Thermal conductivity of hydrate-bearing sediments

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[1] A thorough understanding of the thermal conductivity of hydrate-bearing sediments is necessary for evaluating phase transformation processes that would accompany energy production from gas hydrate deposits and for estimating regional heat flow based on the observed depth to the base of the gas hydrate stability zone. The coexistence of multiple phases (gas hydrate, liquid and gas pore fill, and solid sediment grains) and their complex spatial arrangement hinder the a priori prediction of the thermal conductivity of hydrate-bearing sediments. Previous studies have been unable to capture the full parameter space covered by variations in grain size, specific surface, degree of saturation, nature of pore filling material, and effective stress for hydrate-bearing samples. Here we report on systematic measurements of the thermal conductivity of air dry, water- and tetrohydrofuran (THF)-saturated, and THF hydrate–saturated sand and clay samples at vertical effective stress of 0.05 to 1 MPa (corresponding to depths as great as 100 m below seafloor). Results reveal that the bulk thermal conductivity of the samples in every case reflects a complex interplay among particle size, effective stress, porosity, and fluid-versus-hydrate filled pore spaces. The thermal conductivity of THF hydrate–bearing soils increases upon hydrate formation although the thermal conductivities of THF solution and THF hydrate are almost the same. Several mechanisms can contribute to this effect including cryogenic suction during hydrate crystal growth and the ensuing porosity reduction in the surrounding sediment, increased mean effective stress due to hydrate formation under zero lateral strain conditions, and decreased interface thermal impedance as grain-liquid interfaces are transformed into grain-hydrate interfaces.


1. Introduction

[2] The formation and dissociation of gas hydrate involve a significant change in energy (e.g., 338.7 J g⁻¹ at 273 K in the case of structure I methane hydrate) [Handa, 1986]. Phase transformation, including dissociation for the purposes of energy production from methane hydrates, may therefore be limited by thermal transport in the bulk medium, which includes not only hydrate, but also mineral grains and non-hydrate pore fill. The thermal properties of hydrate-bearing sediments are also critical for estimating regional heat flow from the observed depth of the bottom simulating reflection (BSR) that marks the base of the gas hydrate stability zone in some marine settings [e.g., Yamano et al., 1982; Grevenmeyer and Villinger, 2001] and for analysis of thermal gradients measured within hydrate-bearing sediments [e.g., Tzirita, 1992; Ruppel, 2000]. Adoption of incorrect thermal conductivity values for hydrate-bearing sediments interspersed with hydrate-free sediments can result in errors in estimated heat flow.

[3] Thermal conductivity is the key property that controls the transfer of thermal energy, yet data on the thermal conductivity of hydrate-bearing sediments remain limited. Several studies have focused on determining the thermal conductivity of gas hydrate in the absence of sediments [e.g., Cook and Leaist, 1983; deMartin, 2001; Huang and Fan, 2005; Ross and Andersson, 1982; Waite et al., 2002, 2005] and often at pressure temperature conditions that do not occur in nature. Some of these studies had significant experimental difficulties such as the formation of water ice. Because these studies focus only on the gas hydrate phase, the results sometimes have limited applicability to heat transfer processes in multicomponent natural systems consisting of mineral grains, a hydrate phase, and other pore filling material (gas or liquid).

[4] Researchers have also measured the in situ thermal conductivity of hydrate-bearing sediments in permafrost [Henninges et al., 2005] and marine [e.g., Tréhu, 2006] settings. While such analyses advance understanding of bulk in situ thermal properties, the data are of limited utility for
understanding the impact of various parameters or processes on the thermal conductivity of hydrate-bearing sediments. The primary challenge is the inability to accurately assess in situ hydrate saturations and to constrain the microscale arrangement of mineral grains, hydrate, and other pore filling components. Without such detailed information, evaluating the significance of the in situ thermal conductivity data for other hydrate-bearing sediment regimes is impossible.

