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Electrical Properties of Methane Hydrate + Sediment Mixtures

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As part of our DOE-funded proposal to characterize gas hydrate in the Gulf of Mexico using marine electromagnetic methods, a collaboration between SIO, LLNL, and USGS with the goal of measuring the electrical properties of lab-created methane (CH_4) hydrate and sediment mixtures was formed. We examined samples with known characteristics to better relate electrical properties measured in the field to specific gas hydrate concentration and distribution patterns. Here we discuss first-ever electrical conductivity (σ) measurements on unmixed CH_4 hydrate (Du Frane *et al.*, 2011): 6 x 10-5 S/m at 5 °C, which is ~5 orders of magnitude lower than seawater. This difference allows electromagnetic (EM) techniques to distinguish highly resistive gas hydrate deposits from conductive water saturated sediments in EM field surveys. More recently, we performed measurements on CH_4 hydrate mixed with sediment and we also discuss those initial findings here. Our results on samples free of liquid water are important for predicting conductivity of sediments with pores highly saturated with gas hydrate, and are an essential starting point for comprehensive mixing models.

Background

Seismic methods have traditionally been used to map the spatial distribution of gas hydrate deposits. A bottom simulating reflector (BSR) indicates the lower limit of the stability field, typically marking the gas hydrate to free gas boundary, but provides little information about the

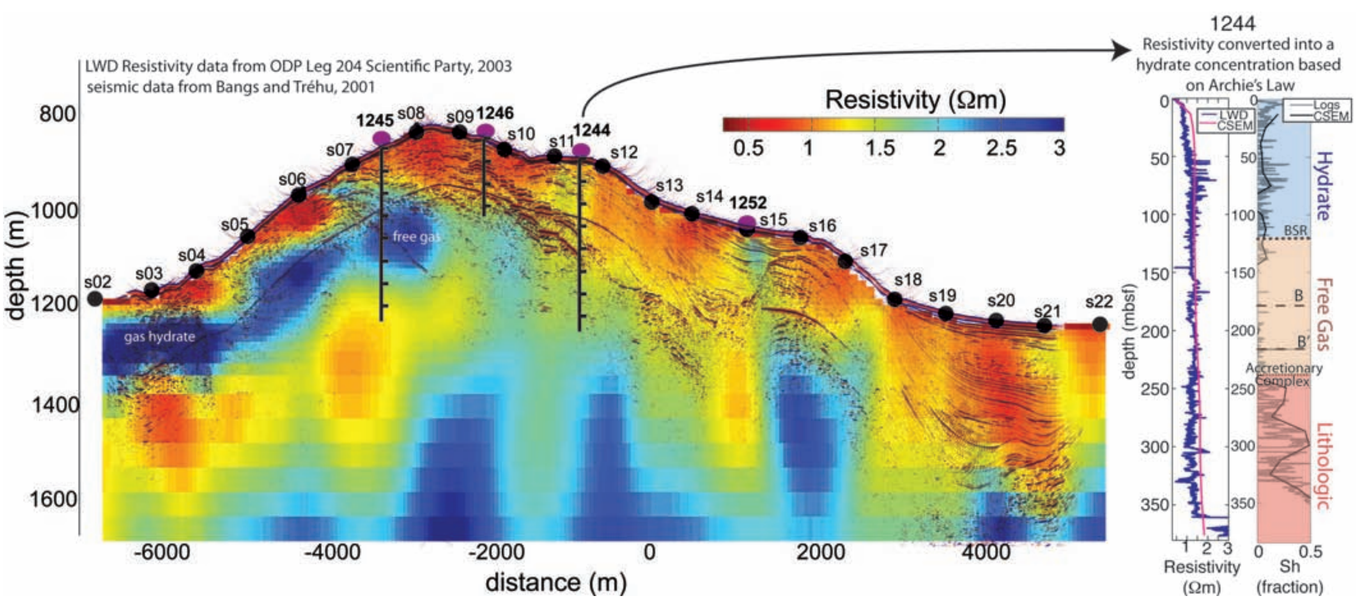

Figure 1: Comparisons of inverted CSEM resistivity data to well log and seismic data at Hydrate Ridge showing the potential of CSEM as a complementary geophysical method for gas hydrate assessment.

occurrence of gas hydrate above it. Seismic blanking zones indicate hydrate or gas only at shallow depths below the seafloor. Besides acoustic properties, electrical properties can also be used to detect gas hydrate, which has high electrical resistance (σ^{-1}) that provides a suitable target for marine controlled source electromagnetic (CSEM) surveys.

