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Brief Report

Data Report: Molecular and Isotopic Compositions of the Extracted Gas from China's First Offshore Natural Gas Hydrate Production Test in South China Sea

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Abstract: Three hundred gas samples recovered from SHSC-4 during China's first gas hydrate production test in the South China Sea were examined for gas component and isotopic composition. According to the gas chromatography analysis, all the gas samples from SHSC-4 are predominated by CH_4, with minor $N_2 + O_2$, as well as trace amounts of CO_2, C_2H_6, and C_3H_8. No H_2S was detected. The molecular and isotopic data of the gas samples fall into the region of "mixed origin" on the plot of $C_1/(C_2 + C_3) - \delta^{13}C_1$, which is close to the microbial origin. The discrimination diagram of $\delta^{13}C_1 - \delta D_{CH4}$ shows that the methane in all of the samples is of microbial origin, and is derived from the CO_2 reduction.

Keywords: isotopic composition; methane; gas hydrate; South China Sea

1. Introduction

In 2017, the first offshore natural gas hydrate (NGH) production test in the South China Sea (SCS) was conducted by the China Geological Survey (CGS). The production test site, SHSC-4, is located in the middle of the continental slope of southeast Shenhu area, northern SCS, about 300 km southeastward away from Hong Kong (Figure 1). The water depth of SHSC-4 is about 1263.5 m, according to the ROV (Remote Operated Vehicle) in situ survey. The production test lasted for 60 days, from 10 May to 9 July. The cumulative gas volume produced during the sixty-day test was approximately 309,000 m^3 (under the atmospheric pressure). The gas production rate was approximately 5454 m^3/day, with a maximum of 35,000 m^3/day. The gas hydrate production test in SCS holds the new record for the longest production time and the highest cumulative volume in the world's offshore gas hydrate production test, which is essential to the future global energy supply.

The core data from site SHSC-4 showed that gas hydrate occurred over a 50-meter interval from 201 mbsf (meter blow the seafloor) to 251 mbsf [1]. The characteristics of gas hydrate-bearing sediment is clayey silt, which accounts for more than 90% of the global NGH [2]. The gas hydrate saturation from both the pore-water freshening and pressure core mass balance is variable throughout the interval, with mean values of 35%. The mean effective porosity of the gas hydrate reservoir is about 34%, and the mean permeability is 2.9 mD [1].

In this document, we report on the shore-based analyses of the produced gas component and isotopic composition from the SHSC-4 site. The objective of this report is to present the gas characteristics of China's first gas hydrate production test in SCS, based on the molecular and isotopic analysis.

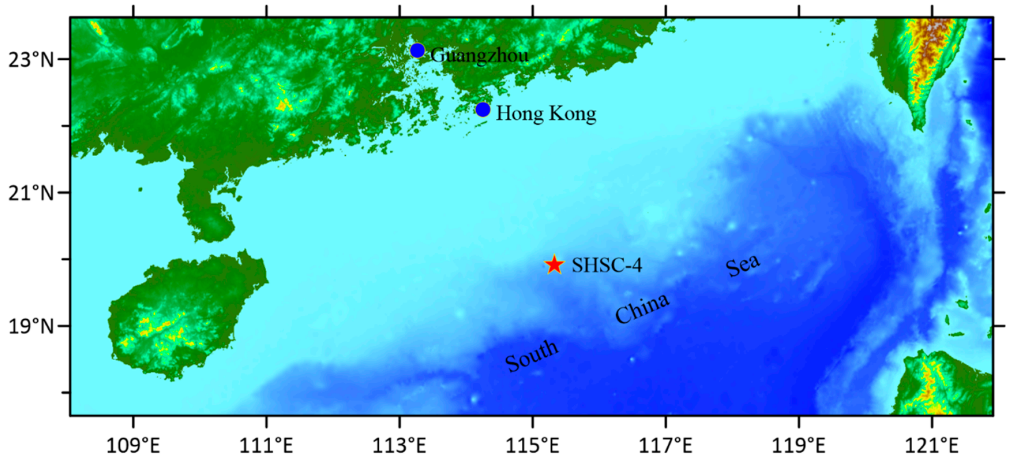

Figure 1. Location of China's first offshore gas hydrate production test in the South China Sea (SCS). The production test site named SHSC-4 (red solid star), which water depth is about 1263.5 m.