A major challenge in the study of hydrate-bearing sediments has been the difficulty of forming methane hydrate in the laboratory on reasonable time scales. In marine settings, most gas hydrate probably forms from aqueous phase, not gaseous, methane [Buffett and Zatsepina, 2000]. This gas-limited process, whether dependent on diffusive or advective transport of the gas, is too slow for routine use in the laboratory, although some recent studies have reported progress in overcoming this obstacle [e.g., Spangenberg et al., 2005; Waite et al., 2008b]. Methane hydrate can be formed rapidly in the laboratory by percolating methane gas through soils [e.g., Helgerud, 2001; Waite et al., 2004] or using the ice seed method [Stern et al., 1996, 1998], and published laboratory studies on the thermal conductivity of methane hydrate-bearing sediments rely on one of these techniques [e.g., Waite et al., 2002; Tzirita, 1992]. Unfortunately, both techniques bias the pore scale distribution of hydrates within the soil matrix, alter the interaction among hydrate, pore fluid and sediment grains, and affect many physical properties, including seismic velocities, mechanical strength, and thermal conductivity [Lee, 2007; Lee et al., 2007; Santamarina and Ruppel, 2008; Yun et al., 2007].

Several previous studies have examined the thermal conductivity of synthetic hydrate-bearing sediments over a limited parameter space. Due to a variety of experimental and logistical constraints, such studies have been conducted with a single soil (i.e., single grain size-specific surface), at a single confining stress, with a single pore filling phase in addition to hydrate (gas or fluid), and/or without comparison to saturated and dry soil samples lacking hydrate [e.g., Stoll and Bryan, 1979; Waite et al., 2002; Huang and Fan, 2005; Henninges, 2007]. Tzirita [1992] conducted experiments on hydrate-bearing sand and pure methane hydrate. His results showed that methane hydrate played an important role in increasing grain-to-grain heat transfer and thus thermal conductivity in hydrate-bearing sands and that increased effective stress led to increased grain-to-grain conduction.

This study documents a systematic approach to the experimental determination of the thermal conductivity of hydrate-bearing samples. We consider the impact of hydrate formation, grain size and effective stress on bulk thermal conductivity. The results highlight the considerable complexity of heat transfer mechanisms in dry, saturated, and hydrate-bearing clay and sand samples and can potentially contribute to an understanding of the results obtained by earlier workers [e.g., deMartin, 2001] in more limited laboratory experiments.

2. Background: Heat Transfer in Granular Media

Heat transfer takes place through convection, radiation, and conduction. In granular media, the relative contribution of free convective heat transport gains relevance in coarse grained soils characterized by a mean grain size greater than 6 mm [Thalmann, 1950]. On the other hand, radiative heat transport occurs through photon emissions and electromagnetic wave propagation and is only significant at temperatures above ~500°C [Guéguen and Palciauskas, 1994]. Therefore, heat transport in fine sands and clays at low temperatures is conductive, and the thermal conductivity is the key parameter governing heat transfer.

The thermal conductivities of grains and fluids vary across several orders of magnitude: mineral grains (order of 10 W m$^{-1}$ K$^{-1}$), water (order of 1 W m$^{-1}$ K$^{-1}$), and air (order of 0.01 W m$^{-1}$ K$^{-1}$). Such a contrast in thermal conductivities leads to preferential particle-level heat transport processes in granular materials: conduction along the mineral, particle-to-particle conduction across contacts, particle-fluid-particle conduction across the fluid near contacts, and conduction along the pore fluid within the pore space (Figure 1) [Yun and Santamarina, 2007]. The main factors that determine the bulk thermal conductivity of soils follow from the particle level transport process and include the volumetric fractions and properties of the constituents and the spatial arrangement and degree of connectivity of the grains.

2.1. Mineralogy

The thermal conductivity of quartz is higher than other common soil forming minerals. Thus, the thermal conductivity of sediments is proportional to the volumetric fraction of quartz [Gangadhara Rao and Singh, 1999; Tarnawski et al., 2002].

2.2. Particle Size

Interparticle conductive heat transfer is proportional to the particle radius and inversely proportional to the
intercontact distance [Batchelor and O’Brien, 1977]. Thus larger particles lead to higher thermal conductivity [Ahuda, 1996; Gangadhara Rao and Singh, 1999; Tarnawski et al., 2002].

