).
$S_u$	undrained shear strength (Pa).
$V$	volume ( $\text{m}^3$ ).
$w$	gravimetric water content, with respect to the specimen's mineral mass (unitless).
$\gamma_w$	unit weight of water ( $\text{N m}^{-3}$ ).
$\theta$	shape and tortuosity factor (unitless).
$\mu$	dynamic fluid viscosity (Pa s).
$\rho$	mass density ( $\text{kg m}^{-3}$ ).
$\sigma_v'$	mean effective stress at failure (Pa).
$\phi$	porosity (% or unitless).
$\Phi_{cv}$	friction angle during constant volume shear (degrees or radians).

### Section 7: thermal properties

$c_p$	specific heat ( $\text{J (kg K)}^{-1}$ ).
$m$	cementation exponent ( $2 \pm 0.5$ for granular media, unitless) [Revil, 2000].
$P$	pressure (Pa).
$R$	universal gas constant ( $8.314 \text{ J (mol K)}^{-1}$ ).
$S_h$	hydrate saturation in the pore space (% or unitless).
$T$	temperature (K).
$Z$	nonideal gas compressibility factor (unitless).
$\Delta H$	enthalpy of reaction ( $\text{J mol}^{-1}$ ).
$\kappa$	thermal diffusivity ( $\text{m}^2 \text{ s}^{-1}$ ).
$\lambda$	thermal conductivity ( $\text{W (m K)}^{-1}$ ).
$\rho$	mass density ( $\text{kg m}^{-3}$ ).
$\phi$	porosity (% or unitless).

### Section 8: permeability and fluid flow

$A$	cross-sectional area ( $\text{m}^2$ ).
$C$	gas slippage or Klinkenberg effect parameter (unitless).
$D_X$	grain diameter at which $X\%$ of the sample is finer (m).
$e$	void ratio (unitless).
$g$	acceleration due to gravity ( $9.8 \text{ m s}^{-2}$ ).
$k$	intrinsic permeability ( $\text{m}^2$ ).
$k_r$	relative permeability (unitless).
$l$	length (m).
$n$	van Genuchten curve-fitting parameter (unitless).
$P$	pressure (Pa).

$q$	flow rate ( $\text{m}^3 \text{s}^{-1}$ ).
$S_s$	specific surface ( $\text{m}^2 \text{kg}^{-1}$ ).
$S_w$	water saturation (unitless).
$S_{w\_eff}$	effective water saturation (unitless).
$S_{w\_irr}$	irreducible water saturation (unitless).
$z$	depth or elevation (m).
$\alpha$	van Genuchten curve-fitting parameter ( $\text{m}^{-1}$ ).
$\Delta P$	capillary pressure (Pa).
$\theta$	shape and tortuosity factor (unitless).
$\mu$	dynamic fluid viscosity (Pa s).
$\rho$	mass density ( $\text{kg m}^{-3}$ ).

