

# Electrical properties of polycrystalline methane hydrate

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[1] Electromagnetic (EM) remote-sensing techniques are demonstrated to be sensitive to gas hydrate concentration and distribution and complement other resource assessment techniques, particularly seismic methods. To fully utilize EM results requires knowledge of the electrical properties of individual phases and mixing relations, yet little is known about the electrical properties of gas hydrates. We developed a pressure cell to synthesize gas hydrate while simultaneously measuring *in situ* frequency-dependent electrical conductivity ( $\sigma$ ). Synthesis of methane (CH<sub>4</sub>) hydrate was verified by thermal monitoring and by post run cryogenic scanning electron microscope imaging. Impedance spectra (20 Hz to 2 MHz) were collected before and after synthesis of polycrystalline CH<sub>4</sub> hydrate from polycrystalline ice and used to calculate  $\sigma$ . We determined the  $\sigma$  of CH<sub>4</sub> hydrate to be  $5 \times 10^{-5}$  S/m at 0°C with activation energy ( $E_a$ ) of 30.6 kJ/mol (−15 to 15°C). After dissociation back into ice,  $\sigma$  measurements of samples increased by a factor of ~4 and  $E_a$  increased by ~50%, similar to the starting ice samples. **Citation:** Du Frane, W. L., L. A. Stern, K. A. Weitemeyer, S. Constable, J. C. Pinkston, and J. J. Roberts (2011), Electrical properties of polycrystalline methane hydrate, *Geophys. Res. Lett.*, 38, L09313, doi:10.1029/2011GL047243.

## 1. Introduction

[2] Clathrate hydrates of natural gas are compounds with an ice-like crystalline framework that encages guest gas molecules, most commonly methane (CH<sub>4</sub>). CH<sub>4</sub> hydrate formation requires cool temperature, high pressure, and sufficient supplies of H<sub>2</sub>O and CH<sub>4</sub>; these conditions are met in both marine and permafrost regions worldwide [Kvenvolden, 1999]. CH<sub>4</sub> hydrate is potentially a significant source of clean, low-carbon energy. However, some naturally occurring hydrate in the arctic exists at the edge of thermodynamic stability posing an environmental hazard that threatens release of potent greenhouse gases [e.g., Shakhova *et al.*, 2010], and posing a more local and immediate threat to drilling and wellbore stability [Dawe and Thomas, 2007].

[3] CH<sub>4</sub> hydrate occurs in vast quantities, with an estimate of 10,000 Gt of CH<sub>4</sub> as the highly cited “consensus value” [Kvenvolden, 1999; Milkov, 2004]; however, other estimates span several orders of magnitude as a result of continued efforts at direct and indirect observation and by the addition

of more complex global models [e.g., Boswell and Collett, 2011; Maslin *et al.*, 2010]. Current geophysical surveying methods for identifying hydrate are limited. Well logging or coring is expensive, invasive, and provides only a point measurement for the direct presence of hydrate. Seismic methods detect hydrate using seismic bottom simulating reflectors, blanking, and bright spots [e.g., Hornbach *et al.*, 2003]. Quantifying the volume fraction of hydrate in sediments may be possible with careful processing and inversion of seismic data [e.g., Hornbach *et al.*, 2003; Zhang and McMechan, 2006], but this approach is complicated.

[4] Well logging indicates that regions containing hydrate are significantly less conductive than water saturated zones [e.g., Collett and Ladd, 2000]. This is consistent with the demonstrated sensitivity of electromagnetic (EM) methods to the concentration and geometric distribution of hydrate and pore fluid [Edwards, 1997; Evans, 2007; Schwabenberg *et al.*, 2005; Weitemeyer *et al.*, 2006a, 2006b]. However, to make quantitative estimates of hydrate volume using EM methods requires knowledge of the electrical conductivity ( $\sigma$ ) of gas hydrates in combination with petrophysical mixing relations, particularly in cases of highly saturated gas hydrate with only minor, poorly connected, pore water.

