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Research paper

Characterization of natural gas hydrate recovered from Pearl River Mouth basin in South China Sea

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ABSTRACT

China carried out a drilling campaign in the eastern part of the Pearl River Mouth (PRM) basin and successfully obtained natural gas hydrate samples in 2013. Laboratory based studies for the characteristics of gas hydrate were carried out on one of the hydrate-bearing sediment sample. The gas hydrate sample shows nodular occurrence with host matrix predominantly composed of silty sand and clay. On the basis of the Raman spectroscopic and X-ray diffraction results, the gas hydrate demonstrates a typical structure I (sI) with cage occupancy of methane is more than 99.5% in large cage and 91.4% in small cage, respectively, corresponding to a hydration numbers of 5.90 by thermodynamic calculation. The molecular compositions of hydrate-bound gas suggest that the guest molecules are predominantly methane (>99.9%), with trace amount of ethane (0.04%) and propane (0.01%). The isotopic analysis indicates that the methane of hydrate-bound gas of the studied drilling well in PRM basin is a typical microbial origin.

1. Introduction

Natural gas hydrate is widely distributed in marine sediments beneath 300 m water depth and the terrestrial permafrost (Kvenvolden, 1995; Makogon et al., 2007). In recent years, several drilling projects have been carried out in South China Sea (SCS) and Qinghai–Tibetan Plateau permafrost regions in China, and successfully obtained gas hydrate samples. These samples are quite different in their occurrences. For example, gas hydrates from Qilian Mountain permafrost only occur as a thin layer within cracks of the rock cores (Zhu et al., 2010; Lu et al., 2011a,b,c), whereas gas hydrates from Shenhu area in SCS disseminate in the sediment pore (Zhang et al., 2007). Several researches focus on the occurrence, gas resource and gas production for Qilian Mountain permafrost hydrates (Lu et al., 2011a,b,c, 2013; Zhao et al., 2013), and the reservoir system of the Shenhu area hydrates (Wu et al., 2008). Song et al. (2014) summarized the natural gas hydrate research in China and gave a preliminary comparison of gas hydrates from Qilian Mountain permafrost and SCS. However, the characteristics of gas hydrate from the PRM basin in SCS has not been mentioned because it was newly recovered in 2013.

The northern SCS is a transitional continental margin, which remains lots of features of continental geological structure due to the comparatively short expansion time (Ludmann et al., 2001). This area experienced intensive neotectonic movements, which resulted in complex base structure and developed complicated fault systems (Wang et al., 2006). In this area, the topography is complex and the slope varies greatly. The water depth is between 800 and 2000 m, with the fathom line roughly parallel to the coast line (Gong et al., 2009). The deposition rate was 17.9–19.6 cm/ka and 9.6–14.6 cm/ka for late Pleistocene and Holocene, respectively, somewhat higher than that for Pliocene (Gong et al., 2009). The geothermal gradient in the studied area is relatively low (45–67.7 °C/km) as compared with other regions (~80 °C/km) in the SCS (Wu et al., 2004, 2009). The occurrence of gas hydrate in SCS was known as postulated from the geophysical and geochemical investigations (Ge et al., 2010; Liu et al., 2011). In June 2007,

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China Geological Survey organized a gas hydrate drilling campaign, GMGS1, in Shenhu Area in SCS, and obtained the natural gas hydrate samples for the first time in China (Zhang et al., 2007). From June to September in 2013, China's second major expedition, GMGS2, was carried out in the eastern part of the Pearl River Mouth basin, which locates at northeast of the Shenhu site (Fig. 1a). It is found that 9 of the 13 investigated sites contain gas hydrates by combining data from logging and core sampling (Fig. 1b). A variety of morphologies of gas hydrate, such as massive, laminated, nodular, vein and disseminated, were found in samples retrieved from GMGS2 drilling sites. The gas hydrate samples are characterized by shallow burying, large thickness, multiple types, high concentration (Zhang et al., 2014).

Laboratory analysis of gas hydrate samples can provide directly the information about the characteristics of hydrates and hydrate-bearing reservoirs (Kneafsey et al., 2011). Three crystallographic structures (i.e. structure I (sI), structure II (sII) and structure H (sH)), have been found for natural gas hydrate. The structures are dependent on the encaged gas components (Davidson et al., 1986; Uchida et al., 2002; Ripmeester et al., 2005). Occasionally, the naturally occurring gas hydrates contain complex gas components and therefore result in sH hydrate (Lu et al., 2007). It is suggested that the characteristics of host sediments, such as the grain-size distribution which determines pore size and permeability have a primary role in control of gas-hydrate morphology and saturation. There are mainly three types of gas-hydrate occurrences: (1) pore-filling gas hydrate in coarse-grained sediments (coarse silt and sand) with generally high saturation (>50% of pore volume), (2) pore-filling gas hydrate in fine-grained sediments with usually low saturation, and (3) grain-displacing gas hydrate which occurs as discreet veins or nodules in fine-grained sediments with variable saturations (Bahk et al., 2011; Boswell et al., 2012; Lee and Collett, 2009, 2012).

