HIGH CONCENTRATION HYDRATE IN DISSEMINATED FORMS OBTAINED IN SHENHU AREA, NORTH SLOPE OF SOUTH CHINA SEA

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ABSTRACT
In April-June of 2007, a gas hydrate drilling expedition was carried out by using M/V Bavenit in Shenhu Area, the north slope of South China Sea. High concentrations of hydrate (>40%) were obtained in a disseminated forms in foram-rich clay sediments at 3 selected sites. The hydrate-bearing sediments ranged several ten meters in thickness are located in the lower part of GHSZ, just above the BGHSZ, and are typically characteristic of higher sonic velocity and resistivity, and lower gamma density in wireline logging profiles. Evidences for gas hydrate include the IR cold spots and temperature anomalies, salinity and chlorite geochemical anomaly of pore water for non-pressurized cores, and X-ray imaging, high p-wave velocity and low gamma density, and high concentration of methane from the pressurized cores. Gasses are mainly methane (max. ethane 0.2-0.3%), therefore only hydrate S1 is formed. It is inferred that the foram content and other silt size grains may provide enough free water for the hydrate to happily occupy both the large spaces in the forams and for it to distribute itself evenly (disseminated) throughout the formation. It is possible that all the forams are hydrate filled. As the forams are visible does this not count for visible white gas hydrates.

Keywords: gas hydrates, high concentration, South China Sea

INTRODUCTION AND OBJECTIVES

The north slope of South China Sea is characteristic of the passive continental margin in Cenozoic and rich of oil&gas bearing basins. As a result, the geological and tectonic settings, the temperature and pressure regimes, and the methane-generating potential from the thick organic-rich sediments are all favorable for gas hydrate formation. Since 2001, Guangzhou Marine Geological Survey (GMGS) has been carring out the geological, geophysical and geochemical investigations for gas hydrate in the northern South China Sea. The evidences for gas hydrate's existence have preliminarily suggested the great promise for gas hydrates.

In order to determine the nature and distribution of gas hydrate, in 18 April –11 June of 2007, a gas hydrate drilling expedition bas been initiated by using M/V Bavenit along with specialized Fugro& Geotek equipments in Shenhu Area, the north slope of South China Sea.

The overall plan for gas hydrate detection, and the quantification of its nature, distribution and concentration, involved the concerted and focused use of different observation and measurement techniques to provide "multiple lines

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of evidence" for gas hydrate. Pressure cores provided "benchmark" spot measurements over approximately one-meter intervals of actual methane concentration, gas hydrate concentration, and background chlorinity. Infrared imaging of non-pressurized cores was used to detect the presence of dissociating/dissociated gas hydrate throughout the hole. Porewater freshening analysis from chlorinity variations was used to quantify the gas hydrate at the centimeterscale. Gas hydrate saturations from the pressure and non-pressurized cores within the cored intervals can then be compared to the resistivity, acoustic, and other well logs for a complete "hydrate picture" of the borehole. We also collected samples from both non-pressure and pressure cores that were likely to contain gas hydrate and preserved them in liquid nitrogen.

Natural gas hydrate dissociates rapidly when recovered in non-pressurized cores as a result of decreasing pressure and increasing temperatures while the cores are raised through the water column. The dissociation of gas hydrate is an endothermic reaction that requires significant heat energy that creates transient negative thermal anomalies (cold spots), which can be detected and imaged using an infrared camera and/or by inserting temperature probes directly into the sediment cores. Initial detection of gas hydrate, therefore, in non-pressurized cores, relies both on visual observation and on measurements of thermal signatures (cold spots or regions) created by the dissociating gas hydrate.

