Data Report: Pore Water Geochemistry at Green Canyon 955, deepwater Gulf of Mexico[1]

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1. Abstract

Two holes were drilled in Green Canyon Block 955 (GC 955) in the deepwater Gulf of Mexico: Hole GC 955 H002 (H002) and Hole GC 955 H005 (H005). Here we present the solute concentrations and oxygen and hydrogen isotope ratios of pore water extracted from sediment whole-round samples collected from these holes. The analytical methods, degree of sample contamination, and the method for contamination correction are discussed as are the general trends in the geochemical data.

2. Introduction

The objective of this report is to present solute concentrations and isotope ratios in pore water extracted from sediment whole-round samples collected during the UT-GOM2-1 Expedition (Flemings et al. 2018). The concentration of dissolved species and the isotopic composition of the pore water provide critical data for the identification of fluid sources and flow pathways, as well as the quantification of fluid-rock reaction rates and the formation of authigenic minerals. In addition, pore water chemical profiles are essential for characterizing methane hydrate distribution and concentrations, methane sources and sinks, and biogeochemical cycling in marine sediments.

Two holes were drilled in Green Canyon Block 955 (GC 955) in the deepwater Gulf of Mexico: Hole GC 955 H002 (H002) and Hole GC 955 H005 (H005). Twenty-one 10 ft (3.05 m) pressure cores were attempted in and near the methane hydrate reservoir. In the first hole, H002, 1 of the 8 cores were

recovered under pressure and there was 34% recovery of sediment (both pressurized and depressurized). In the second hole, H005, 12 of the 13 cores were recovered under pressure and there was 72% recovery of sediment (Thomas et al., 2020). The pressure cores were imaged and logged under pressure.

Sediment samples for pore water extraction were either from pressure cores that were not recovered under pressure or from pressure cores quantitatively degassed either on-board or on-shore to determine the hydrate concentration and the gas composition. To document the pore water geochemistry as a function of depth at both sites, we extracted pore water from whole-rounds sub-sampled from the sediment cores both within and outside of the methane hydrate reservoir and conducted a range of analyses for solutes and isotope ratios useful for characterizing fluid sources, fluid-rock reactions, methane hydrate distribution, and biogeochemical cycling.

3. Methods and Materials

3.1 Field Sampling

Due to space and personnel limitations, pore water was not extracted from whole round samples onboard the D/V *Q-4000 n*or during dockside operations. Thus, the primary focus of on-board and dockside pore water efforts was the preservation of whole-round samples for post-cruise pore water sampling and analysis. While this approach prevents analysis of some time-sensitive pore water constituents (e.g. pH, alkalinity) many constituents can be measured weeks after collection when the whole round sample is stored in an anoxic and refrigerated environment.

Whole round core samples for pore water analysis were collected immediately upon recovery of conventionalized pressure cores (i.e. cores that failed to hold pressure) and immediately after quantitative depressurization of pressure core sections that were processed using the Geotek Pressure Core Analysis and Transfer System (PCATS). These whole round sections were pre-scored with a tubing cutter and then immediately placed within a glove box that was purged of ambient atmosphere and replaced by an anoxic ultra-high purity N_2 atmosphere to prevent oxidation of redox-sensitive elements. All further processing of the core occurred under N_2 atmosphere. The whole rounds were wrapped tightly in plastic wrap to prevent evaporation and were placed in a plastic bag and heat-sealed to retain the N_2 atmosphere during storage and transport. The sealed pore water whole rounds were stored refrigerated at 6 °C. At the end of dockside operations, these samples were shipped overnight in coolers with cold packs to the University of Washington.

The collected pore water samples had the potential to be contaminated by (1) drilling fluids during drilling and coring and (2) PCATS fluid during analysis and cutting of pressure cores. Due to time and laboratory limitations, no tracers were added to mud tanks nor were micro-bead bags used during the expedition. Our approach to identify contamination by drilling fluid relied on comparison of pore water sulfate concentration to drilling fluid sulfate concentration then correcting for contamination based on the composition of the drilling fluid (as discussed below). The intervals recovered from coring (> 400 mbsf) were far below the typical depth of the sulfate-methane transition in the northern Gulf of Mexico 0 to 70 mbsf; (e.g. Presley and Stearns, 1986; Paull et al., 2005; Expedition 308 Scientists, 2006a,b,c,d; Coffin et al., 2008; Kastner et al, 2008; Pohlman et al., 2008; Smith and Coffin, 2014), thus the presence of sulfate can be used as a tracer of contamination. To track PCATS water contamination, 1.9 g of cesium

chloride was added to the ~150 L tanks that supply fresh water to PCATS to create a ~10 ppm (75.23 µM) concentration of cesium (Cs) in the PCATS fluid.

To estimate mixing with contaminating fluids, samples of drilling fluid from the rig floor were collected and PCATS water from the PCATS chamber for most cores. Each fluid sample was split into two 15 mL Nalgene bottles and one 8 mL glass vial. One 15 mL bottle was acidified with 0.05 mL of trace metal grade 16 N nitric acid. The final concentration of nitric acid in the 15 mL acidified sample was approximately 0.053 N. Each bottle was wrapped with Parafilm and stored and refrigerated at 6 °C.