2. Samples and Analytical Methods

All of the gas samples were collected from the flow line on the rig, which was extracted from the gas hydrate interval between 201 mbsf and 251 mbsf with depressurization. All of the samples had no hydrogen sulfide smell. They were sealed in sample bags and were taken back for onshore analysis immediately. Three hundred gas samples were examined for geochemistry by gas chromatography (GC) and isotope ratio mass spectrometer.

An Agilent 7890A GC equipped with a 30 m × 0.53 mm HP-PLOT/Q column was used to measure the hydrocarbon gases from C1 to C5. The Agilent 7890 A is configured with a 1-mL, valve-actuated, sample loop for injection, and a thermal conductivity detector (TCD) for gas detection. The samples were introduced by syringes under atmospheric pressure, and a minimum of 10 mL of gas was used to flush the injection loop. The experiments were initially performed under 50 °C, with an increasing temperature rate of 20 °C/min to 200 °C. Helium was used as the carrier gas at a constant flow rate of 5 mL/min. The TCD temperature was kept under 200 °C. The GC was calibrated using the hydrocarbon gas standards of known concentrations.

Isotopic ratios of carbon and hydrogen in the hydrocarbon gases were measured with a Thermo Fisher Trace GC ultra-gas chromatography coupled to a MAT-253 isotope ratio mass spectrometer via a GC-isolink interface, at Guangzhou Marine Geological Survey Laboratory. The gas components were separated on a 30 m × 0.3 mm ID HP-PLOT/Q column using helium as the carrier gas. The flow rate was 1.5 mL/min. The GC oven was set under 50 °C for 2 min, then programmed to increase to 140 °C at a rate of 30 °C/min, and was maintained under 140 °C for 4 min. The GC injection port was set under 100 °C and then the split ratio was 50:1. The combustion oven temperature was 1000 °C in order to convert all of the hydrocarbons to CO_2, and the high temperature cracked oven temperature was 1420 °C in order to determine the hydrogen isotope. The $\delta^{13}C$ values were reported in the unit of per mil (‰), relative to the VPDB (Vienna Pee Dee Belemnite) standard. The carbon isotope data are more accurate for the hydrocarbon gases (accuracy within ±0.15‰). The δD values were also reported in the unit of ‰ (accuracy within ±1.0‰), relative to VSMOW (Vienna Standard Mean Ocean Water). The carbon and hydrogen isotopic ratio for both methane and ethane were measured, and other hydrocarbon gases were not detected because of the instrument limit.

3. Results

All of the 300 gas samples show similar GC curves, which exhibit a large C1 peak (Methane), but a weak peak of the other components (Figure 2). The GC analysis shows that all of the gas samples are predominated by CH_4 (91.35–97.69%, average = 95.87%) with minor N_2 + O_2 (1.79–8.18%, average = 3.63%), and trace CO_2 (0.007–0.142%, average = 0.013%), C_2H_6 (0.294–0.521%) and C_3H_8

(0.062–0.108%). No H_2S was detected. Among all of the hydrocarbon gases, CH_4 consists 99.38~99.60%, with an average of 99.50% (Figure 3).

