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Cover: Gas hydrates are of keen interest for energy and carbon cycle considerations. Constable et al. (e2020GL087645; <u>https://doi.org/10.1029/2020GL087645</u>) report on electrical properties of lab-made methane hydrate mixtures; shown here is pure methane hydrate. Photo credit: Laura Stern/USGS.



Geophysical Research Letters

RESEARCH LETTER

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Key Points:

- We quantified the electrical conductivity of laboratory-formed methane hydrate mixed with sand or silt plus a fluid phase
- Conductivity measurements of hydrate and sand agree with borehole logs through highly saturated hydrate
- Hydrate saturation in our samples is consistent with a simple version of Archie's law

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Laboratory Electrical Conductivity of Marine Gas Hydrate

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Abstract Methane hydrate was synthesized from pure water ice and flash frozen seawater, with varying amounts of sand or silt added. Electrical conductivity was determined by impedance spectroscopy, using equivalent circuit modeling to separate the effects of electrodes and to gain insight into conduction mechanisms. Silt and sand increase the conductivity of pure hydrate; we infer by contaminant NaCl contributing to conduction in hydrate, to values in agreement with resistivities observed in well logs through hydrate-saturated sediment. The addition of silt and sand lowers the conductivity of hydrate synthesized from seawater by an amount consistent with Archie's law. All samples were characterized using cryogenic scanning electron microscopy and energy dispersive spectroscopy, which show good connectivity of salt and brine phases. Electrical conductivity measurements of pure hydrate and hydrate mixed with silt during pressure-induced dissociation support previous conclusions that sediment increases dissociation rate.

Plain Language Summary Methane hydrate is a frozen mixture of methane gas and water ice and occurs naturally in the seafloor of the continental shelves worldwide. Hydrate is variously considered a source of energy, a natural hazard, or a potential contribution to ocean acidification and climate change. Measurement of seafloor electrical conductivity, either using borehole logs or geophysical prospecting methods, is one of the most reliable ways of estimating hydrate location and abundance, but such methods need to be calibrated using laboratory measurements on hydrate-sediment mixtures. We have made laboratory conductivity measurements on mixtures of hydrate, sand and silt, and seawater. Our results are in good agreement with borehole logs through seafloor sediments fully saturated with hydrate and will allow other scientists to more reliably estimate hydrate concentration from electrical conductivity.

1. Introduction

Gas hydrates are ice-like crystalline structures with encaged molecules, usually methane (CH_4), that forms at temperatures and pressures found on the continental shelves deeper than about 500 m. Although vast amounts of carbon are sequestered as hydrate, 1,000 to 100,000 Gt globally, this total is uncertain (Milkov, 2004). The majority of hydrate is dispersed at low concentrations (Boswell & Collett, 2011), but some marine gas hydrate forms in high concentrations as pore-filling material in clastic sediments such as sands and silts. Such deposits are of interest as a supply of natural gas, particularly for countries that lack conventional hydrocarbons, and several offshore production tests have been made (Fujii et al., 2015; Yamamoto et al., 2014). Dissociation of gas hydrate situated at the edge of its stability field has been implicated in seafloor landslides (e.g., Nixon & Grozic, 2007; Paull et al., 2008), which may potentially generate tsunamis. Rapid release of methane to seawater could contribute to ocean acidification (Biastoch et al., 2011), and even climate change if methane reaches the atmosphere in shallow arctic waters (Wadhams, 2016).

Much of our understanding of seafloor gas hydrate comes from seismic surveys and drilling, either as by-products of conventional hydrocarbon exploration or as targeted scientific studies (e.g., Boswell et al., 2016). These methods are both expensive and subject to limitations. The seismic method is relatively blind to low hydrate concentrations (Waite et al., 2009), especially if grain cementation does not occur, and even high concentrations are difficult to identify and quantify without control from well logs (e.g., Cook & Tost, 2014; Shelander et al., 2012). Drilling provides a good understanding of seafloor geology, but hydrate rapidly changes concentration in a lateral direction, so data along one vertical profile cannot easily be extrapolated. Gas hydrate is electrically resistive, a feature that is exploited in well logging (Collett, 2001; Goldberg et al., 2010), and can be imaged using marine controlled-source electromagnetic (CSEM) methods (e.g., Constable