3.2 Shore-Based Pore Water Collection

Whole round samples were shipped with cold packs (not frozen) to the University of Washington for further processing and analysis, arriving in two batches on 31-May-2017 and 6-June-2017. Samples were immediately flushed with ultra-high purity nitrogen and stored at 4 °C for processing. Whole round samples were removed from the liner and the surface of the sediment scraped in a glove bag under N_2 atmosphere. The cleaned sediment samples were placed into a titanium squeezer modified after the stainless steel squeezer of Manheim and Sayles (1974). Gauge forces to a maximum of 25,000 lb were applied using a Carver hydraulic press to extract pore water. Squeezed pore water was filtered through a pre-washed Whatman No. 1 filter and collected in acid-cleaned plastic syringes. Waters collected in the syringes were further filtered with a 0.2 µm Whatman Puradisc polyethersulfone disposable filter before preservation.

Sample allocation for specific analyses was determined based on the pore water volume recovered and analytical priorities with the analysis of pore water salinity, Cl, contamination tracer (Cs), O/H isotopes, SO_4, and the major cations being the highest priority (Table 1). Sub-samples include 1-2 ml in sealed glass ampoules, 1-2 ml in glass vials, 1-4 ml acidified to pH <2 and stored in acid-cleaned plastic bottles, and 1-4 ml unacidified samples stored in plastic bottles. In addition, pore water subsamples for sulfate concentration analyses were fixed with zinc-acetate and stored in centrifuge tubes. After analysis, pore water sub-samples were stored under appropriate conditions and are available to the broader scientific community.

3.3 Analyses

Salinity and Cl via titration

Salinity was determined with a Reichert temperature-compensated handheld refractometer with a precision of 0.5 practical salinity units (psu). Chlorinity (Cl) was determined via silver nitrate ($AgNO_3$) titration using a Metrohm Dosimat titrator with a precision of 0.3% based on repeated analysis of IAPSO standard seawater and several dilutions of IAPSO.

Cl, Br, and SO_4 concentrations by ion chromatography

Chloride (Cl), bromide (Br), and sulfate (SO_4) concentrations were measured with a Metrohm 882 compact ion chromatograph (IC). Analytical precision was monitored by repeated analysis of four separate dilutions of IAPSO standard seawater that spanned the expected in situ concentration range. The precision of the Cl, Br, and SO_4 analyses were 0.66%, 3.0%, and 0.8% respectively. Analytical accuracy was monitored by evaluation of four in-house reference standards. The average percent

difference between the known and measured concentrations for Cl, Br, and SO$_4$ were 1.0%, 3.0%, and 1.3%, respectively.

Ca, Mg, K, Na, B, Li, Sr, Ba, Fe, and Mn concentrations by inductively-coupled plasma-optical emission spectroscopy (ICP-OES)

Major element samples were prepared with a 1:100 dilution with a 1% trace-metal grade HNO$_3$ solution and measured on a Perkin Elmer Optima 8300 ICP-OES at UW. Standards were prepared from dilutions of IAPSO standard seawater. The analytical precision of the Ca, Mg, K, and Na analyses were <1%, <1%, <1.5%, and <3%, respectively. Minor element analyses were performed on a Perkin Elmer Optima 8300 ICP-OES at UW, and samples prepared in 1:20 dilutions using 1% trace metal-grade HNO$_3$ solution. Calibration, drift, and check standards were prepared from Spex Certiprep reference standards. The analytical precision of the B, Li, Sr, Ba, Fe, and Mn analyses were <3%, <2%, <1%, <1%, <2%, and <2%, respectively.

Cs concentrations by inductively-coupled plasma-mass spectrometry (ICP-MS)

Cesium concentrations were measured on an Agilent 7900 quadrapole ICP-MS with a detection limit of 0.002 μM. Cesium concentrations were determined based on the natural isotope [133]Cs and measurement drift was monitored with three 1 ppb internal standards; [45]Sc, [115]In, and [89]Y. Calibration and off-line drift and check standards were prepared from a Spex CertiPrep certified reference Cs standard. All samples were diluted 1:50 with 1% trace metal-grade nitric acid. The precision of the Cs analyses was <1%.

δ^{18}O and δD stable isotope ratios

The pore water oxygen and hydrogen stable isotope ratios were determined using a Picarro cavity ring-down spectrometer water analyzer at UW. Results reported here are in standard delta (δ) notation relative to Vienna Standard Mean Ocean Water (VSMOW),

$$\delta(\text{‰}) = \left[\frac{R_{sample} - R_{standard}}{R_{standard}}\right] \times 1000 \qquad\qquad \text{(Eq. 1)}$$

where R is the ratio of ^{18}O/^{16}O. The precision of the analyses (based on the standard deviation of repeated analysis of standard seawater and samples) were approximately <0.07‰ for δ^{18}O and <0.5‰ for δD.

3.4 Drilling Fluid Contamination Correction

The pore water major and minor element concentration data, as well as the oxygen and hydrogen isotope ratios were corrected for drill water contamination based on the measured sulfate concentrations in drilling fluid and pore water samples.