CSEM sounding measures the amplitude and phase of EM energy through the seafloor at one or more frequencies; this data can be inverted to resistivity. Pilot CSEM studies at Hydrate Ridge (2004; see Figure 1) and the Gulf of Mexico (2008) indicate that CSEM is highly sensitive to concentration and geometric distribution of gas hydrate; however, to make quantitative estimates of hydrate volume requires knowledge of the conductivity of gas hydrates in combination with petrophysical mixing relations established from theory and experiment. There have been few studies on the electrical properties of sediment/gas hydrate/water mixtures. Liquid water bearing samples help to resolve mixing laws, but lack characterization and are dominated by water with no quantitative information on the conductivity of gas hydrate phase. It is well known that gas hydrates are resistive, but exactly how resistive are they?

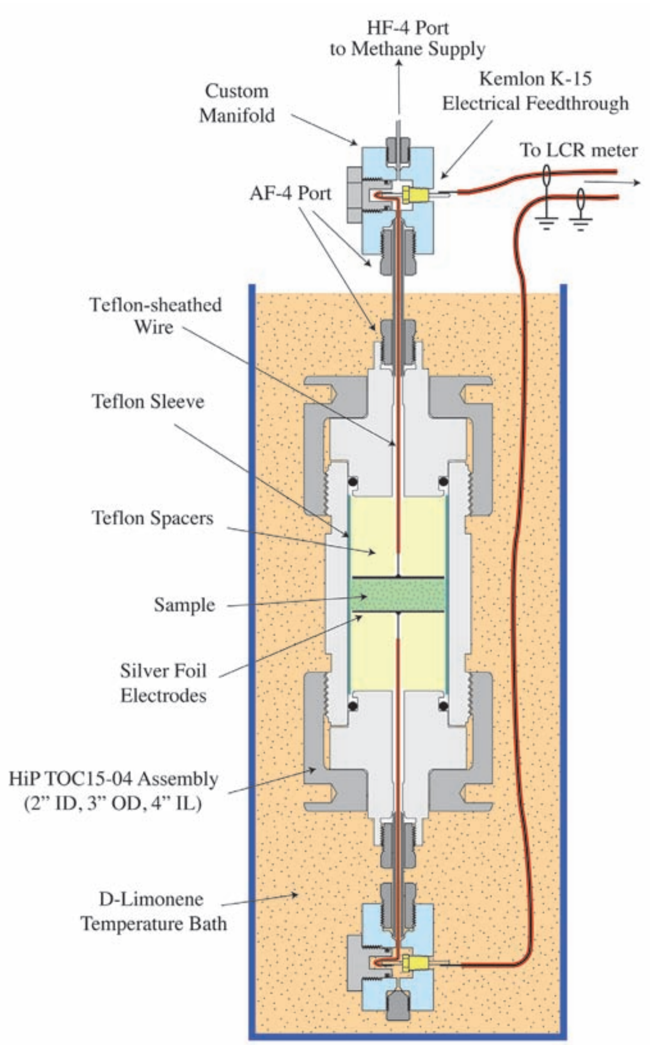

Figure 2: Pressure vessel used to synthesize CH_4 hydrate and measure conductivity.

Making Gas Hydrate

Hydrate was synthesized using a temperature cycling technique developed at USGS to fully-react H_2O ice and pressurized CH_4 (15-30 MPa) into polycrystalline CH_4 hydrate (Stern *et al*., 2004). We developed a pressure cell to synthesize CH_4 hydrate while measuring in situ electrical conductivity (Figure 2). Starting samples were comprised of granular ice that was either free of sediment, mixed with quartz sand (OK#1), or mixed with silica glass beads. Mixtures were made in varying proportions with 100-10vol% ice and 0-90vol% sand or beads. Comparative measurements were performed on some samples after dissociation of hydrate to ice by venting CH_4.

After full reaction to hydrate and subsequent testing, sample characteristics and phase distribution were assessed by cryogenic scanning electron microscopy (cryo-SEM; Figure 3) using techniques and instrumentation first described in *Fire in the Ice Vol. 2, Issue 2*.

Electrical Conductivity

Impedance spectra (20 Hz to 2 MHz) were collected throughout each run and used to calculate conductivity while excluding systemic contributions. Conductivity had typical exponential dependence on temperature:

$$\sigma(T) = \sigma_0 * e^{-Ea/RT}$$

SUGGESTED READING

Du Frane, W.L., Stern, L.A., Weitemeyer, K.A., Constable, S., Pinkston, J.C., and Roberts, J.J., 2011. "Electrical properties of polycrystalline methane hydrate." *Geophys*. Res. Lett., 38, L09313. doi:10.1029/2011GL047243.