2.3. Packing Density and Coordination Number
[12] Interparticle contacts play an important role in heat transfer processes. The higher the packing density and coordination number, the higher the thermal conductivity of the sediment [Tarnawski et al., 2002].

2.4. Water Content
[13] Water acts as a relatively high conductivity bridge between particles. Therefore, the thermal conductivity of partially saturated soils increases with the degree of saturation [Andersland and Ladanyi, 2004; Farouki, 1985; Lu et al., 2007; Singh and Devid, 2000]. This observation applies to hydrate-bearing sediments during dissociation and gas production, when mineral, hydrate, gas, and liquid coexist.

2.5. Effective Stress
[14] The increase in packing density, coordination number, and contact quality with increasing effective stress leads to higher thermal conductivity. Load-bearing granular chains within the soil skeleton greatly facilitate heat transfer [Batchelor and O’Brien, 1977; Lambert and Fletcher, 1997; Sridhar and Yovanovich, 1996; Vargas and McCarthy, 2001].

[15] Numerous theoretical, empirical, and semiempirical models have been developed to predict the effective thermal conductivity of composite natural materials, yet only a few of them account for the interconnectivity of the high thermal conductivity mineral phase and the quality of thermal contacts [e.g., Droval et al., 2006; Yagi and Kunii, 1957]. In fact, thermal conductivity in granular media is often overpredicted because the resistance at contacts is not properly accounted for [Chung, 2001].

3. Laboratory Methods
[16] We measure the thermal conductivity ofhydrate-bearing sediments having different mineral grains and subject to different vertical effective stresses. The selected soils (sand and kaolinite) cover a wide range of grain sizes ($d_{50}$ from 1 µm to 120 µm, where $d_{50}$ refers to the diameter for which 50% of the grains have larger size) and specific surface (0.02 m$^2$ g$^{-1}$ to 36 m$^2$ g$^{-1}$). Table 1 provides details about the soils used for testing, with additional information given by Yun et al. [2007] and Lee et al. [2007].

3.1. Hydrate Former
[17] We use tetrahydrofuran (THF) as the hydrate former. THF (C$_4$H$_8$O) is a clear, colorless, low-viscosity fluid that has an ether-like odor, high volatility, low freezing point (~208 K), and complete miscibility with water. The THF molecule does differ from the methane molecule; in contrast to methane, THF is a structure II, not structure I, hydrate former. Yet the thermal conductivity of methane hydrate [Waite et al., 2005; Krivchikov et al., 2005] and THF hydrate are known to be similar (Table 2), and the behavior of THF as a hydrate former is well understood at both the molecular and pore scales [Lee et al., 2007].

### Table 1. Index Properties of Tested Soils as Reported by Guimaraes [2001], Klein [1999], and Santamarina and Cho [2001]$^a$

<table>
<thead>
<tr>
<th>Soil</th>
<th>$d_{50}$ (µm)</th>
<th>Specific Gravity</th>
<th>Specific Surface (m$^2$ g$^{-1}$)</th>
<th>$n_{max}/n_{min}$</th>
<th>Sphericity</th>
<th>Roundness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand (F110)</td>
<td>120</td>
<td>2.65</td>
<td>0.019</td>
<td>0.46/0.35</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Clay (SA1 kaolinite)</td>
<td>1.1</td>
<td>2.6</td>
<td>36–37</td>
<td>—</td>
<td>0.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>

$^a$SEM photos of the soils and additional information can be found in Yun et al. [2007] and Palomino and Santamarina [2005].