[5] To date, there have been few published measurements on the electrical properties of sediment-gas hydrate-water mixtures and none on unmixed, single-phase CH<sub>4</sub> hydrate. Spangenberg and Kulenkampff [2006] examined the  $\sigma$  of glass beads as a function of CH<sub>4</sub> hydrate saturation in the pore space at ~13°C. Lee *et al.* [2010] published a systematic examination of  $\sigma$  and permittivity of tetrahydrofuran hydrate (an analog for natural gas hydrate) mixed with sand, silts, and clay at ~0°C. Ren *et al.* [2010] studied a mixture of sand, CH<sub>4</sub> hydrate, and seawater from 5–30°C, however temperature was not controlled independently of CH<sub>4</sub> hydrate saturation. Studies on mixed samples help to resolve mixing laws, but the  $\sigma$  of these samples are dominated by the water and/or sediment, with no quantitative information on the  $\sigma$  of the gas hydrate. In this study we present the first  $\sigma$  measurements on unmixed CH<sub>4</sub> hydrate over a large temperature range that encompasses that of natural hydrate formations.

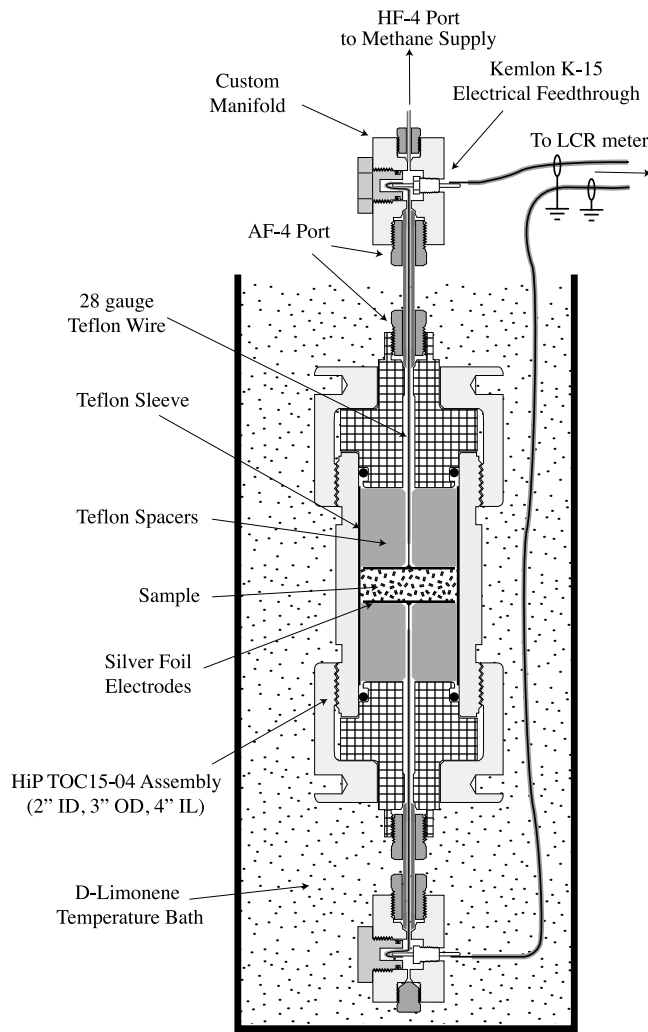
## 2. Experimental Techniques

[6] We designed a specialty pressure cell to form polycrystalline CH<sub>4</sub> hydrate for *in situ* impedance ( $Z$ ) measurements (Figure 1). An Agilent E4980A LCR (inductance-capacitance-resistance) meter was used to measure complex  $Z$  spectra between 20 Hz to 2 MHz with a relative accuracy 0.01% degrading to 1% for  $Z$  of 10 M $\Omega$ . The assembly was tested for electrical leakage using a blank sample made of Teflon, ice frozen from reagent grade water, and a variety of parallel resistor-capacitor (R-C) circuits (10–316 k $\Omega$ ;

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**Figure 1.** Schematic of  $\sigma$  cell, built around a commercially available double-ended pressure vessel manufactured by High Pressure Equipment Co. with a pressure rating of 5,000 psi (34.5 MPa). Silver foil electrodes are connected by Teflon insulated wire to high pressure electrical feedthroughs (Kemlon brand K-15) on the inner (high pressure) side and the Agilent E4980A LCR meter on the outer side. The cell encloses a  $5 \times 1.25$ -cm disc-shaped sample, with electrodes at each end and capped by Teflon spacers and surrounded by a Teflon sleeve.