The field observation found that gas hydrates recovered from the PRM basin have various morphologies. The sample analyzed in our laboratory is a distinct grain-displacing gas hydrate, recovered from site GMGS2 08F, at 71.13 m depth from the seafloor (Fig. 2). In this paper, studies for characterizing gas hydrate from the PRM basin were carried out on this sample. We combined the results of grain size analysis of the hosting sediments, the crystallographic structure and gas composition of the gas hydrate for individual sample and provide a specification of the characteristics of the gas hydrate occurring in the PRM basin, SCS.

2. Experimental methods

The gas hydrate sample was preserved in liquid nitrogen when transported or prepared for measurement in our laboratory. The sample is a kind of grain-displacing gas hydrate with obvious small pieces of natural gas hydrate in silt clay (Fig. 2). The sub-samples were used for grain size and mineralogy analysis, Raman, X-ray Diffraction (XRD) and gas composition measurement.

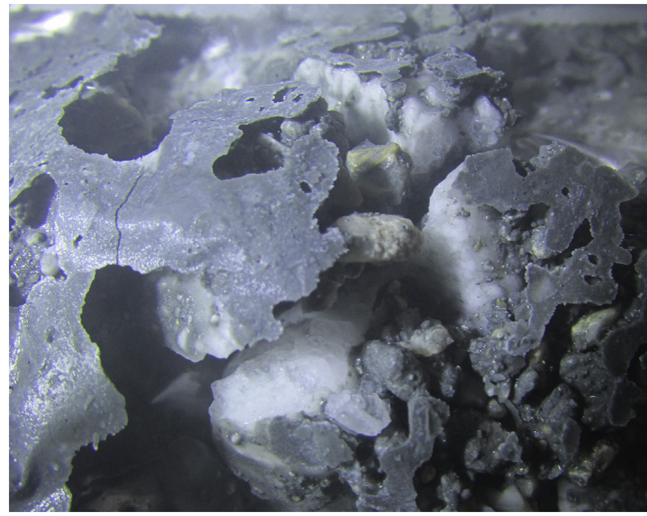

Figure 2. Gas hydrate Sample from PRM basin preserved in liquid nitrogen.

2.1. Grain size and mineralogy analysis

Grain-size of sediment was measured using a laser granularity analyzer (Malvern, model: MS2000). The Chinese national standard for grain size analysis (GB/T 19077.1-2008) was referred for the measurement. About 0.5 g sediment sample was dispersed in 1000 ml water with sodium hexametaphosphate (0.5 mol/L) as dispersant, the mixture was stirred for about 1 min and then measured for particle size distribution. The measurement of particle size range is from 0.02 μm to 2000 μm, with the Relative Standard Deviation (RSD) less than 1% and the reproducibility (median particle diameter, Φ50) less than 1% (Liu et al., 2012).

The air-dried powder sediment specimen was investigated for the mineral composition. The analysis was performed using X-ray diffraction (model: D/Max-2500) with a Cu radiation in conditions of 40 kV and 100 mA. The scanning angle was 3.0°−60° (2 theta) at a rate of 0.2 s/step (2 theta/s). For the XRD analysis, the computer software (TOPAS) based on Rietveld quantification method was used.

2.2. Raman and XRD measurement

Raman spectroscopic measurements were carried out using a confocal microscopic Raman spectrometer (Renishaw, model:

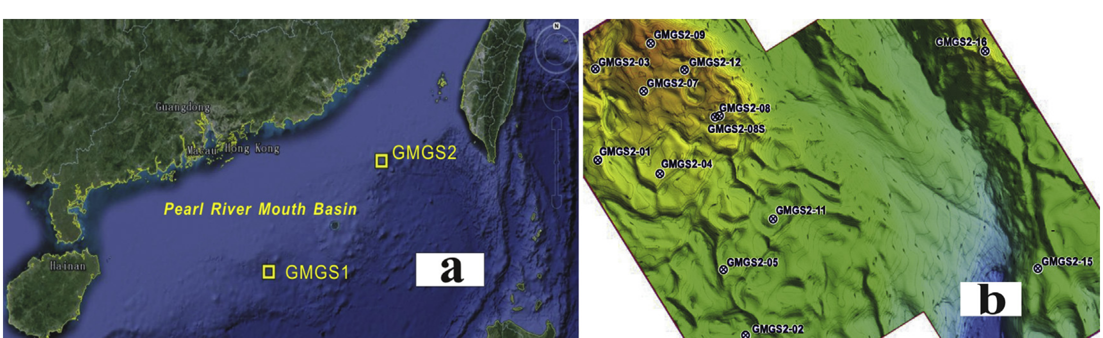

Figure 1. Map of PRM basin, SCS, showing: (a) locations of GMGS1 and GMGS2 expeditions and (b) the locations of GMGS2 drilling sites (modified from Zhang et al., 2014).