Gas hydrate dissociates into light hydrocarbon gas, which expands to create gas voids and cracks within sediment cores, and fresh water, which can be detected as a freshening of pore fluids relative to background as well as sometimes visually by wet or moussy sediment textures. To ensure that any fully-dissociated gas hydrate was detected in non-pressurized cores, an exhaustive porewater sampling plan was undertaken. Porewater freshening was used not only as a method for detecting the occurrence of gas hydrate but as a technique to quantify the gas hydrate concentration. Porewater salinity and chlorinity were measured to gauge the extent of porewater freshening due to hydrate dissociation. Porewater sulfate was measured as a tracer of surface seawater used in drilling so that any chlorinity variations due to infiltration of drilling fluids could be removed from the data set. Porewater samples from pressure cores were used

to confirm the *in situ* (baseline) chlorinity.

Detection of gas hydrate in pressurized cores relies on a combination of nondestructive testing and dissociation tests. Nondestructive tests on static pressurized cores included measurements of gamma density, P-wave velocity, and X-ray images on the cores at near in situ pressure & temperature conditions, where any gas hydrates inside the core were stable. These data together with the amount of gas released during active depressurization/dissociation experiments, allowed the fine-scale nature of the gas hydrate as well as its average concentration in the pressure cores to be determined.

Natural gas mass balance from pressure cores was used to estimate the saturation of gas hydrate or free gas, by quantifying the total amount of light hydrocarbon gas present in pressure cores. Mass balance from pressure cores is the only way to quantify the total concentration of natural gas in a core, from which the gas hydrate saturation of sediment can then be calculated assuming dissolved gas, free gas, and gas hydrate phases are in thermodynamic equilibrium. Gases released from pressure cores during depressurization experiments were collected and their composition measured. The total amount of gas contained in a pressure core was then compared to the pore volume of the core, and gases that were present at a level beyond saturation at *in situ* conditions were assumed to exist as a gas hydrate or free gas phase.

PROCEDURES
General operations & strategy

Two holes were planned at each site investigated. The first hole drilled was a pilot hole that was drilled to determine if there were any shallow gas hazards present at the site. Each pilot hole was then logged with a suite of slim wireline logging tools. At most sites, this was followed by drilling an adjacent sampling/testing hole. This sampling hole was generally offset about 10-15 m from the pilot hole along the geological strike (WSW-ENE).

The objectives of the sampling hole were to sample layers with and without gas hydrate to determine the concentration, nature, and distribution of gas hydrate within the section; determine the temperature gradient and hence the base of methane gas hydrate stability; determine the depth of the sulfate methane interface (SMI); sample representative lithologies for correlation

with seismic profiles and wireline logs; and, in particular, recover cores containing gas hydrate for description and sample storage. The sampling and testing plan was initially determined fromthe available seismic data but was refined based on the details obtained from the wireline logging. Sediment samples were obtained with the Fugro Hydraulic Piston Corer (FHPC) and Fugro Corer (FC) as well as without release of in situ pressure with the Fugro Pressure Corer (FPC)and the Fugro Rotary Pressure Corer (FRPC). The temperature profile was determined from temperature measurements using either the Wison EP temperature probe or from the temperature measurements on the Fugro Pore Water Sampler (FPWS).

Coring plan

Due to limited time for GMGS Expedition 1, boreholes could not be cored continuously. The initial coring plan for each site was generated by picking coring targets from the seismic section, which was done in concert with the client. This coring plan was refined once the data for the wireline logging was completed. Sites were cored near the surface to determine the nature and depth of the sulfate-methane interface, at intermediate depths to hit seismic or wireline log targets and to collect baseline geochemical data, and above and below the estimated depth of the BSR to detect gas hydrate or free gas near the base of gas hydrate stability.

Preservation of gas hydrate samples in liquid nitrogen

Samples of gas hydrate bearing sediment were preserved in liquid nitrogen for further analyses. Samples were either rapidly cut from the non-pressure cores (FHPC or FC), following the infrared thermal scan, or removed from rapidly depressurized pressure cores (FPC or FRPC). These samples were wrapped in aluminum foil, placed in Tyvek sample bags, and submerged in liquid nitrogen to rapidly freeze the samples.