1.15–22 pF). We performed 3 runs with  $\text{CH}_4$  hydrate: run 1 with a thermocouple installed in the cell to verify the synthesis process and extent of reaction, and then runs 2 and 3

to measure  $\sigma$ . Samples of  $\text{CH}_4$  hydrate were synthesized from a granular ice +  $\text{CH}_4$  gas mixture at  $25 \pm 5$  MPa using a temperature cycling method described previously by Stern *et al.* [1996, 2004]. The reactant ice was made from a block of nearly gas-free ice grown from distilled-deionized water, then crushed and sieved to  $180\text{--}250\ \mu\text{m}$ . We measured  $Z$  and  $\sigma$  in runs 2 and 3 during the first heating cycle, after full reaction to  $\text{CH}_4$  hydrate, and after samples were dissociated back into polycrystalline ice. Heating was isochoric such that the pore pressure of  $\text{CH}_4$  gas increased during the measurement (pressure ranges are listed in Table 1). While heating or cooling, temperature in the center of the run 1 sample lagged slightly behind bath temperature by  $1\text{--}5^\circ\text{C}$ , leading to slight uncertainty in sample temperature during heating for runs 2 and 3. We addressed this in run 3 by monitoring  $Z$  at a single frequency after each heating increment and recording  $\sigma$  after it stopped changing. In Table 1 this is called “step-dwell.”

[7] Cryogenic scanning electron microscopy (cryo-SEM) was used to observe the grain size and appearance of the final  $\text{CH}_4$  hydrate formed in run 1. For this procedure, the vessel was cooled sufficiently with liquid nitrogen prior to depressurization and opening of the cell. A thermocouple embedded in the sample was used to ensure stability of the hydrate during the quenching procedure, recovery, and transfer to the cryo-preparation station (Gatan Alto Model 2100). The sample was cleaved under vacuum in the preparation station to produce fresh surfaces uncontaminated by water condensation, and then transferred under vacuum to a LEO982 field emission SEM. A thermocouple embedded in the SEM sample stage monitored temperature throughout the imaging process. Imaging was conducted at temperature  $< -185^\circ\text{C}$  K, vacuum  $< 10^{-6}$  kPa, and accelerating voltage of 2 kV. Further details are given by Stern *et al.* [2004].

### 3. Results

[8] Cryo-SEM images of the crystal morphology and thermal monitoring of run 1 confirmed the synthesis of  $\text{CH}_4$  hydrate (Figure 2). The resulting polycrystalline material has  $20\text{--}70\ \mu\text{m}$  average grain diameters and  $\sim 20\%$  intergranular porosity. The porosity is also known independently from mass measurements of the reactant ice prior to loading the cell. Most of the porosity occurs as isolated and virtually unconnected cavities (Figure 2a), and so will have minimal effect on  $\sigma$ . Ice was not observed in the interior of the sample.

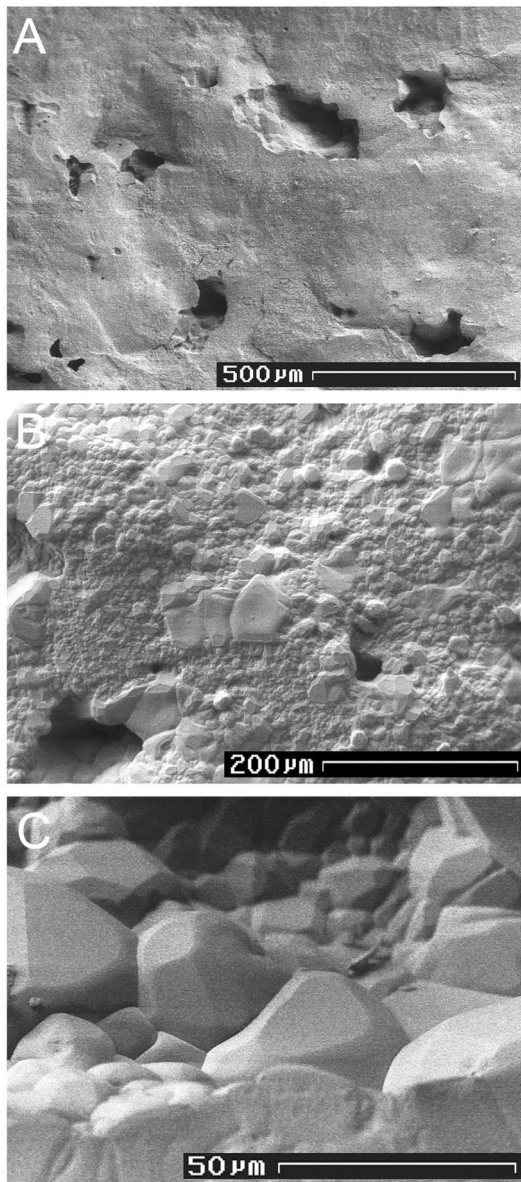
[9] Plots of complex  $Z$  from runs 2 and 3 consist of two overlapping, semicircular arcs (Figure 3a). The silver foil electrodes were polarizing and did not allow transfer of charge from the samples (i.e., “blocking”), resulting in large