Below the sulfate-methane transition zone, sulfate is depleted in the pore fluids, and any sulfate present in a sample is a result of contamination with drill water that was pumped down the hole while drilling. Drilling fluid was sampled during coring at both Sites H002 and H005 and analyzed at the University of Washington. Based on the sulfate concentration of each pore water sample, we used the chemical

composition of the drilling water to correct each analysis for contamination using the following equations:

$$F_{DW} = [SO_4]_{meas}/[SO_4]_{DW} \qquad \text{(Eq. 2)}$$

$$f_{Pf} = 1 - f_{DW} \qquad \text{(Eq. 3)}$$

and

$$[X]_{corr} = [[X]_{meas} - (f_{DW} \times [X]_{DW})]/f_{Pf} \qquad \text{(Eq. 4)}$$

where f_{DW} is the fraction of a pore fluid sample that is contaminated with drilling fluid and f_{PW} is the fraction of uncontaminated pore water in a sample. The subscripts *DW*, *Pf*, and *meas* denote drill water, pore fluid, and measured, respectively. $[X]_{corr}$ is the corrected value of a solute (e.g., Cl, Ca, Sr, etc.), $[X]_{meas}$ is the measured concentration of that solute, and $[X]_{DW}$ is the concentration of the solute in the drilling fluid.

3.5 Hydrate saturation calculations

We used chlorinity measurements and calculations of chlorinity anomalies to estimate the hydrate saturation (S_h) of the collected samples, using the equation of Ussler and Paul, 2001:

$$S_h = \frac{\beta(C_{cb} - C_c)}{C_C + \beta(C_{cb} - C_c)} \qquad \text{(Eq. 5)}$$

where C_c is the sample pore water chlorinity and C_{cb} is the baseline pore water chlorinity. β is a dimensionless coefficient equal to 1.257 that accounts for the density change from methane hydrate to water (Malinverno et al., 2008). Because there were insufficient coring points to establish a baseline Cl profile, we use a value of C_{cb} equal to 559 mM, average seawater Cl concentration.

4. Results

The uncorrected geochemical data are shown in Table 2, and the corrected data, based on the composition of the drill water collected during coring at Sites H002 and H005, are presented in Table 3. There is large variability in the drill water composition in drilling fluid samples collected between the two sites, and it was significantly altered with respect to surface seawater composition. Typically, surface seawater is used as a drilling fluid. As such, we also provide corrected data in Table 4 assuming the drilling fluid had a composition of average seawater.

Onboard the UT-GOM2-1 expedition, the shipboard scientific party prepared a cesium tracer solution for the PCATS system at a concentration of 75.23 µM. The three pore water samples that underwent quantitative degassing within the PCATs have Cs concentrations ranging from below detection limit to 0.014 µM, thus exhibited very low PCATS contamination ranging from <0.003-0.02% contamination.

4.1 Site H002

All of the whole round samples for pore water geochemistry from Site H002 were recovered from pressure cores that did not maintain pressure to the rig floor. Sulfate concentrations ranged from 5.37 mM to 9.11 mM (Table 2), indicating drill water contamination of 19-33% (Table 3). Cl concentrations corrected for drill water contamination range from 47 to 280 mM (Tables 4-5). Considering that the Cl ion behaves conservatively at the in situ temperatures at this site, the Cl values indicate freshening of 50-92% of average seawater value (seawater Cl concentration = 559 mM). Thus, all of the other solutes are also diluted 50-92% from the addition of freshwater (by methane hydrate dissociation during core recovery and potentially clay dehydration at depth), and any deviations from diluted values are the result of diagenetic reactions that either increase or decrease their concentrations. Also see http://www-udc.ig.utexas.edu/gom2/H002/7_Geochemistry/Pore_Water/

4.2 Site H005

The five pore water whole round samples collected at Site H005 produced 1 to 11 mL of pore water for geochemical analyses (Table 1). Sulfate concentrations ranged from 0.5 mM in the whole round sample recovered from Core 1FB Section 3 well above the reservoir to 11.9 mM within the reservoir (Table 2), indicating that the fine-grained sample well above the main hydrate-bearing interval had minimal drilling contamination (2%), whereas samples collected within the hydrate-bearing interval were contaminated up to 41% with drilling fluid (Tables 3-4). The one sample collected above the gas hydrate reservoir had the highest Cl concentration, 499 mM, whereas samples from within the reservoir have much lower Cl concentration ranging from 57 mM to 264 mM (up to 90% less than modern seawater values), mainly due to gas hydrate dissociation upon core recovery and pressure core depressurization shipboard.

Similar to the Cl values, salinity is lower than seawater in all samples, most dramatically in the hydrate reservoir due to pore water freshening during core recovery and hydrate dissociation (Figure 1). Core 1FB Section 3 had negligible hydrate saturation from quantitative degassing (Phillips et al., 2020) and a salinity of 28 parts per thousand (ppt) (approximately 80% of typical seawater, 35 ppt). Slow, specialized quantitative degassing experiments immediately after the expedition were used to estimate the in situ salinity in the reservoir based on sample pressure behavior during depressurization, and constrained the pre-dissociation salinity to be relatively near seawater concentrations (34 to 45 ppt or 97 to 128% of typical seawater) (Phillips et al., 2020) (Figure 1b). All salinity values measured from post-dissociation pore waters are substantially lower than seawater salinity (3 to 18.5 ppt or 9 to 53% of typical seawater) (Figure 1b).