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Methane Hydrate Synthesis Conditions, Conductivity (0) at +5°C, and Armenias Fits (Ed and 00)				
Sample name	Sample conditions	σ (S/m)	Ea (kJ/mol)	$\log(\sigma_0)$
MH ^a	CH ₄ hydrate synthesized from ice	3.49E-05	33.62	1.861
MH + NaCl0.25 ^a	$\rm CH_4$ hydrate from ice with 0.25 wt% NaCl	2.85E-04	36.62	3.362
MH + NaCl1.0 ^a	CH ₄ hydrate from ice with 1.0 wt% NaCl	1.31E-03	35.52	3.281
MH + Sand10 ^b	CH ₄ hydrate from ice with 10 vol% Sand	7.80E-05	31.31	1.779
MH + Sand45 ^b	$\rm CH_4$ hydrate from ice with 45 vol% Sand	9.98E-05	43.18	4.122
MH + Silt10	CH ₄ hydrate from ice with 10 vol% Silt	1.50E-04	30.58	1.973
MH + Silt50	$\rm CH_4$ hydrate from ice with 50 vol% Silt	2.03E-04	37.82	3.442
SH ^a	CH ₄ hydrate synthesized from frozen seawater	3.02E-01	86.38	15.58
SH + Sand50	$\rm CH_4$ hydrate from seawater with 50 vol% Sand	6.40E-02	76.11	13.12
SH + Silt50	$\rm CH_4$ hydrate from seawater with 50 vol% Silt	3.63E-02	80.26	13.67

Table 1

Methane Hydrate Synthesis Conditions. Conductivity (σ) at +5°C, and Arrhenius Fits (Ea and σ_{-})

^aSample data from Lu et al. (2019). ^bSample data from Du Frane et al. (2015).

et al., 2016; Schwalenberg et al., 2010; Wang et al., 2017; Weitemeyer et al., 2006). While CSEM data can be useful as a stand-alone method, because resistivity and seismic properties sample geology in very different ways, the combination of electrical and seismic methods can be very useful (e.g., Kannberg & Constable, 2020).

The interpretation of CSEM and well log data requires the support of laboratory studies of conductivity (e.g., Lee et al., 2010; Li et al., 2012; Priegnitz et al., 2015; Spangenberg & Kulenkampff, 2006). In a series of previous papers we investigated electrical conductivity as a function of temperature for pure methane hydrate (Du Frane et al., 2011), hydrate with sand (Du Frane et al., 2015), and hydrate with salt (NaCl) (Lu et al., 2019). Here we conclude these studies by comparing the effect of sand and silt with hydrate synthesized from pure water and flash frozen seawater, and examining conductivity during pressure-induced dissociation. Combined with the previous studies, our results provide a comprehensive picture of methane hydrate conductivity. Sediments increase the conductivity of methane hydrate, silt more than sand when mixed at the same volume percent. We infer that the charge carriers contributed by sediment to be sodium and/or chlorine ions, since the activation energy with temperature is similar to samples with NaCl added. Samples with hydrate synthesized from flash frozen seawater are 1–2 orders of magnitude more conductive, presumably because of connected brine. The simplest version of Archie's law with a cementation exponent of 2 predicts the conductivity of samples synthesized with 50% sediment and seawater.