Core temperature measurement

Core temperature was measured to identify negative thermal anomalies created from dissociating gas hydrate. These measurements were used primarily as a tool to rapidly identify parts of the cores that contained, or had contained, gas hydrate, both for possible gas hydrate preservation and to direct the porewater sampling. Liner temperatures were measured as soon as the core was brought into the processing container using a FLIR infrared (IR) camera on an automated track. A visual image was collected at the same time so that the voids in the core could clearly be seen and correlated with positive thermal anomalies in the IR image. Composite IR and visual images of each core were saved. Sediment temperature was measured using digital recording temperature probes inserted for 5 minutes into the center of the core immediately after it was cut into sections.

Porewater sampling, porewater analyses, & gas hydrate from porewater freshening

Samples of all cores were taken for porewater analysis, in the case of the FHPC and FC guided by the core liner temperatures from infrared imaging, and in the case of the FPC and FRPC guided by the MSCL-P data. Samples were taken in sediments that might contain gas hydrate (negative thermal anomalies or high P-wave velocities) as well as in adjacent sediments with no evidence of gas hydrate. Plug samples of sediment were taken from the centers of cores and squeezed in a hydraulic press to separate the porewater for chemical analyses. Porewater salinity was measured on board by refractometry; the error on salinity measurements was ±0.5 ppt (precision of refractometer). Porewater chloride concentration was measured on board by titration with silver nitrate using a chromate indicator; repeatability of chloride concentration measurements was ±0.5%.

Sulfate was measured to account for any dilution of porewater from drilling fluid. Sulfate eventually drops to zero in sedimentary porewaters at depths varying from less than 5 to more than 50mbsf due to microbial sulfate reduction, as seen throughout the world's ocean basins. If the decline of sulfate is monitored, once below the depth of zero sulfate, sulfate can be used as a tracerof drilling fluid. The drilling fluid signature can be removed through a two-component mixingmodel. Sulfate was measured by barium sulfate nephelometry. Samples of drill water were processed in the same manner as porewater samples.

Approximately 1 ml of most water samples was archived, should further analyses be required. Samples were filtered through a 0.2 micron ion-chromatography-certified filter and are suitable for major ion analyses. Water samples can be identified by sequential water sample identification number. Residual sediments ("squeeze cakes") were saved forgrain size measurement or other analyses and are also identified by water sample identification number.

Porewater freshening was calculated from the difference between measured chlorinity and the estimated *in situ* baseline chlorinity. Baseline chlorinity profiles were constructed using the maximum measured chlorinities from the non-pressurized cores as well as data from pressure cores. Gas hydrate saturation, as a percent of pore volume, was calculated from porewater freshening and the density and water content of gas hydrate. The mixing model used assumes that thepore space can be occupied by porewater or gas hydrate but not both. Gas hydrate saturation has an estimated error of ±2% of pore volume (empirical estimate based on sediment sections containing no gas hydrate). While negative values of gas hydrate saturation do not indicate "negative" gas hydrate, the values do show the errors in the calculation.

Gas sampling and analyses

Gas voids in non-pressure cores (FHPC & FC) were sampled to detect light hydrocarbon gases. Core liners were punctured with a sampling probe, gas samples collected in a plastic syringe, and the gas analyzed for methane, and ethane, propane, isobutane, and butane by gas chromatography. Gas samples taken from pressurized cores were also analyzed to determine both the total amount and type of gas present. These gas compositions reflect the composition of the gas ex-solved from pore fluids, free gas, and dissociating gas hydrate.

Headspace samples were taken from near-surface cores to determine the depth of the sulfate-methane interface. A 5 ml plug of sediment was sealed in a 26 ml glass vial using a teflon-coatedseptum and an aluminum crimp seal. After addition of 2 ml of saturated NaCl solution to the vial, the sediment was slurried and the vial placed in a 60°C for two hours. The vials were allowed to cool to room temperature, the headspace of the vial analyzed, and the concentration ofhydrocarbon gases in the porewaters calculated.

Gas composition was measured using an Agilent MicroGC 3000A gas chromatograph with molecular sieve and PLOT U columns and thermal conductivity detectors. Oxygen, nitrogen, methane, ethane, propane, and butane were measured. Air contamination during sampling was removed from gas totals. Selected gas samples were archived in salt-water-filled, rubber-stoppered glass serum bottles and labeled with the full section name and section depth from which they were taken.