### Table 2. Thermal Conductivity of Sample Components and Related Materials$^b$

<table>
<thead>
<tr>
<th>Thermal Conductivity (W m$^{-1}$ K$^{-1}$)</th>
<th>Temperature (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>273</td>
<td>Kaye and Laby [2007]</td>
</tr>
<tr>
<td>Water</td>
<td>273</td>
<td>Kaye and Laby [2007]</td>
</tr>
<tr>
<td>Ice</td>
<td>353</td>
<td>Kaye and Laby [2007]</td>
</tr>
<tr>
<td>THF-17H$_2$O Liquid</td>
<td>268</td>
<td>Kaye and Laby [2007]</td>
</tr>
<tr>
<td>THF-17H$_2$O Hydrate</td>
<td>261</td>
<td>This study</td>
</tr>
<tr>
<td>CH$_4$ Hydrate</td>
<td>273</td>
<td>Huang and Fan [2005]</td>
</tr>
<tr>
<td>Water-Saturated Sand</td>
<td>293</td>
<td>This study</td>
</tr>
<tr>
<td>Sand Saturated With THF-17H$_2$O Liquid</td>
<td>293</td>
<td>This study</td>
</tr>
<tr>
<td>Sand With 100% THF-17H$_2$O Hydrate</td>
<td>261</td>
<td>This study</td>
</tr>
<tr>
<td>Dry Clay</td>
<td>293</td>
<td>This study</td>
</tr>
<tr>
<td>Water-Saturated Clay</td>
<td>293</td>
<td>Becker et al. [1992]</td>
</tr>
<tr>
<td>Clay Saturated With THF-17H$_2$O Liquid</td>
<td>293</td>
<td>This study</td>
</tr>
<tr>
<td>Clay With 100% THF-17H$_2$O Hydrate</td>
<td>261</td>
<td>This study</td>
</tr>
<tr>
<td>Quartz</td>
<td>298</td>
<td>Kaye and Laby [2007]</td>
</tr>
</tbody>
</table>

$^b$When a range of values is reported for soil samples, the lowest and highest values, respectively, represent the thermal conductivities corresponding to the lowest and highest vertical effective stresses used in this study.

$^b$Above freezing.
is then placed on top of the specimen, followed by the loading the desired height, excess pore fluid is removed. Filter paper regularly to attain a uniform density. When the sand reaches surface to avoid air entrainment. The specimen is tamped are then poured using a funnel held very close to the fluid intended pore fluid into the stainless steel cell. Sand particles of THF 17H2O, which corresponds to 19% THF to 81% thermal conductivity. Here, we use a target fluid composition state of effective stress) that can play an important role in other important geological conditions (e.g., evolution of the synthesis of specimens and allows us to properly reproduce mixed at the beginning of the experiment. This facilitates the evaporation losses during mixing [Lee et al., 2007; Yun et al., 2007], solutions in this study are mixed at 22% THF. This also ensures that ice does not form [Waite et al., 2005; Lee et al., 2007].

3.2. Sample Preparation and Configuration

Sediments are confined within a cylindrical stainless steel cell (inside diameter 63.5 mm, height 187.95 mm) to impose zero-lateral strain conditions (Figure 2a). We measure the vertical displacement of the top cap and compute the instantaneous porosity. Excess pore fluid can drain freely through the upper boundary; we use a supernatant oil layer seal to minimize THF evaporation throughout the testing period. During phase transformation, we maintain a constant force to attain a constant vertical effective stress condition. Pore pressure is constant at the boundaries, but may change randomly within the specimen.

Sand specimens are prepared by first placing the intended pore fluid into the stainless steel cell. Sand particles are then poured using a funnel held very close to the fluid surface to avoid air entrainment. The specimen is tamped regularly to attain a uniform density. When the sand reaches the desired height, excess pore fluid is removed. Filter paper is then placed on top of the specimen, followed by the loading cap and the thermal conductivity probe instrumentation. Kaolinite specimens are formed by mixing kaolin powder with the pore fluid at a mass ratio of 0.8, which is above the liquid limit (LL) of the soil, which is LL = 0.7 for water as pore fluid. A filter paper saturated in the pore fluid is placed along the inner perimeter of the stainless steel cell to facilitate consolidation. The kaolinite paste, held within a plastic liner, is placed inside the cell against the saturated filter paper. The liner is carefully pulled up while holding the paste in place by exerting pressure at the surface. Finally, a saturated filter paper and the loading cap are set on top of the sediment. There is no target density for the kaolinite specimen.