2. Sample Preparation

Samples were prepared from granular "seed" ice + CH_4 gas \pm SiO₂ (sand or silt) to produce polycrystalline methane hydrate both with and without a sediment component, using the thermal-cycling method developed by Stern et al. (1996, 2004) and modified for the current work by Du Frane et al. (2011, 2015) and Lu et al. (2019). Seed ice was prepared from either triple-distilled water or synthetic seawater containing 3.5 wt% salts that was flash frozen in liquid nitrogen (Lu et al., 2019). For two samples here, pure H₂O seed ice was premixed with silica silt to produce final samples containing 10 and 50 vol% silt, respectively, relative to the methane hydrate component (MH + Silt10 and MH + Silt50). A third sample was prepared with 50 vol% silt mixed with seawater ice (SH + Silt50), and a fourth from 50 vol% quartz sand mixed with seawater ice (SH + Sand50). Silt used here was Min-U-Sil40 supplied by U.S. Silica, with >99.5% purity SiO₂ and 10.5 µm average particle size. Sand was Oklahoma #1, >99% purity SiO₂ with 84% grain-size distribution of 106–250 µm, also used in Du Frane et al. (2015). In addition to the four samples described above, Table 1 lists six previous experiments from Du Frane et al. (2015) and Lu et al. (2019) relevant to the current work and discussion. The sample naming convention is MH for hydrate synthesized from high purity ice, and SH for hydrate synthesized from seawater, followed by the added product (silt, sand, or NaCl) and the percentage by weight or volume.

All experiments were conducted in a custom pressure vessel in which gas hydrate is synthesized while simultaneously collecting in situ impedance (Z) spectroscopy measurements similar to those of Du Frane et al. (2011). Initial porosity for all samples was \approx 36 vol% prior to reaction, and the resulting material after synthesis is a cohesive aggregate of methane hydrate + sediment with \approx 25% porosity. Porosity reduction is due to volumetric expansion and restructuring of H₂O during ice-to-hydrate conversion in a closed system. In samples formed from seawater ice, a liquid brine component also develops. Further details can be found in Lu et al. (2019).

Each sample underwent at least six thermal cycles during synthesis, until electrical impedance stopped changing significantly between cycles. A final incremental "step-dwell" heating cycle involved a 1-hr hold at each target temperature to allow thermal equilibration of the sample before making electrical impedance measurements. With the exception of Sample MH + Silt50, all samples were then quenched in liquid nitrogen for postrun analysis (described below).

Following step-dwell impedance measurements on Sample MH + Silt50, this sample was partially dissociated to generate H_2O pore water within it to monitor impedance changes relative to the sample's original fluid-free state and to compare with those samples formed from seawater ice that developed a liquid brine component. The sample was depressurized across the methane hydrate phase stability boundary while holding external temperature at +5°C, forcing it to partially dissociate to water + gas in a relatively uniform manner (Lu et al., 2019). Pressure was first reduced from 20 to 5 MPa, allowing sufficient time for sample equilibration following isochoric cooling effects, and was then reduced again to 3.8 MPa, 0.6 MPa below the equilibrium boundary. After 45 min, the sample was quenched in liquid nitrogen.

All samples were recovered for analysis of phase distribution and grain-scale characteristics by cryogenic scanning electron microscopy (cryo-SEM) and energy dispersive spectroscopy (EDS) methods (Lu et al., 2019; Stern et al., 2004). Imaging was conducted at less than -185° C, 10–15 kV, in low-vacuum mode with chamber pressure of \approx 20 Pa.

3. Cryo-SEM and EDS

Figure 1 shows representative cryo-SEM images and EDS measurements from four samples, all containing sediment. Ice-derived methane hydrate with 10% silt (Figure 1a) exhibits dense regions of methane hydrate (smooth, darker regions) surrounded by individual grains or small clusters of silt (small, brighter particles). The identification of hydrate and silt is verified by the presence of carbon and silica peaks, respectively, in EDS spot measurements (blue insets). The run of ice-derived methane hydrate with 50% silt (Figure 1b) was extensively dissociated prior to quenching, and the EDS measurements show minimal carbon remaining. In the run containing 50% silt and hydrate synthesized from seawater (Figure 1c), silty regions cluster locally but are well distributed at the sample-wide scale. Here hydrate often appears rounded or botryoidal where remaining briny fluid crystallizes or "freezes" on or proximal to it, as exposed along open cavities. Peaks in Na and Cl show increased brine or salt concentration in the silty clusters, which may imply that hydrate formation is inhibited in the lower porosity regions of sediment.