MSCL-P measurements

Gamma density measurements, P-wave velocity measurements, and X-ray images of FPC &FRPC cores were automatically collected using the Geotek MSCL-P (Pressure Multi-Sensor Core Logger). MSCL-P data on pressure cores were collected for two basic purposes: to determine the nature and distribution of gas hydrate within the sediment core and to provide parameters for the mass balance calculations of gas from pressure cores.

Gamma density was measured with a ^{137}Cs source and a sodium iodide detector; the error in density was ±2%. P-wave velocity was measured using a pulse transmission technique at 250 kHz;the error in velocity was ±1%. X-ray images were collected with a microfocal source and imageintensifier; the pixel resolution was approximately 120 microns. The voltage and current on thepolychromatic X-ray source was tuned to provide best image quality and should not be used toestimate density. All data in the MSCL-P was collected at 0.5 cm spacings. The center 0.5 cm section from each X-ray image was concatenated to form a single image for each core.

The details of the MSCL-P data were used to determine the nature and distribution of gas hydrate in relation to the sediment structure. Grain-displacing gas hydrate structures, such as veins and lenses, are normally visible in density and X-ray data as low-density structures and, if they were large enough, visible in the P-wave velocity data as high velocities. Pore-filling disseminated gas hydrate is often not evident in density and X-ray data, as gas hydrate has a similar density to pore fluid, but often produces an anomalously high P-wave velocity if the sediment is cemented with gas hydrate.

Depressurization experiments & quantification of gas hydrate from total methane

Most pressure cores were depressurized in a controlled fashion inside the MSCL-P to quantify the total amount of hydrocarbon gas in all phases, including gas hydrate, within the cores and todetermine the distribution of gas hydrate within the sediment. First, MSCL-P measurements (gamma density, P-wave velocity, and X-ray images) were collected along each pressure core at 0.5 cm intervals to characterize the core and to identify any gas hydrate structures. Once baseline measurements had been made, the pressure core was carefully positioned inside the MSCL-P so that the end of the core was immediately below the gas collection point. The pressure wasthen slowly

and incrementally reduced through a manifold and expelled gas and fluid were collected.

Gas was collected during depressurization and analyzed using the on-board gas chromatograph to determine the composition of the gas released. The total released volume of methane and other hydrate-forming gases was determined by measuring the volume of gas expelled from the system and adding the volume of fluid expelled from the system. Gas remaining in the core orelse where in the system must displace fluid; the volume of fluid expelled by the system alone from changes in volume or air coming out of solution was empirically determined and subtracted from the total fluid volume. Total gas volumes were used to calculate *in situ* gas concentrations within sediment. For instance, methane concentration was calculated from total methane evolved from each pressure core and the pore volume of the core.

The calculated concentration of methane was compared to methane saturation for in-situ conditions; *in situ* temperatures were taken from the Fugro Temperature Probe or the temperature measurement on the Fugro Pore Water Sampler, and *in situ* pressures were assumed to be hydrostatic. Any methane present beyond dissolved methane saturation (excess methane) was assumed to be in a methane hydrate phase or a free methane gas phase, depending on the calculated thermodynamic phase boundaries. The primary evidence that this was a fair assumption comes from the observation that the P-wave attenuation was not substantial in the pressure cores recovered in the gas hydrate stability zone. Even when a small amount of free gas exists in sediments (probably less than 0.2%), the attenuation of a 250 kHz signal increases quite dramatically. This was not observed until the cores were at least partially depressurized.