3.3. Thermal Conductivity Measurements

The thermal conductivity of the specimens is measured with a needle probe using the technique first outlined by Von Herzen and Maxwell [1959]. We use an East 30 Sensors needle probe mounted on the upper cap (Figure 2a) and containing a heating wire and thermocouple (Figure 2b). A transient heat pulse is generated by imposing a DC current through the heating wire while the thermocouple monitors the temperature within the needle. The needle’s length (60 mm) is much greater than its diameter (1.5 mm) so that radial conduction conditions prevail. Temperature is recorded continuously throughout the duration of the test, including during the periods of hydrate formation and dissociation. A thermal conductivity measurement consists of monitoring the input power and temperature increase every second during a 100-s-long heating interval. The typical temperature-time evolution for a given vertical effective stress is shown in Figure 3.

3.4. Experimental Sequence

1. Subject the specimen to the vertical effective stress (0.05, 0.1, 0.25, 0.5 or 1 MPa, which corresponds to depths as great as ~100 m below seafloor) and allow it to consolidate at constant force until there is no further volume change. This phase endures from less than an hour in sand to over 24 h in kaolinite.

2. Determine the thermal conductivity for the consolidated unfrozen specimen under the applied vertical effective stress at room temperature during 3 separate measurements.

3. In specimens containing a mixture of THF and water, cool the specimen to a temperature between 258 and 268 K to form hydrate.

4. Determine the thermal conductivity of the hydrate-bearing sediment during four separate measurements.

5. Warm the specimen to room temperature to dissociate thehydrate. Phase transformation for THF hydrate occurs at 277 K.

6. Increase the vertical effective stress and repeat steps 1 through 5.

4. Data Reduction

The general analytical solution to the line source problem in an infinite medium can be simplified for long-duration measurements to obtain the expression \[ \Delta T = A + B \ln(t/t_0) \] [Jones, 1988], where \( \Delta T \) denotes the change in temperature, \( A \) and \( B \) are fitting parameters, \( t \) denotes time [s] and the [s] in the denominator of the logarithm's
argument is included to make the total argument dimensionless. The parameter \( B = \frac{q}{4\pi \lambda} \) is a function of the thermal conductivity \( \lambda \) [W m\(^{-1}\) K\(^{-1}\)] of the medium and the power \( q \) [W m\(^{-1}\)] supplied to the needle probe. Therefore the thermal conductivity can be determined from the slope of the data plotted in \( \Delta T \) versus \( \ln(t) \) space. It is often cumbersome to select the proper time range for fitting the experimental data due to the complexity of signatures recorded with real sediments and the wide range in resulting \( B \) values that can be extracted by fitting parts of the experimental data. Data fitting can be constrained using the intercept, but \( A \) is a function of the medium properties, including the thermal conductivity itself, as well as the effective heat transfer coefficient between the probe and the medium, a factor that is difficult to assess [Jones, 1988]. To improve data reduction, we represent the cell, the specimen, and the needle probe using finite elements, and solve the heat equation

\[
\rho C \frac{dT}{dt} - \nabla \cdot (\lambda \nabla T) = Q, \tag{1}
\]

in COMSOL Multiphysics\(^\text{\textregistered}\) software. In (1) the parameters are density \( \rho \) [kg m\(^{-3}\)], temperature \( T \) [K], heat capacity \( C \) [J kg\(^{-1}\) K\(^{-1}\)], thermal conductivity \( \lambda \) [W m\(^{-1}\) K\(^{-1}\)], and power input \( Q \) [W m\(^{-1}\)]. The initial density of the medium is known, and the heat capacity is computed as a volumetric weighted average of the components. The needle probe is modeled with an inner copper core of 0.2 mm radius surrounded by a 0.2-mm-thick wax layer. Both the copper core and the wax layer are enclosed within a 0.25-mm-thick stainless steel cylindrical shell. The outer wall of the stainless steel cell (31.7 mm inner radius and 6.32-mm-thick) encloses a homogeneous medium that represents the sediment under study. Other model parameters are given in Table 3.