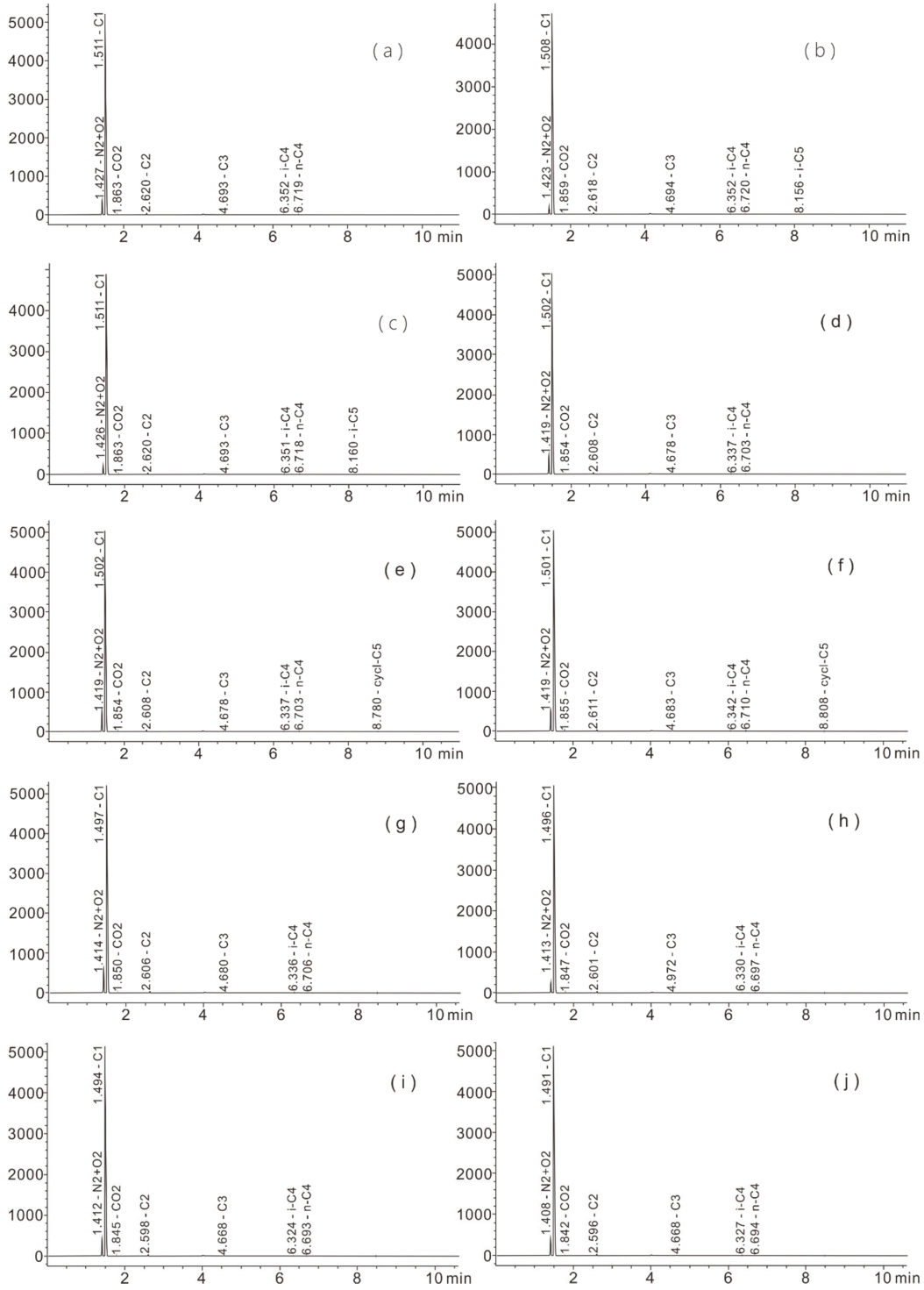

Figure 2. The representative GC curves of the gas samples from China's first offshore gas hydrate production test in SCS. (**a**,**b**) stand for the GC curves of gas extracted from the early depressurization; (**c**–**h**) are the curves of the gas samples from the middle production; (**i**,**j**) are the samples from the late production. All of the samples exhibit a large C1 peak and other weak peaks, which show that all of the gas samples are predominated by CH_4.

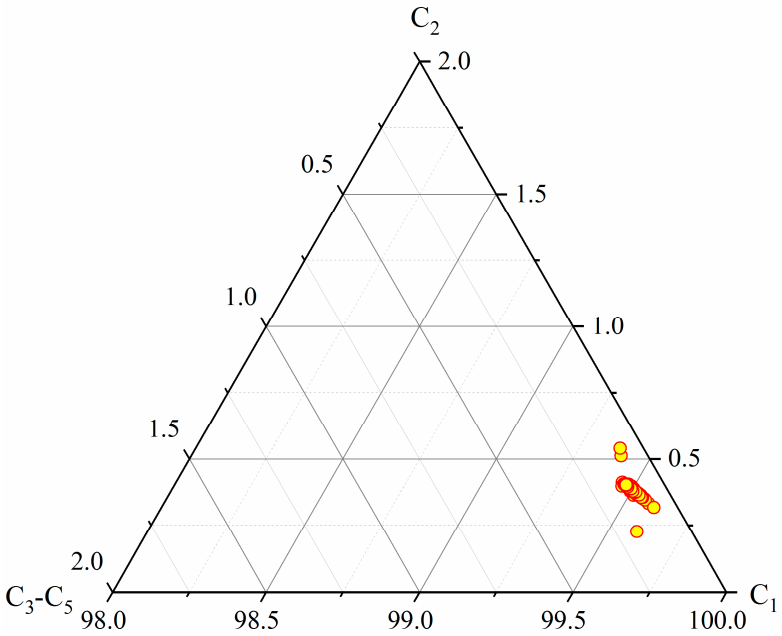

Figure 3. Ternary diagram of hydrocarbons from China's first offshore gas hydrate production test in SCS. All of the data points fall into the C1 end member, which indicate that methane is the main component of gas.