The Cl anomalies were used to calculate hydrate saturations (Sh) ranging between 44 and 83% of the pore space in samples from the reservoir and an Sh of 14% in Core 1FB in the overlying mud (Figure 1a). Sh derived from porewater matches well with the Sh estimated from well logs in the reservoir (Lee and Collett, 2012). Three of the core sections from Hole H005 measured with quantitative degassing were also sampled and analyzed for pore water composition after depressurization, allowing for a comparison between Sh measured by quantitative degassing and calculated from Cl anomalies. There is a strong correlation between Sh derived from the two approaches (Figure 2a) with Cl derived values 12 to 16% higher than quantitative degassing. The assumption of seawater salinity for Sh calculations could result in overestimated Cl anomalies and Sh, if in situ Cl is lower than seawater. Core 1FB in the overlying mud has a near-zero Sh based on quantitative degassing, but the Cl concentration of the whole-round collected from this core was 499 mM. The disagreement between the Sh estimated from quantitative

degassing and the pore water Cl concentration in Core 1FB suggests the background Cl concentrations may indeed be less than modern seawater value.

Considering that Cl behaves conservatively at the in situ temperature at this site, the decrease in Cl concentrations from seawater value is the result of pore water dilution from the addition of freshwater. Thus, plots of other solutes ratioed to Cl provide information on differences in pore fluid composition within the hydrate-bearing reservoir compared to the fine-grained sediments above the reservoir. The reservoir fluid is strongly depleted in K, Mg, and Sr concentrations and highly enriched in Ba, B, and Li concentrations (Figure 3), reflecting either differing in situ fluid-rock reactions within the reservoir compared to the sediments above or migration of deeper-sourced fluids within the reservoir. Also see http://www-udc.ig.utexas.edu/gom2/H005/7_Geochemistry/Pore_water/

5. Acknowledgements

6. References

Coffin, R., Hamdan, L., Plummer, R., Smith, J., Gardner, J., Hagen, R., and Wood, W., 2008, Analysis of methane and sulfate flux in methane-charged sediments from the Mississippi Canyon, Gulf of Mexico: Marine and Petroleum Geology, v. 25, no. 9, p. 977-987.

Expedition 308 Scientists, 2006a, Site U1319, *in* Flemings, P. B., Behrmann, J. H., John, C. M., and the Expedition 308 Scientists, eds., Proceedings of the Integrated Ocean Drilling Program, Volume 308: College Station TX (Integrated Ocean Drilling Program Management International, Inc.).

Expedition 308 Scientists, 2006b, Site U1320, *in* Flemings, P. B., Behrmann, J. H., John, C. M., and the Expedition 308 Scientists, eds., Proceedings of the Integrated Ocean Drilling Program, Volume 308: College Station TX (Integrated Ocean Drilling Program Management International, Inc.).

Expedition 308 Scientists, 2006c, Site U1322, *in* Flemings, P. B., Behrmann, J. H., John, C. M., and the Expedition 308 Scientists, eds., Proceedings of the Integrated Ocean Drilling Program, Volume 308: College Station TX (Integrated Ocean Drilling Program Management International, Inc.).

Expedition 308 Scientists, 2006d, Site U1324, *in* Flemings, P. B., Behrmann, J. H., John, C. M., and the Expedition 308 Scientists, eds., Proceedings of the Integrated Ocean Drilling Program, Volume 308: College Station TX (Integrated Ocean Drilling Program Management International, Inc.).

Flemings, P.B., Phillips, S.C, Collett, T., Cook, A., Boswell, R., and the UT-GOM2-1 Expedition Scientists, 2018. UT-GOM2-1 Hydrate Pressure Coring Expedition Summary. In Flemings, P.B., Phillips, S.C, Collett, T., Cook, A., Boswell, R., and the UT-GOM2-1 Expedition Scientists, Proceedings of the UT-GOM2-1

Hydrate Pressure Coring Expedition, Austin, TX (University of Texas Institute for Geophysics, TX). https://dx.doi.org/10.2172/1647223.

Kastner, M., Claypool, G., and Robertson, G., 2008, Geochemical constraints on the origin of the pore fluids and gas hydrate distribution at Atwater Valley and Keathley Canyon, northern Gulf of Mexico: Marine and Petroleum Geology, v. 25, no. 9, p. 860-872.

Lee, M. W., and T. S. Collett, 2012, Pore- and fracture-filling gas hydrate reservoirs in the Gulf of Mexico Gas Hydrate Joint Industry Project Leg II Green Canyon 955 H well: Marine and Petroleum Geology, v. 34, no. 1, p. 62–71, doi:10.1016/j.marpetgeo.2011.08.002.

Malinverno, A., Kastner, M., Torres, M.E., and Wortmann, U.G., 2008, Gas hydrate occurrence from pore water chlorinity and downhole logs in a transect across the northern Cascadia margin (Integrated Ocean Drilling Program Expedition 311), Journal of Geophysical Research, 113, B08103, doi:10.1029/2008JB005702

Paull, C. K., Ussler, W., Lorenson, T., Winters, W., and Dougherty, J., 2005, Geochemical constraints on the distribution of gas hydrates in the Gulf of Mexico: Geo-Marine Letters, v. 25, no. 5, p. 273- 280.