30 Initially, the soil cell system is considered at equilibrium and at temperature \( T_o \) throughout. The cell wall is maintained at constant temperature \( T_o \) throughout the model run. Heat flux is imposed at the boundary between the copper core and the wax layer at \( t > 0 \). Continuity is satisfied at all other internal boundaries. No boundary effects are observed during the first 300 s when either perfectly conductive or perfectly insulating cell walls are imposed.

31 We calibrate our laboratory measurement system against the numerical model using data gathered for water that was gelled to avoid convection. This calibration allows us to determine the magnitude of the heat flux associated with a given input voltage applied to the needle probe. The calibrated numerical model is used for data reduction by performing successive forward simulations until model predictions fit experimental data. The resolution in conductivity obtained with this procedure is better than \( \pm 0.1 \lambda \). Figure 4 shows data and a set of numerical results generated during data reduction. The main advantage of applying a numerical simulation rather than available analytical solutions is increased confidence in data analysis. In particular, the FEM simulations give us the ability to properly capture boundary conditions, to study their impact, and to reproduce the whole time series rather than selecting a priori the range of data to be fit.

5. Results

5.1. Air Dry Sediments

32 Thermal conductivity values for all tested sediments under air dry conditions are shown as a function of vertical effective stress in Figure 5. These data highlight the role of coordination number and contact quality, which increase with effective stress (i.e., the bottlenecks for heat conduction). The extrapolation to higher vertical effective stress levels can be taken into consideration through changes in porosity. Volume change is monitored throughout the testing history to recover the instantaneous porosity in the sediment. All specimens experience volume contraction during loading, but volume change is more pronounced in kaolinite specimens. The porosity in air dry kaolinite decreases from 0.74 to 0.61 when the vertical effective stress changes from 0.05 MPa to 1 MPa. The associated change in thermal conductivity is 0.074 W m\(^{-1}\) K\(^{-1}\) to 0.21 W m\(^{-1}\) K\(^{-1}\). For the same vertical effective stress interval, the porosity change in air dry sand...
is small (0.45 to 0.44), but the increase in thermal conductivity is pronounced (0.28 W m\(^{-1}\) K\(^{-1}\) to 0.48 W m\(^{-1}\) K\(^{-1}\)). For comparison, the rate of change of thermal conductivity relative to porosity \(n\), as given by \(\frac{\Delta \lambda}{\Delta n}\), is -1 W m\(^{-1}\) K\(^{-1}\) in the kaolinite and 20 W m\(^{-1}\) K\(^{-1}\) in sand.

5.2. Water Saturated Sediments (Without Hydrate)

[33] Figure 5 also shows the results for water saturated unfrozen specimens. Thermal conductivity values are much higher than for air dry conditions, highlighting the contribution of water in facilitating heat transport across contacts. The thermal conductivity of the saturated sand shows no measurable sensitivity to changes in vertical effective stress. Saturated kaolinite exhibits an increase in thermal conductivity (2.1 W m\(^{-1}\) K\(^{-1}\) to 2.8 W m\(^{-1}\) K\(^{-1}\)) for vertical effective stress increasing from 0.05 MPa to 1 MPa. The associated change in porosity is 0.67 to 0.51.

5.3. Specimens With THF Solution (With and Without Hydrate)

[34] The thermal conductivity data for room temperature sediments mixed with the stoichiometric THF solution as the pore-filling fluid are also shown in Figure 5. The thermal conductivity of stoichiometric THF solution at room temperature is very close to the value for water (Table 2). Therefore, the conductivity in the unfrozen state differs little between the THF- and water-saturated specimens. Differences reflect changes in porosity and fabric due to pore fluid chemistry (in the kaolin specimen) or due to densification (in the sand specimen).