Figure 1d shows a similar seawater-derived sample where silt is replaced by 50% sand, exhibiting similar appearance apart from less clumping of the sediment. The SEM image is matched with EDS "maps" of the same region, separated here by individual elements O, Si, C, and Na (panels d1–d4, respectively): O corresponds to both hydrate and sand: Si to sand only, C to hydrate only, and Na to frozen brine or salt. While not quantitative, the elemental maps illustrate the general distribution and connectivity of each component in the SEM image, including excellent distribution of brine. The shading is a result of the low angle of the incident radiation. Additional SEM images of methane hydrate \pm quartz sand \pm NaCl-bearing phases, including hydrate formed from seawater ice, are shown in Lu et al. (2019).

4. Electrical Characterization

For each run and each temperature, complex electrical impedance was measured at 27 frequencies between 0.5 and 300 kHz, evenly spaced in log (frequency) and limited by the impedance meter, as described in Lu et al. (2019), and plotted as "Cole-Cole" plots in the complex plane. Figure 2 shows examples of such plots at representative temperatures for four runs considered here. Such impedance spectroscopy is necessary to separate the effect of charge polarization at the silver electrodes (chosen for compatibility with NaCl) and the resistance/capacitance of the actual sample (e.g., Roberts & Tyburczy, 1994, 1999). For all but the simplest complex impedance measurements, equivalent circuit modeling (ECM) is required to model sample





Figure 1. Cryo-SEM images and EDS measurements from methane hydrate plus sediment (sand and silt). Methane hydrate made from H_2O ice, plus (a) 10 vol% silt and (b) 50 vol% silt. Methane hydrate made from seawater ice and (c) 50 vol% silt and (d) 50 vol% sand. Insets d1 to d4 show EDS maps for oxygen, silicon, carbon, and sodium that correspond to the SEM image shown in (d). See text for further descriptions.

impedance. In ECM modeling, complex impedance data are typically fit by a series of pairs of resistors (R) and capacitors (C) in parallel. A single such RC circuit generates a semicircular arc in the complex plane extending from the origin and with the center of the arc on the real axis. Here we used the ECM software of Bondarenko and Ragoisha (2005) to fit the measurements. Besides allowing the separation of electrode impedance, ECM also provides insight into conduction mechanisms (e.g., Lu et al., 2019).

Methane hydrate synthesized from pure ice (MH) is characterized by two RC circuits, the left-most (highest frequency) arc associated with the resistance and capacitance of the dielectric hydrate sample and the right-most (low frequency) arc associated with electrode polarization. In ECM, if the center of the impedance arc falls below the real axis, the capacitor element needs to be replaced with a constant phase element (CPE). For a lone capacitor, the Cole-Cole plot is a line at 90° to the real axis. For a single CPE, the line is at a constant phase of less than 90°. With the addition of a resistor in parallel, the center of the impedance arc falls below the real axis by this difference in phase. There are various physical reasons for this, which include an imperfect (dispersive) dielectric, an electro-chemical double-layer formed from ions adsorbed onto grain





Figure 2. Cole-Cole plots of data (imaginary component of impedance, or reactance, plotted against the real component, or resistance) and equivalent circuit model (ECM) fits at different temperatures for pure methane hydrate with 0% NaCl (MH) and three methane hydrate samples synthesized from frozen seawater. Column titles correspond to sample names in Table 1. Frequency = 1-30 kHz. R = resistor; CP = constant phase element; C = capacitor. The lowest frequency arcs, and number 2 components, are associated with electrode polarization.

surfaces, and rough or porous electrodes (e.g., Brug et al., 1984). A CPE is needed to model MH sample conductivity at the warmest temperatures, which we interpret as an imperfect dielectric because it is not associated with the electrodes and there is no fluid to form a double layer.

For methane hydrate synthesized from seawater (SH), the Cole-Cole plots are dominated by electrode polarization, which requires a CPE, possibly to account for roughness or lack of uniform contact. The sample part of the model lacks a capacitive element, presumably because conductivity is dominated by a connected brine phase (Lu et al., 2019), and there is little change in sample impedance (R1) with temperature.