Phillips, S. C., P. B. Flemings, M. E. Holland, P. J. Schultheiss, W. F. Waite, J. Jan, E. G. Petrou, and H. Hammon, 2020, High concentration methane hydrate in a silt reservoir from the deep-water Gulf of Mexico: AAPG Bulletin, v. 104, no. 9, p. 1971–1995, doi:10.1306/01062018280

Pohlman, J. W., Ruppel, C., Hutchinson, D. R., Downer, R., and Coffin, R. B., 2008, Assessing sulfate reduction and methane cycling in a high salinity pore water system in the northern Gulf of Mexico: Marine and Petroleum Geology, v. 25, no. 9, p. 942-951.

Presley, B. J., and Stearns, S., 1986, Interstitial Water Chemistry, Deep Sea Drilling Project Leg 96, *in* Bouma, A. H., Coleman, J. M., Brooks, J., Bryant, W. R., Constans, R., Cremer, M., Droz, L. I., Ishizuka, T., II, M. C. K., Kohl, B., Meyer, A. W., Normark, W. R., O'Connell, S., Parker, M., Pickering, K. T., Schroeder, C., Stelting, C. E., Stow, D. A. V., Sweet, W. E., Wetzel, A., and Whelan, J. K., eds., Initial Reports of the Deep Sea Drilling Project 96: Washington (U.S. Government Printing Office), p. 697-709.

Smith, J., and Coffin, R., 2014, Methane Flux and Authigenic Carbonate in Shallow Sediments Overlying Methane Hydrate Bearing Strata in Alaminos Canyon, Gulf of Mexico: Energies, v. 7, no. 9, p. 6118.

Thomas, C., S.C. Phillips, P.B. Flemings, M. Santra, H. Hammon, T. Collett, A. Cook, T. Pettigrew, and P. Schultheiss, P., 2020, Pressure coring operations during Expedition UT-GOM2-1 in Green Canyon Block 955, northern Gulf of Mexico, AAPG Bulletin, v. 104, no. 9, p. 1877-1901, doi: 10.1306/02262019036

Ussler, W., III, and C. K. Paull, 1995, Effects of ion exclusion and isotopic fractionation on pore water geochemistry during gas hydrate formation and decomposition, Geo Mar. Lett., 15, 37–44.