**Table 1.** Summary of Experimental Conditions and Equation (1) Fit Parameters for  $\sigma_0$  and  $E_a$

Run	Sample Condition	Heating Cycle	Heating Rate ( $^\circ\text{C/hr}$ )	$\text{CH}_4$ Pore Pressure (MPa)	$\text{Log}(\sigma_0 \text{ (S/m)})$	$E_a \text{ (kJ/mol)}$
1	Synthesis Test	n/a	6.2	16.9–25.8 <sup>a</sup>	n/a	n/a
2	Ice w/ $\text{CH}_4$	1	7.4	21.7–26.2	1.16 <sup>b</sup>	25.8 <sup>b</sup>
	$\text{CH}_4$ hydrate	11	5.9	18.3–21.3	0.965	27.9
	Dissociated to ice	12	4.7	0	6.63 <sup>b</sup>	54.5 <sup>b</sup>
3	Ice w/ $\text{CH}_4$	1	9.8	23.0–26.7	0.376 <sup>b</sup>	21.8 <sup>b</sup>
	$\text{CH}_4$ hydrate	7	Step-Dwell	16.2–18.5	1.50	30.6
	Dissociated to ice	8	Step-Dwell	0	5.00 <sup>b</sup>	45.3 <sup>b</sup>

<sup>a</sup>Pressure range over entire run.

<sup>b</sup>Fits only include data below ice melting point.



**Figure 2.** Cryo-SEM images of CH<sub>4</sub> hydrate formed in run 1, showing (a) overall sample appearance and (b, c) closer views of individual grains.

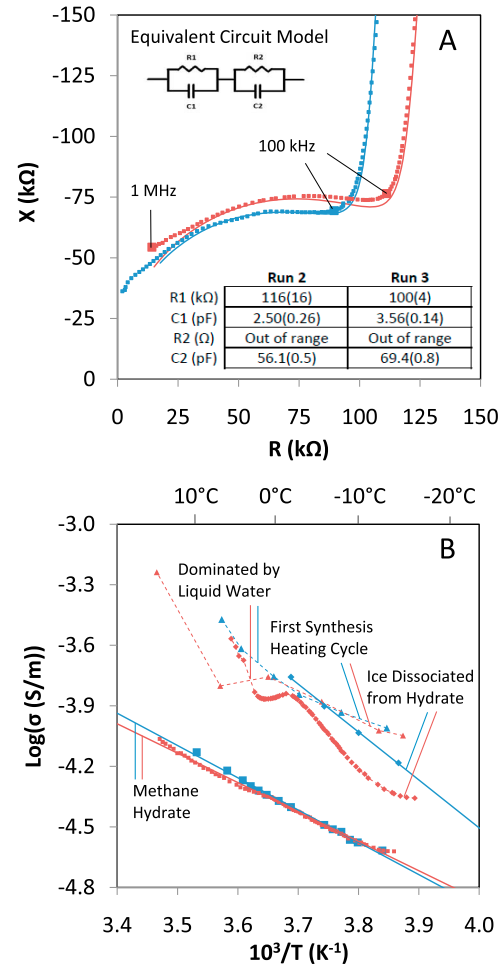
low frequency arcs (shown partially in Figure 3a). We attribute the smaller, high frequency arcs to sample properties [Roberts and Tyburczy, 1993].  $Z$  spectra were fit with an equivalent circuit of two R-Cs in series [Roberts and Tyburczy, 1991], which demonstrated that  $\sigma$  could be reliably measured with the frequency associated with the smallest phase angle to eliminate electrical response related to the vessel, leads or electrodes (Figure 3a).