[35] Figure 6 shows the thermal conductivity for THF-saturated sand and kaolinite specimens before and after hydrate formation. There is a marked increase in conductivity at low vertical effective stress in both sand (3.7 W m\(^{-1}\) K\(^{-1}\) to 4.5 W m\(^{-1}\) K\(^{-1}\)) and kaolinite (1.6 W m\(^{-1}\) K\(^{-1}\) to 2.8 W m\(^{-1}\) K\(^{-1}\)) specimens upon hydrate formation at vertical effective stress of 0.05 MPa. For these experiments, samples having 100% hydrate saturation experience volume...
expansion during hydrate formation and volume contraction upon dissociation.

6. Discussion

The compiled experimental results imply that several factors affect the thermal conductivity of soils with different pore filling material and at different vertical effective stress under zero-lateral strain conditions. First, we consider the air dry specimens, whose thermal conductivities are plotted as a function of porosity in Figure 7. Two causal links between effective stress and thermal conductivity are readily identified: (1) For coarse-grained soils (sand), increased effective stress results in little porosity reduction. Thus, the increase in thermal conductivity with effective stress $\sigma'$ reflects enhanced heat transfer across contacts due to the higher interparticle contact force $F$, which is proportional to $d^2 \sigma'$, where $d$ is the grain diameter. (2) For fine-grained soils (kaolinite), the increase in thermal conduction is primarily caused by the large reductions in porosity, which leads to an increase in coordination number.

Next we consider the saturated specimens. The liquid in the pore space contributes to thermal conduction within the fluid along the pores and creates a thermal bridge between particles, leading to particle-fluid-particle conduction (Figure 1). Replacing air with either water or the liquid THF solution increases the effective thermal conductivity of the bulk samples by a factor of $C_{\text{THF}}^2$ (Figure 5). Clearly, the presence of liquid in pores in the samples exerts a far greater effect on thermal conductivity than does the change in effective stress. The effect of water should extend to relatively low water saturation levels as anticipated from Figure 1. Such low saturation conditions are characteristic of hydrate dissociation and gas production in natural settings.

Finally, we consider the case of hydrate-bearing sediments. The thermal conductivity of THF hydrate is close to that of a liquid phase mixture of THF and water, in sharp contrast to the situation for ice and water (Table 2). It might therefore be assumed that the presence of hydrate should have little impact on bulk soil thermal conductivity. The increase that we observe in thermal conductivity in the presence of hydrate for both coarse- and fine-grained sediments therefore requires further analysis. We consider several hypotheses that may explain the thermal conductivity relationships noted in our data.

6.1. Experimental Bias

The design or implementation of the laboratory experiments might have produced systematic problems that lead to increased thermal conductivity in the hydrate-bearing sediments. For example, if excess water were present, ice would have formed in pore space and increased the thermal conductivity of the sample. Our experiments were carefully prepared to ensure a condition of excess THF, not free water, if hydrate formation did not run to full theoretical completion (i.e., 100% occupancy of pore space). Furthermore, none of the temperature measurements (e.g., Figure 3) reveals a second phase transition plateau as would be expected in the case of a water-ice transition. Noise in the data and uncertainty in data reduction can also not account for the measured increase in thermal conductivity in the presence of hydrate; in all cases, the raw data show clear and consistent differences between specimens before and after hydrate formation.

6.2. Cryogenic Suction and Segregation

The literature on ice in fine-grained soils shows that ice forms first in the larger pores. Then, the pore fluid migrates from the smaller pores toward the nucleating ice, causing cryogenic suction (Andersland and Ladanyi, 2004; Hutchinson, 1974; Konrad, 1989; McRoberts, 1975; Miller, 1980). Therefore, while soils experience global volume expansion during freezing, the local porosity decreases near the freezing front.
Figure 8. Fluid-saturated sediment of initial porosity \( n_0 \) and volume \( A \cdot L \) is shown on the left. Hydrate forms at constant mass, undergoing volume expansion \( (A \cdot \Delta L) \) and occupies a segregated volume \( A \cdot t_l \) on the right side of the diagram. The porosity \( n_1 \) of the neighboring, unfrozen saturated soil has decreased compared to initial porosity \( n_0 \) as fluid migrated to the hydrate phase.