Lee, J.Y., Santamarina, J.C., and Ruppel, C., 2010. "Parametric study of the physical properties of hydrate-bearing sand, silt, and clay sediments: 1. Electromagnetic properties." *J. Geophys. Res.* 2010;115:B11104, doi:10.1029/2009JB006669.

Stern, L.A., Kirby, S.H., Circone, S., and Durham, W.B., 2004. "Scanning electron microscopy investigations of laboratory-grown gas clathrate hydrates formed from melting ice, and comparison to natural hydrates." *Am. Mineral.* 2004;89(8-9):1162-1175.

Weitemeyer, K.A., and Constable, S., 2010. "Tests of a new marine EM survey method at Mississippi Canyon 118, Gulf of Mexico." *Fire in the Ice, Methane Hydrate Newsletter,* US Department of Energy Office of Fossil Energy National Energy Technology Laboratory, 10(1), 13-17.

Weitemeyer, K.A., Constable, S., and Tréhu, A.M., 2011. "A marine electromagnetic survey to detect gas hydrate at Hydrate Ridge, Oregon." *Geophys. J. Int.*, doi: 10.1111/j.1365-246X.2011.05105.x.

where σ_0 is a pre-exponential constant, E_a is activation energy, R is the gas constant, and T is temperature. Plotting log(σ) versus $10^3/T(K)$ gives slopes that are proportional to E_a which characterizes the temperature dependence (Figure 4).

Conductivity measurements of unmixed CH_4 hydrate (i.e. no sediment, shown in blue) ranged between 10^{-5} to 10^{-4} S/m. After the unmixed hydrate was dissociated, we measured conductivity of unmixed ice which was ~400% higher, with ~50% higher activation energy. The conductivity of CH_4 hydrate is much less than seawater (~ 10^{-1} to 10^{1} S/m) and much greater than quartz (< 10^{-18} S/m).