The molecular $\{C_1/(C_2 + C_3)\}$ compositions of the 300 gas samples collected from the production test range from 165 to 259 (ave. = 209). The $\delta^{13}C$ and δD in methane are within the range of −66.09–−63.14‰ (average = −64.88‰) and −195.8–−186.0‰ (average = −191.3‰), respectively, which are similar to those of the methane experimentally released from the natural gas hydrate samples collected from the Shenhu Area ($\delta^{13}C_1$ = −64.38–−61.57‰, δD_{CH4} = −220.00–−191.00‰ [3]).

The relationship between the C_1/C_{2+} ratios and the $\delta^{13}C$ values of methane is a good way to distinguish the origin of hydrocarbon. High C_1/C_{2+} ratios ($C_1/C_{2+} \geq 1000$) and low methane $\delta^{13}C$ values ($\delta^{13}C \leq -55$‰) are characteristic of a microbial origin, while low C_1/C_{2+} ratios ($C_1/C_{2+} \leq 100$) and high methane $\delta^{13}C$ values ($\delta^{13}C \geq -50$‰) are characteristic of a thermogenic origin [4–10]. On the plot of $C_1/(C_2 + C_3) - \delta^{13}C_1$, all of the gas samples from the production test fall into the "mixed origin" region close to the microbial origin (Figure 4), which is different from the gas hydrate from Blake Ridge, Hydrate Ridge, Mexico gulf, and a Japan gas hydrate prodution test site in Nankai Trough, but close to the Ulleung basin of Korea. Moreover, the discrimination diagram of $\delta^{13}C_1 - \delta D_{CH4}$ (Figure 5) shows that the methane in all of the samples is of microbial origin and is derived from a CO_2 reduction, which is different from the nearby LW3-1-1 gas well with methane thermogenic origin in SCS, but is the same as Blake Ridge, Hydrate Ridge, and the Ulleung basin of Korea. The information from Figures 4 and 5 indicate that the gas extracted from China's first gas hydrate production test possibly originate from bacterial and thermogenic gas mixtures, but have more of a bacterial component.