Methane hydrate synthesized from seawater ice and in the presence of sand and silt look similar to SH at warm temperature, but as the sample conductivity drops at colder temperatures, the sample begins to dominate the impedance of the sample + electrode measurement, and we begin to resolve a capacitive (actually CPE) element in the sample. The effect is greater for silt than sand, suggesting a relationship with surface area, and possibly that there might be an electro-chemical double-layer forming.

The resistance of the sample part of the ECM (R1) is combined with the geometry of the sample to compute the electrical resistivity of the material. Electrical conductivity, the reciprocal of resistivity, is proportional to the product of the number of charge carriers and the mobility of the charge carriers. Both the carrier density and mobility are thermally activated and described by a Boltzmann relationship, and so conductivity σ for a single charge carrier as a function of temperature is given by

$$\sigma = \sigma_o e^{-A/kT} = \sigma_o e^{-E_a/RT},$$





Figure 3. Conductivity versus reciprocal temperature (Arrhenius) plot for all samples. Blue symbols represent methane hydrate with no sediment, but with between 0 to 1.0 wt% NaCl (see legend box). Green symbols represent samples with sand. Red symbols represent samples with silt. Samples synthesized from seawater are shown as diamonds. Colored lines are activation energy fits as given in Table 1. Colored arrows indicate the change in conductivity after 45 min of partial dissociation to generate pore water. The vertical black arrow indicates the expected loss of conductivity given by Archie's law and 50% porosity.

where k is Boltzmann's constant (1.381 \times 10⁻²³ J/K), R is the gas constant (8.314 J/mol/K), T is absolute temperature, and σ_o is a pre-exponential constant. The A and E_a are both activation energies, in electron volts and kJ/mol, respectively. Here we shall use the latter. This is the Arrhenius equation, which can be linearized by plotting the logarithm of σ versus 1/T to create an Arrhenius plot, the slope of which gives E_a . Figure 3 presents an Arrhenius plot for the samples introduced in this paper, along with hydrate synthesized from pure water (MH) and the salt-bearing samples MH + NaCl0.25 and MH + NaCl1.0 from Lu et al. (2019) and the sand-bearing samples MH + Sand10 and MH + Sand45 from Du Frane et al. (2015) for comparison. Du Frane et al. (2015) did not carry out ECM modeling on MH + Sand45, but calculated conductivity from the impedance with the smallest angle from the real axis, which approximated the value of R1. Here we were able to conduct ECM modeling of the original data at temperatures above -1° C, resulting in lower conductivities and activation energy.

5. Results

The electrical conductivity of MH + Silt10 and MH + Silt50, methane hydrate made from pure ice with added silt, is essentially the same for both samples in spite of the different proportion of sediments (10% vs. 50%). Having recomputed the conductivities for MH + Sand45, the same is true of the corresponding sand samples, although the sand conductivities are about a factor of 2 lower than the silt. For both silt and sand, the activation energy is slightly higher for the samples with greater sediment content, but this difference is close to what we can resolve. For all four samples, the activation energy (31 to 43 kJ/mol) is similar to the sample

prepared with 0.25% NaCl (37 kJ/mol), so we infer that the charge carriers are derived from NaCl. Indeed, the activation energy for hydrate synthesized from "pure" ice is also similar, 34 kJ/mol, as noted by Lu et al. (2019), again suggesting that contaminant NaCl provides the dominant charge carrier. A sample with methane hydrate mixed with glass beads had high concentrations of Na₂CO₃ present, but little enhancement of electrical conductivity over methane hydrate by itself (Du Frane et al., 2015). This suggests the presence of chlorine ions may play a bigger role in hydrate conductivity than sodium.

Silt samples are more conductive than sand samples, even though tests of rinse water show that sand provides more salt than the silt, per unit volume. This suggests that it is surface area, rather than available NaCl, that determines hydrate conductivity. There is a limit to the amount of NaCl that hydrate can incorporate, because below the liquidus (0°C), the conductivity of the 1% and 0.25% NaCl samples is essentially the same. It is unlikely that hydrate incorporates 0.25% NaCl. Rinse water conductivity from 10% silt suggests that 0.01% NaCl is available to the hydrate. Du Frane et al. (2015) report that hydrate synthesized from seed ice had about 0.005% contaminant NaCl. Factoring these by conductivity differences, we infer that a maximum of between 0.02% and 0.05% NaCl contributes to the conductivity of pure methane hydrate. The silts used in this study were primarily silica, and the effects of silt containing clays on electrical conductivity are likely more complicated.