[10] For runs 2 and 3,  $\sigma$  was measured during the initial heating cycle and after CH<sub>4</sub> hydrate was fully synthesized (i.e., after  $\geq 6$  heating cycles). The samples were then dissociated to polycrystalline ice by venting the pressurized CH<sub>4</sub> from them at  $-15^\circ\text{C}$  (1 day for run 2, and 13 days for run 3). In both runs,  $\sigma$  of the samples as CH<sub>4</sub> hydrate were a factor of  $\sim 3$ – $4$  lower than  $\sigma$  of the samples as ice. For both ice and CH<sub>4</sub> hydrate,  $\sigma$  exhibited typical Arrhenius behavior

(Figure 3b). Therefore, we fit the  $\sigma$  data as a function of absolute temperature ( $T$ ) using

$$\sigma(T) = \sigma_0 e^{-E_a/(RT)} \quad (1)$$

where  $\sigma_0$  is a pre-exponential constant corresponding to  $T = \infty$ ,  $E_a$  is activation energy, and  $R$  is the gas constant (fitting



**Figure 3.**  $Z$  and  $\sigma$  measurements from runs 2 (red) and 3 (blue) with data fits shown as solid lines (corresponding colors). (a) Complex  $Z$  spectra of polycrystalline CH<sub>4</sub> hydrate from runs 2 and 3 at  $4^\circ\text{C}$ , modeled with two parallel R-C pairs in series. Real  $Z$  ( $R = Z \cdot \cos(\theta)$ ) is plotted vs. imaginary  $Z$  ( $X = Z \cdot \sin(\theta)$ ), where  $|Z|^2 = R^2 + X^2$  and  $\theta = \tan^{-1}(X/R)$ . Fitting results are given in lower inset, with errors provided in parentheses.  $Z$  spectra consist of overlapping semicircular arcs. The smaller arcs at high frequency ( $\geq 100$  kHz at  $4^\circ\text{C}$ ) resulted from the material properties of the samples ( $R1$ ,  $C1$ ). The larger arcs at low frequency (shown partly as a rapid change in  $X$  for  $R > \sim 100$  kΩ and frequencies  $\leq \sim 100$  kHz at  $4^\circ\text{C}$ ) were caused by electrode polarization ( $R2$ ,  $C2$ ). Modeling indicates that  $\sigma$  can be calculated from  $|Z|$  corresponding to the smallest value of  $|Z|$ . (b)  $\sigma$  collected during the first heating cycle (triangles), after methane hydrate synthesis (squares), and after dissociation to ice (diamonds). CH<sub>4</sub> hydrate is  $\sim 0.6$  log units below ice, and has  $\sim 33\%$  lower  $E_a$  (proportional to the slope of data fits, results in Table 1).

results listed in Table 1). Larger error is associated with  $E_a$  calculated during active heating, because of the variable amount by which the bath temperature lagged sample temperature. We consider the  $E_a$  calculated from run 3 using the “step-dwell” approach to be the more reliable, nevertheless there is good agreement between runs 2 and 3 (Figure 3b).

#### 4. Discussion

[11] Previous experience indicates that most sample transformation to hydrate occurs while passing the melting point of ice during the first heating cycle [Stern *et al.*, 2004]. Our  $\sigma$  results during the first cycle are consistent with this, assuming that ice dominated the electrical properties of the sample below its melting point, and the small amount of unreacted liquid water dominated above the ice point (Figure 3b).

[12] After several more heating/cooling cycles we do not observe a discontinuity in  $\sigma$  or  $E_a$  below or above the melting point of ice, suggesting that samples had fully reacted into  $\text{CH}_4$  hydrate. This is consistent with previous observations that all ice reacts within 1–5 heating/cooling cycles, depending in part on the grain size and packing density of the initial ice grains [Stern *et al.*, 1996, 2004]. In both runs 2 and 3, synthesis of  $\text{CH}_4$  hydrate resulted in lower  $\sigma$  and  $E_a$  in our samples compared to the first heating cycle. Using the Hashin-Shtrikman mixing model we calculate that  $\sigma$  of nonporous  $\text{CH}_4$  hydrate would be a factor of 1.37 (0.137 log units) higher than our measurements for 20% porous gas hydrate.