7. Figures
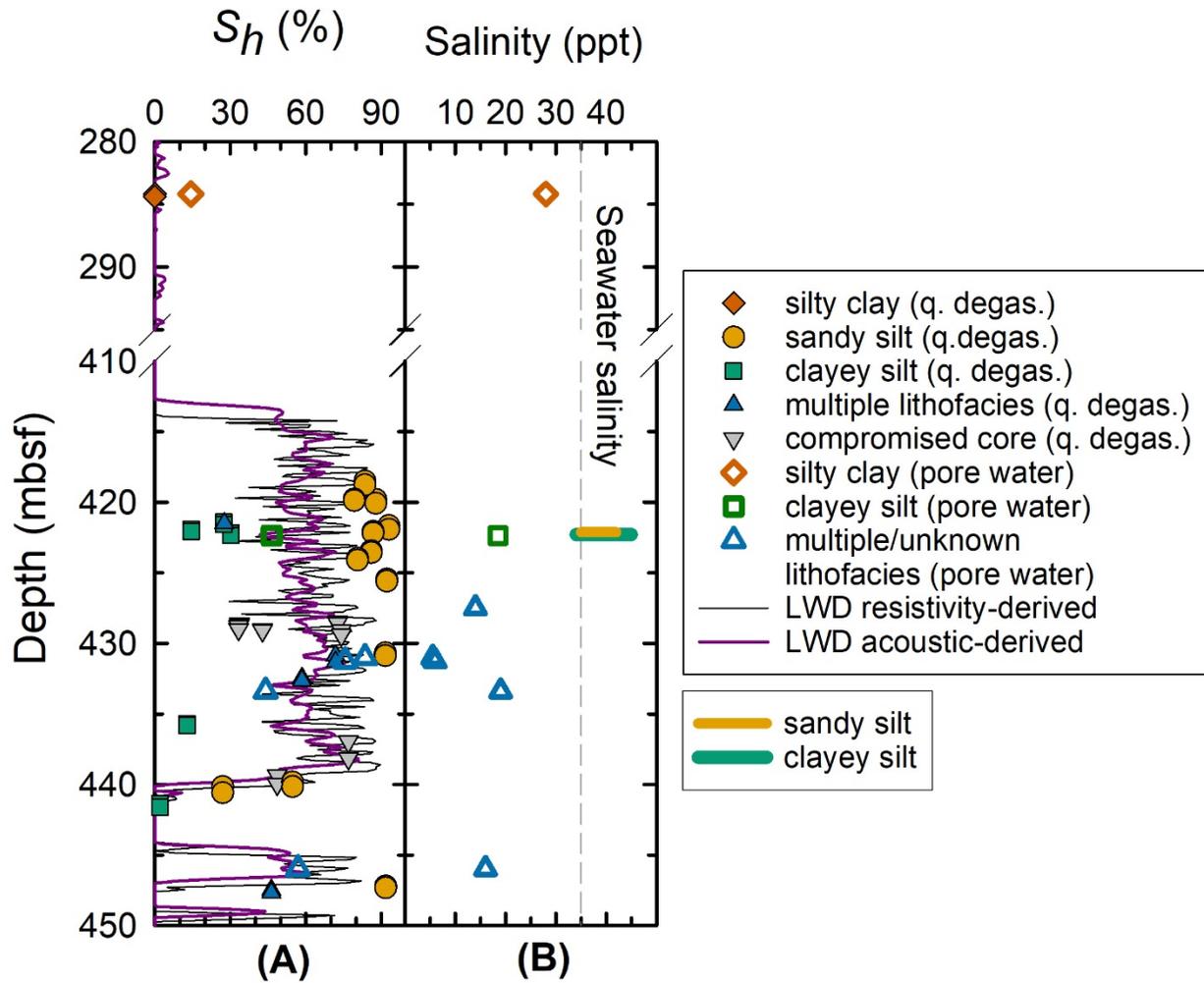
Figure 1. A) Hydrate saturation (Sh) derived from chlorinity (open symbols, this study), quantitative degassing (solid symbols. Phillips et al., 2020) and logging while drilling (Lee and Collett, 2012). B) Salinity measured on pore water (open circles, this study) and salinity ranges estimated from dissociation behavior (horizontal lines, Phillips et al. 2020).
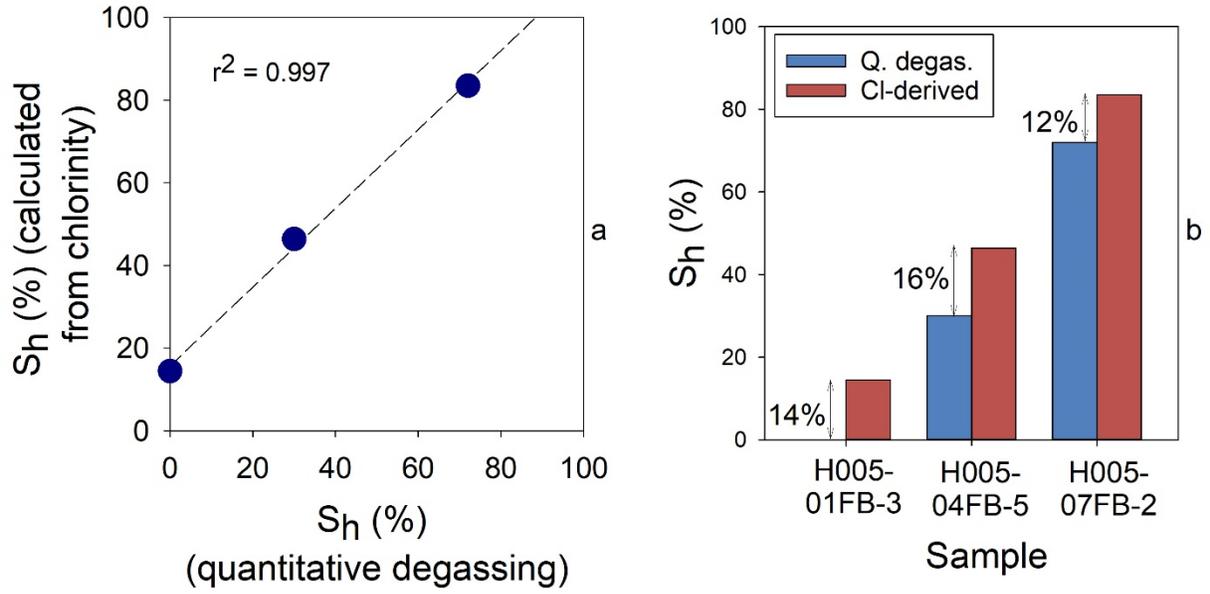
Figure 2. Direct comparisons of hydrate saturation (Sh) dervied from chlorinity (this study) and quantitative degassing (Phillips et al., 2020) from the same pressure core sections. A) Sh from the two methods are highly correlated. B) Sh calculated from chlorinity is 12 to 16% higher than from quantitative degassing.
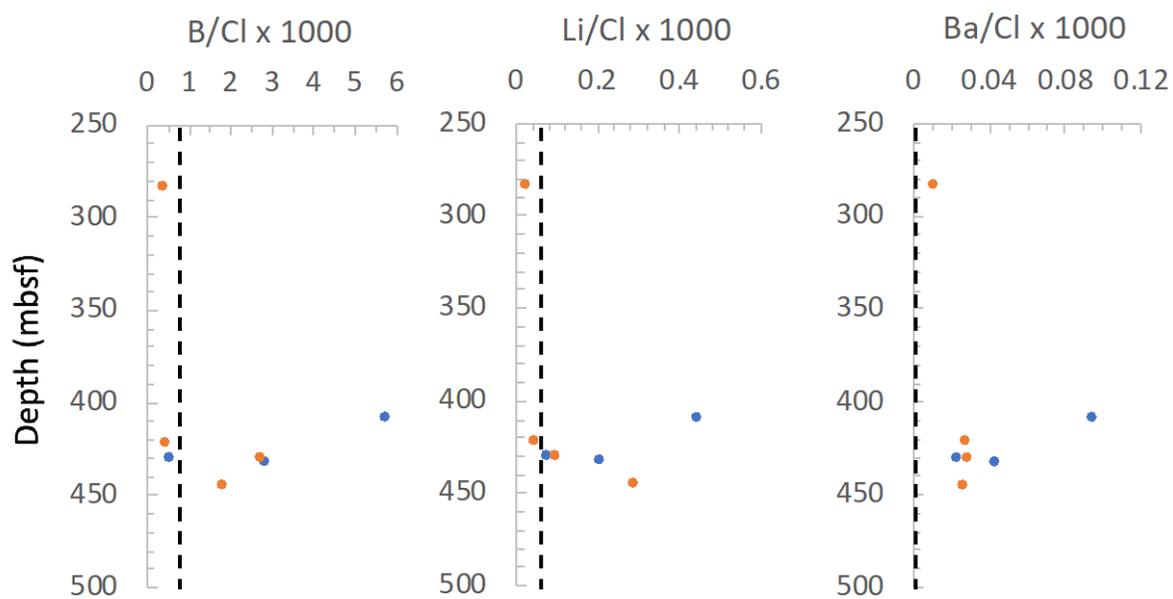
Figure 3. Contamination corrected B/Cl, Li/Cl, and Ba/Cl concentration ratios versus depth at Sites H002 and H005. Note that the ratios are multiplied by 1000 as the minor element concentrations are μM and Cl concentrations are mM. Orange dots are Site H005 data and blue dots are Site H002 data. The vertical dashed line denotes the average seawater ratio.