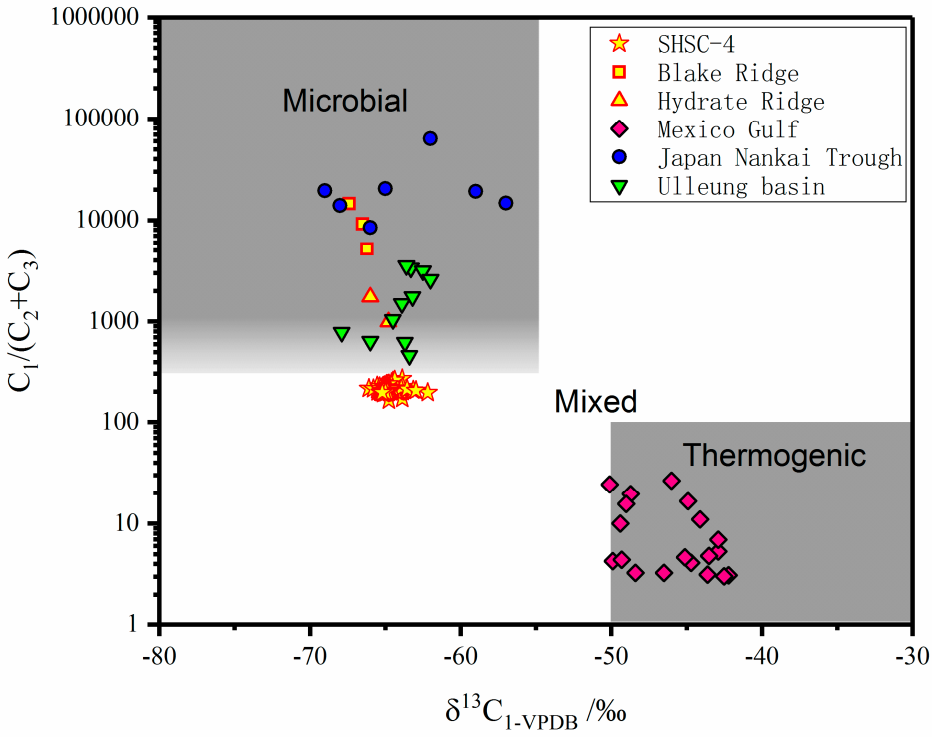

Figure 4. Relationship between $C_1/(C_2 + C_3)$ and $\delta^{13}C$-C_1 of hydrocarbon from China's first offshore gas hydrate production test in SCS (adapted from Whiticar et al. [6]). The data from the Blake Ridge [11], the Hydrate Ridge [7], the Mexico Gulf [12], the Japan Nankai Trough [13], and the Ulleung Basin [14] were plotted for comparison.

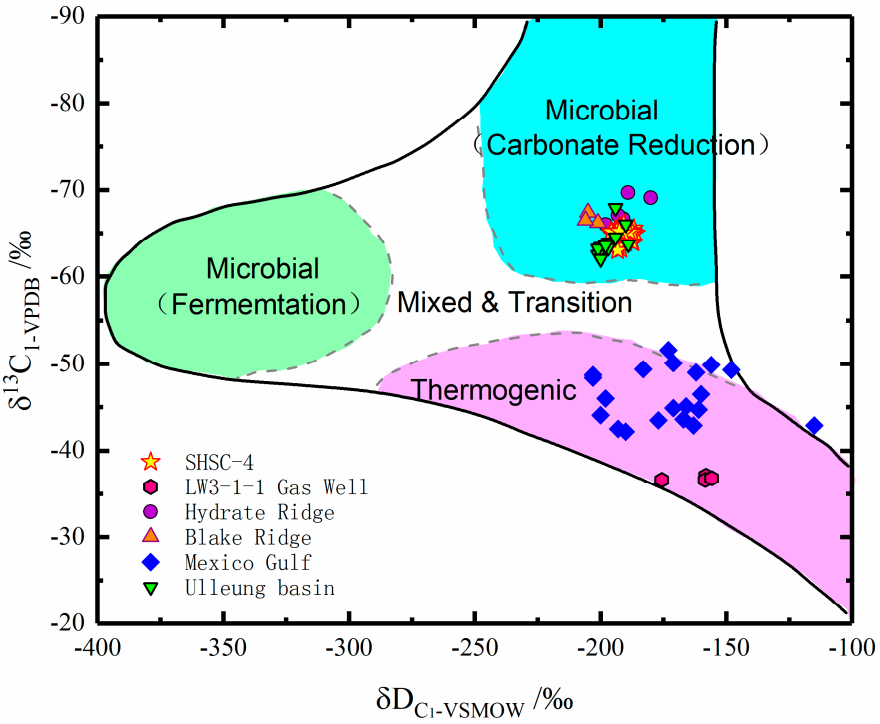

Figure 5. Relationship between $\delta^{13}C$ and δD of CH_4 from China's first offshore gas hydrate production test in SCS (base map from Whiticar et al. [6]). The data from the LW3-1-1 gas well in SCS [15], the Hydrate Ridge [16], the Blake Ridge [11], the Mexico Gulf [12], and the Ulleung Basin [14] were plotted for comparison.

4. Summary and Conclusions

The extracted gas from China's first natural gas hydrate production test in SCS are predominantly by methane, which accounts for 99.38~99.60% of all of the hydrocarbon gases. The $\delta^{13}C$ and δD in methane are within the range of −66.09–−63.14‰ and −195.8–−186.0‰, respectively. Different from those of the nearby LW3-1-1 gas well with a thermogenic origin, these values imply that the methane of the natural gas hydrate in the Shenhu area was mainly derived from the bacterial reduction of CO_2. Nevertheless, the contribution of the thermogenic origin cannot be excluded in this study. It is possible that the bacterial gas is the main gas origin for gas hydrate formation in SHSC-4.

Author Contributions: J.Y. made the substantial contributions of research conception and design. X.Q. contributed to made the critical revision. H.Q. contributed to data collection. W.X. made the contribution of data interpretation. H.L. drafted the article and made final approval of the article. C.L., J.Z. and J.L. analysed the component of samples. T.Y. collected the gas samples. J.C. and R.S. made the isotope analysis.

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Conflicts of Interest: The authors declare no conflicts of interest.

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