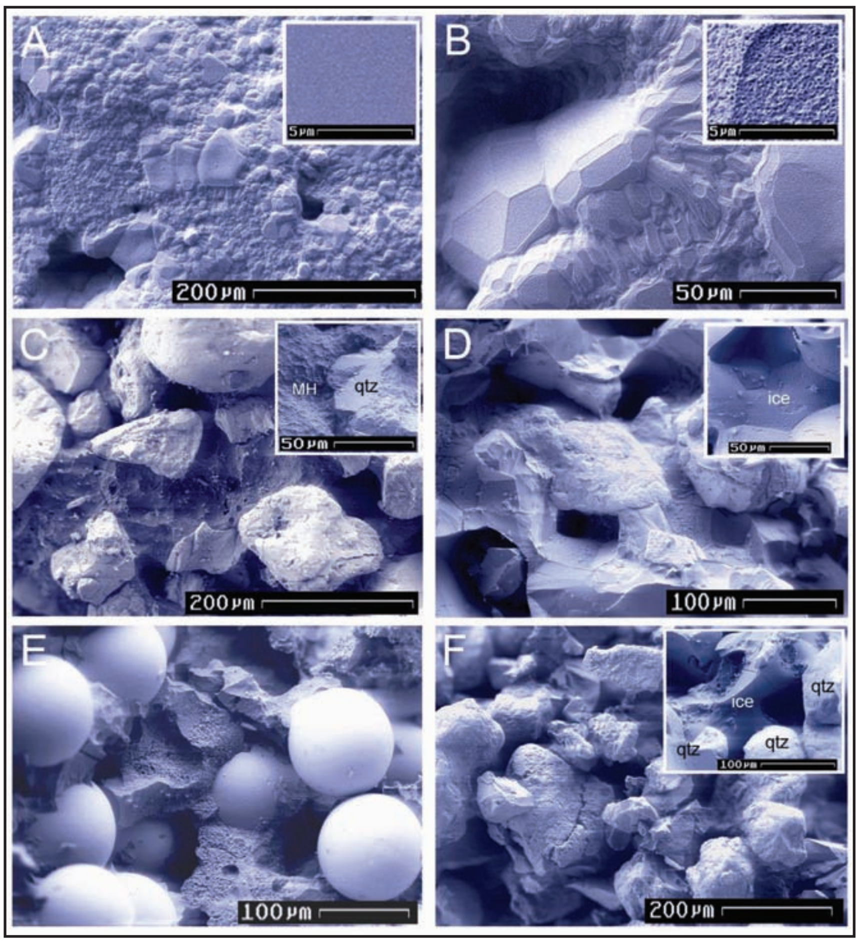

Figure 3: Cryo-SEM images of hydrate-sediment mixtures. A and B show single-phase (unmixed), polycrystalline CH_4 hydrate with 20% porosity. Hydrate grains typically range 10-80 microns in diameter and are fully dense as-grown (A, inset) but develop surface pitting with time in the high-vacuum SEM column (B, inset). C shows a 50:50vol% hydrate:sand sample and D shows a 50:50vol% ice:sand sample. Significant annealing of the ice grains accompanies dissociation at our test conditions (compare D and C insets), but there is no significant migration of sand, thus enabling comparison of measurements before and after dissociation. E shows a 50:50vol% hydrate:beads sample. SEM shows uniform distribution of phases in all three samples (C, D, and E) as well as similarities in the nature of the grain contacts, helping establish a basis for comparison of conductivity measurements. F shows a 10:90vol% ice:sand sample, with some of the connecting ice expanded in the inset.

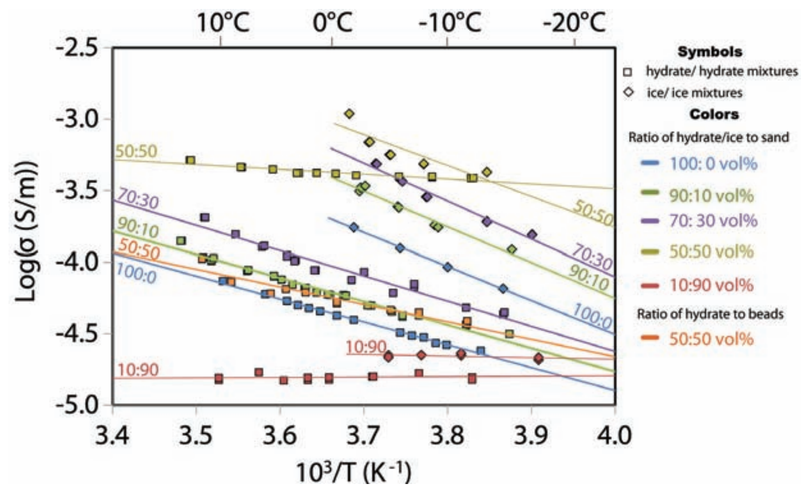

Figure 4: Electrical conductivity measurements versus inverse temperature for CH_4 hydrate and CH_4 hydrate-sediment mixtures.

To evaluate the effects of sediments we measured the conductivity of CH_4 hydrate mixed with either quartz sand or glass beads. We immediately noticed that hydrate samples containing quartz sand had higher conductivity than samples without sand, which is counterintuitive because the quartz sand by itself is highly resistive. Increased sand concentrations, up to 50vol%, resulted in increased conductivity and decreased E_a (green, purple, yellow). Sand had similar affect on samples with dissociated ice. However the sample with 10:90vol% hydrate: sand had much lower conductivity. Lower conductivity likely resulted from poorly connected hydrate, whereas sand connectivity had a smaller effect on conductivity. This indicates that the majority of electrical current conducts through the hydrate/ice rather than the sand.

Fine particles on the weathered surfaces of the sand likely increased the concentrations of impurities and charge carriers in the surfaces of hydrate/ ice grains, which lead to increased surface conductivity. To evaluate this mechanism further we measured a sample with 50:50vol% hydrate: beads (shown in orange). The synthetic glass beads are significantly more uniform and of higher purity than the natural quartz sand, and hence we observed a less pronounced surface conductivity contribution.

Next Steps

Our measurements have been successful in determining the electrical conductivity of single-phase CH_4 hydrate and reveal general trends by comparison of various ice/sediment mixtures to hydrate/sediment mixtures. Such factors as chemical impurities, surface conductivity, sediment angularity, and porosity-permeability issues – just to name a few – still require greater investigation to fully understand their contributions and competing mechanisms. For more fundamental materials science perspective, we can examine defect structure of CH_4 hydrate using different electrode materials. Other specific directions of interest for future work involve measuring CO_2 hydrate (±sediment), where CSEM may play a role in monitoring CO_2 sequestration in storage sites such as at Snøhvit.

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