8. Tables

	glass			plastic				
	O/H	**DOC**	**Halogens and NH4**	**SO4**	**Cations**	**B and Si**	**Residue**	
								total
code	**GOMOH**	**GOMDOC**	**GOMHAL**	**GOMSO4**	**GOMCAT**	**GOMBSi**	**GOMIW**	
subsample container	1-2 ml ampoule	1.5 ml amber screw top	2ml screw top	10 ml Corning Cent. Tube; 0.1 ml sample from hal bottle to 9.9 ml Zn-acetate solution	4 ml acid-cleaned bottles	4 ml acid-cleaned bottles	5 ml acid-cleaned cryo-tubes	
treatment	**No Treatment**	**Frozen**	**No Treatment**	**Zn-acetate**	**acidify with 10 ul HNO3**	**No Treatment**	**acidify with 10 ul HNO3**	
20 ml	2	2	2	0.1	4	4	5	**19.1**
15 ml	2	2	2	0.1	4	4	1	**15.1**
10 ml	1	0	2	0.1	4	3	0	**10.1**
5 ml	1	0	1	0.1	2	1	0	**5.1**
4 ml	1	0	1	0.1	2	0	0	**4.1**
3 ml	1	0	0	0.1	2	0	0	**3.1**
2 ml	1	0	0	0.1	1	0	0	**2.1**
1 ml	1	0	0	0	0	0	0	**1**

Table 1. Distribution of pore water samples

Table 2. Pore water geochemical data not corrected for drill water contamination

Expedition	Hole	Core	Type	Section	Volume Recovered (ml)	Salinity	Cl (mM) AgNO₃ Titration	Cl (mM)	Br (mM)	SO₄ (mM)	δ¹⁸O (‰)	δD (‰)	Ca (mM)	Mg (mM)	K (mM)	Na (mM)	B (µM)	Li (µM)	Sr (µM)	Ba (µM)	Fe (µM)	Mn (µM)
UT-GOM2-1	H002	1	CS	1	8	8	150	148	0.746	6.67	-	-	2.21	6.06	2.17	156	217	15.4	12.55	1.99	0.916	2.02
UT-GOM2-1	H002	2	CS	2	1	3	-	-	-	-	0.71	13.98	-	-	-	-	-	-	-	-	-	-
UT-GOM2-1	H002	6	CS	4	2	14	-	279	0.484	5.41	-	-	4.94	15.01	3.62	255	272	25.1	28.93	5.68	1.07	3.83
UT-GOM2-1	H002	8	CS	1	11	19	344	350	2.24	9.11	-0.38	6.09	6.15	20.59	3.20	308	224	21.6	34.33	3.89	0.919	2.91
UT-GOM2-1	H002	8	CS	4	4.5	6	161	163	0.291	5.37	0.11	10.81	2.38	7.78	2.37	159	239	16.9	14.61	2.47	0.928	3.14
UT-GOM2-1	H005	1	FB	3	11	28	493	500	0.925	0.495	-1.90	-3.36	5.75	36.60	3.88	435	195	14.4	69.48	5.44	0.904	1.44
UT-GOM2-1	H005	4	FB	5	9	18.5	331	339	0.588	6.59	-1.01	-1.17	5.47	18.25	3.10	290	185	16.3	39.03	5.74	0.916	1.37
UT-GOM2-1	H005	7	FB	2	8	5.5	111	107	0.219	3.11	-0.11	3.32	1.48	4.11	2.20	108	185	8.0	8.512	1.47	0.895	0.609
UT-GOM2-1	H005	12	FB	2	1	13	-	-	-	-	0.20	8.21	-	-	-	-	-	-	-	-	-	-
UT-GOM2-1	H005	12	FB	3	7	16	273	281	0.516	11.9	-0.26	6.59	5.33	17.27	3.17	256	251	23.1	22.58	1.16	8.99	5.37
UT-GOM2-1	H002	1	CS	Drill Water	-	-	474	483	-	27.7	-0.43	-1.99	16.19	44.79	9.57	458	335	23.6	20.15	BDL	1.09	96.7
UT-GOM2-1	H005	1	FB	Drill Water	-	-	-	590	0.977	30.4	0.95	7.98	11.23	56.61	12.00	506	439	30.2	82.37	BDL	BDL	0.322
UT-GOM2-1	H005	2	FB	Drill Water	-	-	580	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
UT-GOM2-1	H005	2	FB	PCATS	-	-	-	33.5	0.142	1.72	0.86	8.67	0.89	3.44	2.12	33.2	32.1	2.11	BDL	BDL	BDL	2.49
UT-GOM2-1	H005	4	FB	PCATS	-	-	-	5.49	0.018	0.743	-5.34	-32.46	1.07	0.89	1.61	8.83	97.3	3.22	5.671	BDL	BDL	1.99
UT-GOM2-1	H005	7	FB	PCATS	-	-	-	26.6	0.114	1.27	0.89	9.06	0.87	2.31	1.69	26.8	88.4	3.15	3.745	BDL	BDL	2.44