MSCL-S measurements

Gamma density, P-wave velocity, magnetic susceptibility, and electrical resistivity of FHPC & FC cores were measured using the Geotek MSCL-S (Standard Multi-Sensor Core Logger). The measurement interval was normally 2 cm. Gamma density and P-wave velocity measurements were similar to those made with the MSCL-P, except the P-wave frequency in the MSCL-S was 230 kHz. P-wave velocities are only available near the top of each hole; as the methane concentration increased downhole, gas exsolving from sediments created bubbles, cracks, and voids which strongly attenuates the acoustic transmission through the sediment. Magnetic susceptibility was measured with a 8 cm diameter Bartington loop sensor; the error in magnetic susceptibility was ±5%. Electrical resistivity was measured using a custom non-contact inductive resistivity sensor; the electrical resistivity was susceptible to the same issues as the P-wave velocity andthe data is severely degraded once gas cracks appear in the cores.

CONCLUSION

A gas hydrate investigation was performed in the Shenhu area, South China Sea, between, 2007, from the SDV Bavenit. Geotek's primary role was to quantify gas hydrate in sediment cores and determine the nature and distribution of gas hydrate within the sedimentary sequence at each site that was sampled. Eight sites were investigated: SH3, SH6, SH1,SH2, SH7, SH5, SH9, and SH4 (in chronological order). At each site, a pilot hole was drilled first that was subsequently wireline logged. A sampling and testing hole was drilled at five of these locations: Sites SH3, SH1, SH2, SH7, and SH5. The remaining sites, SH6, SH9, and SH4,were not sampled as it was considered that there was little or no prospect of finding any gas hydrate after the wireline logs had been examined. Both non-pressure cores and pressure cores were retrieved from the sampling holes with a variety of tools at depths guided by the detailed wireline logs and the available seismic data. Temperature measurements were collected at intervals appropriate for determining the base of gas hydrate stability. The core analysis program focused on determining the occurrence of gas hydrate using both nondestructive and destructive techniques. Non-pressure cores were rapidly scanned with an infrared camera to detect thermalanomalies caused by dissociating hydrate and then sampled extensively for porewater analysis to quantify any porewater freshening caused by dissociated gas hydrate. A very cold sample from one non-pressure core was rapidly stored in liquid nitrogen. Each pressure core was nondestructively tested for density & P-wave velocity and X-ray imaged, all at in situ temperatures & pressures, to examine the cores for the characteristic signatures of gas hydrates. Most pressure cores were slowly depressurized and the released gases captured, to accurately measure the amount of methane present and to calculate the concentration of gas hydrate.

Three pressure cores that were rich in gas-hydrate-bearing sediments were rapidly depressurized and subsamples from two of these were stored in liquid nitrogen for later shore based analysis.

The calculated base of gas hydrate stability (from temperature, pressure, and salinity measurements) at all the sites was near the estimated depth of the BSR on the seismic profiles. Gas composition measurements showed that methane was the dominant gas, with 0.01-0.1% ethane present, so that calculations based on Structure I methane hydrate are appropriate. The sulfate-methane interface at the sites cored varied between 17-27 mbsf. Significant and very distinct gas-hydrate-bearing layers of sediments were found at three of the sites investigated (SH3, SH2, and SH7) but the remaining sites cored (SH1 and SH5) showed no detectable levels of gas hydrate. At Site SH3, gas hydrate was found in two cores just above the base of gas hydrate stability (206 mbsf), with a maximum gas hydrate concentration of 25% of pore volume, calculated from porewater freshening. The resistivity anomaly from the wireline logs indicated that this layer was approximately 10 meters thick. At Site SH2, a 25-meter-thick layer of gas-hydrate-bearing sediment was found at 195-220 mbsf. The gas hydrate concentration in this interval was consistently high (over 25% of pore volume) with maximum calculated concentrations of 47% of pore volume. At Site SH7, another 25-meter-thick layer of gas-hydrate-bearing sediment was found at 155-180 mbsf. The gas hydrate concentration in this interval was more variable than at Site SH2 but had maximum calculated concentrations of 44% of pore volume. Nearly all the evidence from both the pressure cores and the non-pressure cores indicated that the gas hydrate existed at all three sites in a disseminated, non-grain-displacing form that cannot be seen with the naked eye. It should be noted that the concentration of gas hydrate in these 3 sites in what appears to be relatively fine-grained sediments is, in our experience, unprecedented.