[41] Cryogenic suction and segregation may also play an important role in controlling the thermal conductivity of hydrate-bearing sediments. The effective thermal conductivity will depend on the conductivity of the hydrate phase, the conductivity of the lower-porosity unfrozen sediment, and the relative spatial distribution of the frozen and unfrozen areas within the sample.

[42] Consider a fluid saturated sediment of initial porosity \( n_0 \) and volume \( A \cdot L \), where \( A \) denotes area and \( L \) length (Figure 8). Hydrate forms at constant mass and occupies a segregated volume \( A \cdot t_l \). The porosity of the neighboring, unfrozen saturated soil decreases as fluid driven by cryogenic suction migrates to the hydrate phase. Invoking mass conservation and incorporating volume expansion \( \beta \) of 9.89% during hydrate formation [Sloan, 1998], the reduced porosity \( n_1 \) for the unfrozen sediment becomes:

\[
n_1 = n_0 \frac{1 + \beta (1 - \alpha_L)}{1 + \beta} - \alpha_L,
\]

where \( \alpha_L \) is the volume fraction of segregated hydrate determined from \( \alpha_L = t_l/(L + \Delta L) \) with \( \Delta L \) denoting the change in the specimen’s length.

[43] The effective media properties of the hydrate-bearing sediment will depend on the spatial distribution of the segregated hydrate in the sample. Two of the most commonly used effective media models, parallel and series, predict different results for the case of cryogenic suction during hydrate formation. A series model, given by

\[
\lambda_{\text{series}} = \left[ \frac{\alpha_L \lambda_h + (1 - \alpha_L) \lambda_{\text{soil}}}{1 - \alpha_L} \right]^{-1},
\]

predicts a decrease in bulk thermal conductivity \( \lambda_{\text{series}} \). Subscripts \( h \) and “soil” refer to hydrate and mineral grains, respectively. The parallel model

\[
\lambda_{\text{parallel}} = \alpha_L \lambda_h + (1 - \alpha_L) \lambda_{\text{soil}},
\]

6.3. Increase in Effective Stress

[44] The increase in thermal conductivity of fine-grained soils following cryogenic suction and hydrate segregation processes should be less pronounced at high effective stress. Indeed, our experimental results show smaller changes in conduction upon hydrate formation at high effective stress in the kaolinite sample.

6.4. Reduced Interface Thermal Impedance

[45] Cryogenic suction loses relevance in the case of coarse-grained soils (sand), and it therefore cannot be invoked to explain the observed increase in thermal conductivity during hydrate formation. However, volume expansion during hydrate formation produces a large increase in radial effective stress in the sample, which is maintained under zero-lateral strain conditions. Note that during volume expansion the principal stresses may even rotate, with the effective vertical stress becoming the radial stress. For coarse-grained soils, the change in thermal conductivity recorded in Figure 5 may primarily reflect the improvement in the quality of intergranular contacts during the increase in effective stress.

7. Conclusions

[47] 1. The analytical solution for a line source in an infinite medium can be used to fit our data, but with poor resolution. We achieved lower uncertainty in thermal conductivity using a numerical model of the tested needle medium cell system.

[48] 2. Increasing the effective confining stress on granular media increases both the number of contacts (prevalent in clayey soils) and the quality of contacts (prevalent in sandy soils). A tenfold increase in vertical effective stress from an initially low stress level can cause an increase in thermal conductivity by a factor of 2 or 3.

[49] 3. Changing the pore fluid from gas (dry) to liquid (saturated) allows for additional conduction paths, namely grain-liquid-grain and through the percolating liquid phase. This results in a pronounced increase in thermal conductivity, typically by a factor of ~10 or greater, between dry and
References


Andersland, O. B., and B. Ladanyi (2004), or recommendations expressed herein are those of the authors and do not endorse by the U.S. Government. Any opinions, findings, conclusions, product, or firm name is for descriptive purposes only and does not imply sediments at Georgia Institute of Technology. Comments by W. Waite and additional support from the Goizueta Foundation. C.R. thanks the Petro-

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