## Section 9: electromagnetic properties

$c$	ionic concentration ( $\text{mol m}^{-3}$ ).
$C$	salinity (practical salinity unit).
$e$	void ratio (unitless).
sed	subscript indicating a property of hydrate-free sediment.
$S_i$	pore space saturation of phase $i$ (% or unitless).
$S_s$	specific surface ( $\text{m}^2 \text{kg}^{-1}$ ).
$sw$	subscript indicating a property of standard seawater.
$T$	temperature (K).
TDS	total dissolved solids ( $\text{kg L}^{-1}$ ).
$V$	volume ( $\text{m}^3$ ).
$z$	depth (m).
$\alpha$	empirical parameter in Archie's law (unitless).
$\beta$	empirical parameter in Archie's law (unitless).
$\epsilon_0$	permittivity of free space ( $8.85 \times 10^{-12} \text{ F m}^{-1}$ ).
$\zeta$	ionic mobility ( $(\text{S m}^2) \text{mol}^{-1}$ ).
$\kappa^*$	complex electrical permittivity (relative to "free space," $\epsilon_0$ ) (unitless).
$\kappa'$	real component of the relative electrical permittivity (unitless).
$\kappa''$	imaginary component of the relative electrical permittivity (unitless).
$\lambda_{ddl}$	surface conduction (S).
$\mu^*$	complex magnetic permeability (relative to "free space," $\mu_0$ ) (unitless).
$\mu'$	real component of the relative magnetic permeability (unitless).
$\mu''$	imaginary component of the relative magnetic permeability (unitless).
$\mu_0$	magnetic permeability of free space ( $1.25 \times 10^{-6} \text{ N A}^{-2}$ ).
$\rho$	electrical resistivity ( $\Omega \text{ m}$ ).
$\sigma$	electrical conductivity ( $\text{S m}^{-1}$ ).
$\sigma_{AC}$	alternating current conductivity ( $\text{S m}^{-1}$ ).
$\sigma_{DC}$	direct current conductivity, zero frequency ( $\text{S m}^{-1}$ ).
$\phi$	porosity (% or unitless).
$\chi$	empirical parameter in Archie's law (unitless).
$\omega$	frequency (Hz).

## Section 10: seismic wave velocity, attenuation, and small-strain stiffness

$G$	shear modulus (Pa).
$K$	bulk modulus (Pa).
$S_i$	pore space saturation of phase $i$ (% or unitless).
$sk$	subscript indicating a property of the sediment skeleton.
$V_p$	compressional wave velocity ( $\text{m s}^{-1}$ ).
$V_s$	shear wave velocity ( $\text{m s}^{-1}$ ).

$\alpha$	shear stiffness at 1 kPa effective stress (Pa).
$\beta$	sensitivity of the shear stiffness to the effective stress (unitless).
$\nu$	Poisson's ratio (unitless).
$\rho$	mass density ( $\text{kg m}^{-3}$ ).
$\sigma'$	mean effective stress (Pa).
$\phi$	porosity (% or unitless).

## Section 11: strength and deformation

$c$	cohesion (Pa).
$E$	Young's modulus (Pa).
$E_{50}$	secant Young's modulus at 50% failure stress (Pa).
$P_p$	pore pressure (Pa).
$S_h$	hydrate saturation in the pore space (% or unitless).
$S_{h(crit)}$	critical hydrate saturation, typically between 25% and 45%, indicating the transition from hydrate as a pore fill to hydrate as a structural component of the sediment (%).
$S_{h(occ)}$	hydrate saturation beyond which pores become occluded, typically $\sim 80\%$ (%).
$\alpha$	failure plane angle from horizontal (degrees or radians).
$\nu$	Poisson's ratio (unitless).
$\nu_{50}$	Poisson's ratio at 50% failure stress (unitless).
$\sigma'_1$	maximum principal effective stress (Pa).
$\sigma'_3$	minimum principal effective stress (Pa).
$\sigma'_n$	normal effective stress acting on the failure plane (Pa).
$\tau$	shear stress (Pa).
$\tau_f$	shear stress at failure (Pa).
$\Phi$	friction angle (degrees or radians).
$\psi$	dilatancy angle (degrees or radians).

## Section 12: volume change upon dissociation

$C_c$	coefficient of compressibility (unitless).
$e_0$	initial void ratio (unitless).
$k_a$	Rankine's active Earth pressure coefficient (unitless).
$k_o$	stress ratio "at rest," meaning under zero lateral strain (unitless).
$V$	volume ( $\text{m}^3$ ).
$\beta$	reduction factor pertaining to the volumetric strain (unitless).
$\Delta P$	pressure change induced by depressurization (Pa).
$\epsilon_{vol}$	volumetric strain (unitless).
$\epsilon_z$	vertical strain (unitless).
$\sigma'_{z0}$	initial vertical effective stress (Pa).

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