[13] After venting the samples, most of the  $\text{CH}_4$  hydrate dissociated to ice within several hours; however, the dissociation rates for the last remaining hydrate is complicated by the effects of self preservation or self buffering of the hydrate [Stern *et al.*, 2001]. For run 2 a small amount of hydrate may have remained in the samples at the center of grains, in which case this secondary phase would be poorly connected and have little contribution to the measured electrical properties. Run 3 dissociated for a much longer period and likely had no hydrate remaining in the sample when  $\sigma$  was measured. In both runs  $\sigma$  and  $E_a$  were lower for  $\text{CH}_4$  hydrate than for the dissociated ice product.

[14] The  $\sigma$  of ice is known to be determined by the concentration of intrinsic Bjerrum defects (L and D) and extrinsic protonic defects ( $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ ) resulting from ionic impurities, with higher concentrations/mobilities of these defects in grain surfaces than in the bulk grains [e.g., Petrenko and Whitworth, 1999]. Assuming similar defects conduct charge in hydrate suggests the magnitude of  $\sigma$  is also likely to be dependent on impurities. Although we did not characterize the impurity of our samples, the same ionic impurities existed in the bulk samples as either ice or hydrate. Good reproducibility of  $\sigma$  measurements suggests similar concentrations of impurities were in samples from runs 2 and 3.

[15] Lower  $\sigma$  in hydrate than ice is consistent with greater site spacing. Accommodation of a large hydrocarbon molecule in the clathrate structure potentially reduces the site densities of all point defects relative to the ice structure ( $I_h$ ) which would increase the energy necessary for defects to hop to neighboring sites. This would result in reduced defect mobilities and may explain why both  $\sigma$  (this study) and

thermal conductivity [deMartin, 2001; Waite *et al.*, 2007] are lower for hydrate than ice.

#### 5. Conclusion

[16] We have performed the first electrical measurements of unmixed, polycrystalline  $\text{CH}_4$  hydrate (with ~20% unconnected intergranular porosity), over the temperature range of  $-15$  to  $15^\circ\text{C}$ ; the  $E_a$  is 30.6 kJ/mol. We measure  $\sigma$  of  $\text{CH}_4$  hydrate at  $0^\circ\text{C}$  to be  $5 \times 10^{-5}$  S/m, which helps to verify that EM surveys may be used to map hydrates in seafloor sediments and provides a more quantitative basis for modeling using mixing laws. Future experiments will be conducted on  $\text{CH}_4$  hydrate + sediment aggregates ( $\pm$  seawater) to measure electrical properties of mixed-phase samples.

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#### References

- Boswell, R., and T. Collett (2011), Current perspectives on gas hydrate resources, *Energy Environ. Sci.*, 4, 1206–1215, doi:10.1039/c0ee00203h.
- Collett, T. S., and J. W. Ladd (2000), Detection of gas hydrate with down-hole logs and assessment of gas hydrate concentrations (saturations) and gas volumes on the Blake Ridge with electrical resistivity log data, *Proc. Ocean Drill. Program Sci. Results*, 164, 179–191.
- Dawe, R. A., and S. Thomas (2007), A large potential methane source—Natural gas hydrates, *Energy Sources, Part A*, 29(3), 217–229, doi:10.1080/009083190948676.
- deMartin, B. J. (2001), Laboratory measurement of the thermal conductivity and thermal diffusivity of methane hydrate at simulated in-situ conditions, M.S. thesis, *Sch. Earth Atmos. Sci.*, Georgia Inst. Tech., Atlanta.
- Edwards, R. N. (1997), On the resource evaluation of marine gas hydrate deposits using sea-floor transient electric dipole-dipole methods, *Geophysics*, 62(1), 63–74, doi:10.1190/1.1444146.
- Evans, R. L. (2007), Using CSEM techniques to map the shallow section of seafloor: From the coastline to the edges of the continental slope, *Geophysics*, 72(2), WA105–WA116, doi:10.1190/1.2434798.
- Hornbach, M. J., W. S. Holbrook, A. R. Gorman, K. L. Hackwith, D. Lizarralde, and I. Pecher (2003), Direct seismic detection of methane hydrate on the Blake Ridge, *Geophysics*, 68(1), 92–100, doi:10.1190/1.1543196.
- Kvenvolden, K. A. (1999), Potential effects of gas hydrate on human welfare, *Proc. Natl. Acad. Sci. U. S. A.*, 96(7), 3420–3426, doi:10.1073/pnas.96.7.3420.
- Lee, J. Y., J. C. Santamarina, and C. Ruppel (2010), Parametric study of the physical properties of hydrate-bearing sand, silt, and clay sediments: 1. Electromagnetic properties, *J. Geophys. Res.*, 115, B11104, doi:10.1029/2009JB006669.
- Maslin, M., M. Owen, R. Betts, S. Day, T. Dunkley Jones, and A. Ridgwell (2010), Gas hydrates: Past and future geohazard?, *Philos. Trans. R. Soc. A*, 368, 2369–2393, doi:10.1098/rsta.2010.0065.
- Milkov, A. V. (2004), Global estimates of hydrate-bound gas in marine sediments: How much is really out there?, *Earth Sci. Rev.*, 66(3–4), 183–197, doi:10.1016/j.earscirev.2003.11.002.
- Petrenko, V. F., and R. W. Whitworth (1999), *Physics of Ice*, Oxford Univ. Press, New York.
- Ren, S. R., Y. Liu, and W. Zhang (2010), Acoustic velocity and electrical resistance of hydrate bearing sediments, *J. Petrol. Sci. Eng.*, 70, 52–56, doi:10.1016/j.petrol.2009.09.001.
- Roberts, J. J., and J. A. Tyburczy (1991), Frequency dependent electrical properties of polycrystalline olivine compacts, *J. Geophys. Res.*, 96(B10), 16,205–16,222, doi:10.1029/91JB01574.