Hole	Core	Type	Section	Cl(mM) AgNO₃ Titration	Cl(mM)	Br(mM)	SO4(mM)	δ18O (‰)	δD (‰)	Ca (mM)	Mg (mM)	K (mM)	Na (mM)	B (mM)	Li (µM)	Sr (µM)	Fe (µM)	Mn (µM)	f_{dw}	f_{pf}
H002	1	CS	1	47.1	41.6	-	0	-	-	BDL	BDL	BDL	60.4	180	12.8	10.13	0.86	BDL	0.24	0.76
H002	2	CS	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H002	6	CS	4	-	229	-	0	-	-	2.21	7.78	2.18	206	256	25.5	31.06	1.07	BDL	0.20	0.80
H002	8	CS	1	280	285	-	0	-0.35	10.1	1.23	8.72	0.08	234	170	20.6	41.28	0.83	BDL	0.33	0.67
H002	8	CS	4	85.7	86.2	-	0	0.24	13.9	BDL	BDL	0.64	87.3	216	15.2	13.28	0.89	BDL	0.19	0.81
H005	1	FB	3	492	498	0.924	0	-1.94	-3.55	5.66	36.27	3.75	434	191	14.1	69.27	-	1.4617285	0.02	0.98
H005	4	FB	5	262	269	0.480	0	-1.56	-3.70	3.88	7.63	0.64	230	115	12.5	27.03	-	1.6631926	0.22	0.78
H005	7	FB	2	57.6	51.7	0.133	0	-0.23	2.79	0.37	BDL	1.08	63.0	156	5.5	0.10	-	0.6415131	0.10	0.90
H005	12	FB	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H005	12	FB	3	74.1	81.1	0.219	0	-1.04	5.69	1.52	BDL	BDL	94.1	130	18.5	BDL	-	8.627347	0.39	0.61

- indicates not corrected for drill water contamination

f_{dw} = fraction of pore water sample that is contaminated with drill water

f_{pw} = fraction of uncontaminated pore water in a sample

BDL = below detection limit

Table 3. Pore water geochemical data corrected for drill water contamination

Hole	Core	Type	Section	Cl (mM) AgNO₃ Titration	Cl (mM)	Br (mM)	SO4 (mM)	$\delta^{18}O$ (‰)	δD (‰)	Ca (mM)	Mg (mM)	K (mM)	Na (mM)	B (mM)	Li (∝M)	Sr (∝M)	Ba (∝M)	Fe (∝M)	Mn (∝M)	f_{SW}	f_{PW}
H002	1	CS	1	27.2	24.6	0.712	0	-	-	BDL	BDL	BDL	59.1	155	12.2	BDL	2.56	1.19	2.63	0.23	0.77
H002	2	CS	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H002	6	CS	4	-	214	0.398	0	-	-	3.65	6.04	2.06	203	237	24.9	15.6	6.96	1.32	4.72	0.19	0.81
H002	8	CS	1	245	254	2.87	0	-0.55	8.90	4.12	5.20	BDL	228	132	19.5	10.1	5.63	1.34	4.25	0.32	0.68
H002	8	CS	4	70.2	72.8	0.161	0	0.13	13.28	0.51	BDL	0.53	86.0	197	14.8	BDL	3.01	1.14	3.86	0.19	0.81
H005	1	FB	3	492	499	0.926	0	-1.93	-3.42	5.67	36.30	3.77	435	191	14.2	69.2	5.54	0.92	1.47	0.02	0.98
H005	4	FB	5	264	274	0.508	0	-1.31	-1.51	3.97	7.68	0.94	234	114	13.5	24.9	7.40	1.19	1.78	0.23	0.77
H005	7	FB	2	57.0	52.2	0.142	0	-0.13	3.72	0.39	BDL	1.20	63.5	156	5.9	BDL	1.63	1.00	0.68	0.11	0.89
H005	12	FB	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H005	12	FB	3	71.2	85.1	0.275	0	-0.44	11.22	1.66	BDL	BDL	98.0	129	21.0	BDL	1.90	15.31	9.14	0.41	0.59

- indicates not corrected for drill water contamination

f_{SW} = fraction of pore water sample that is contaminated with drill water

f_{PW} = fraction of uncontaminated pore water in a sample

BDL = below detection limit

Table 4. Pore water geochemical data corrected for contamination assuming drilling fluid had composition of average seawater