Samples with 50% sand and silt with hydrate synthesized from flash frozen seawater (SH + Sand50 and SH + Silt50) exhibit similar activation energies (76.1 and 80.2 kJ/mol), which are higher than for the hydrate from H₂O ice, along with higher conductivities. The sand sample is about a factor of 2 higher conductivity than the silt sample. The conductivity of the seawater sample without sediment (SH) is generally independent of temperature, which Lu et al. (2019) interpreted as a fully interconnected brine network. However, we note that the three highest temperature data points for this sample have an activation energy similar to the silt/sand samples (86.4 kJ/mol), suggesting that the conductivity of the sand/silt samples is determined by brine released during hydrate formation. That the conductivity of the sand/silt samples does not become temperature independent suggests that sediment inhibits the full interconnection of brine, perhaps through capillary forces. A simple Archie's law (Archie, 1942) calculation, $\sigma = \sigma_0 \phi^2$, where ϕ is porosity and here

equal to 0.5, σ is the conductivity of the sample, and σ_o is the conductivity of the brine/hydrate system, correctly predicts the conductivity of the sediment samples from the high-temperature SH data (see arrow in Figure 3), supporting the proposal that the conduction mechanism is similar in the three samples.

Sample MH + Silt50 was partially dissociated in a similar pressure-drop manner to the way sample MH was dissociated by Lu et al. (2019). The electrical conductivity of both samples 45 min after dissociation is plotted on Figure 3 for direct comparison. The dissociation rate was faster for the sediment sample, which is consistent with the observations of Circone et al. (2004), who measured faster dissociation rates in methane hydrate containing either homogeneously mixed or interlayered quartz sand, compared to pure methane hydrate. The quartz sand in that study was the same OK#1 used here.

6. Discussion and Conclusions

The similarity in conductivity for hydrate-from-ice samples with 10% and 50% sediment fractions suggests that the reduction in the conductive phase (hydrate) in the 50% samples is compensated for by an increased availability of charge carriers from the increased amount of sediment. That the silt samples are more conductive than sand samples suggests that the surface area of the sediment is the defining parameter, perhaps by distributing charge carriers though hydrate more efficiently than by adding sand. In the marine environment the availability of salt is not restricted by sediment, and so in an open system where brine can be excluded during hydrate formation, pure hydrate would be expected to have a conductivity similar to that of MH + NaCl0.25.

Our results provide an upper bound on the resistivity of pure methane hydrate and hydrate in clastic sediments. In natural systems where brine has been excluded during hydrate formation, electrical resistivity of hydrate-saturated sediment at seafloor temperatures could be as high as $3,000-10,000 \ \Omega m$, depending on grain size. Such high resistivities are rarely seen in well logs or CSEM resistivity models. Full exclusion of fluids may be uncommon, but logging tools are generally not designed to measure such high resistivities, and CSEM soundings average resistivity over length scales comparable to the depth of investigation. However, Matsumoto et al. (2017) observed peak resistivities of $1,000 \ \Omega m$ or more in logging-while-drilling data from seafloor chimneys off eastern Japan that contained high saturations of gas hydrate.

Samples synthesized using seawater represent the opposite extreme of a closed system where brine formed during hydrate formation remains in the sediment. Here the resistivity at seafloor temperatures is about 20 Ω m for samples with 50% sediment. While it is difficult to imagine large deposits of hydrate formed in this manner, it is possible that pockets or layers of brine-enriched hydrate might develop in association with more resistive hydrate deposits. This could create a large amount of electrical anisotropy, and indeed, we have observed large anisotropy in hydrate, with horizontal resistivities 20 times smaller than vertical resistivities (Constable et al., 2020).

Data Availability Statement

Data published in this paper are available on the Open Source Framework repository (at https://doi.org/10. 17605/OSF.IO/SCJNG).

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