- Roberts, J. J., and J. A. Tyburczy (1993), Impedance spectroscopy of single and polycrystalline olivine: Evidence for grain-boundary transport, *Phys. Chem. Miner.*, **20**(1), 19–26, doi:10.1007/BF00202246.
- Schwalenberg, K., E. Willoughby, R. Mir, and R. N. Edwards (2005), Marine gas hydrate electromagnetic signatures in Cascadia and their correlation with seismic blank zones, *First Break*, **23**, 57–63.
- Shakhova, N., I. Semiletov, A. Salyuk, V. Yusupov, D. Kosmach, and O. Gustafsson (2010), Extensive methane venting to the atmosphere from sediments of the East Siberian Arctic Shelf, *Science*, **327**(5970), 1246–1250, doi:10.1126/science.1182221.
- Spangenberg, E., and J. Kulenkampff (2006), Influence of methane hydrate content on electrical sediment properties, *Geophys. Res. Lett.*, **33**, L24315, doi:10.1029/2006GL028188.
- Stern, L. A., S. H. Kirby, and W. B. Durham (1996), Peculiarities of methane clathrate hydrate formation and solid-state deformation, including possible superheating of water ice, *Science*, **273**(5283), 1843–1848, doi:10.1126/science.273.5283.1843.
- Stern, L. A., S. Circone, S. H. Kirby, and W. B. Durham (2001), Anomalous preservation of pure methane hydrate at 1 atm, *J. Phys. Chem. B*, **105**(9), 1756–1762, doi:10.1021/jp003061s.
- Stern, L. A., S. H. Kirby, S. Circone, and W. B. Durham (2004), Scanning electron microscopy investigations of laboratory-grown gas clathrate hydrates formed from melting ice, and comparison to natural hydrates, *Am. Mineral.*, **89**(8–9), 1162–1175.
- Waite, W. F., L. A. Stern, S. H. Kirby, W. J. Winters, and D. H. Mason (2007), Simultaneous determination of thermal conductivity, thermal diffusivity and specific heat in sl methane hydrate, *Geophys. J. Int.*, **169**(2), 767–774, doi:10.1111/j.1365-246X.2007.03382.x.
- Weitemeyer, K. A., S. C. Constable, and K. W. Key (2006a), Marine EM techniques for gas-hydrate detection and hazard mitigation, *Lead. Edge*, **25**, 629–632, doi:10.1190/1.2202668.
- Weitemeyer, K. A., S. C. Constable, K. W. Key, and J. P. Behrens (2006b), First results from a marine controlled-source electromagnetic survey to detect gas hydrates offshore Oregon, *Geophys. Res. Lett.*, **33**, L03304, doi:10.1029/2005GL024896.
- Zhang, Z. J., and G. A. McMechan (2006), Elastic inversion for distribution of gas hydrate, with emphasis on structural controls, *J. Seismic Explor.*, **14**(4), 349–370.

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