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Research paper

Contribution of thermogenic organic matter to the formation of biogenic gas hydrate: Evidence from geochemical and microbial characteristics of hydrate-containing sediments in the Taixinan Basin, South China Sea

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ABSTRACT

High-saturation (40–100%), microbial gas hydrates have been acquired by expedition GMGS2 from the Taixinan Basin. In this study, geochemical and microbial features of hydrate-containing sediments from the drilling cores (GMGS2-09 and GMGS2-16) were characterized to explore their relationships with gas hydrate formation. Results showed that the average TOC content of GMGS2-09 and GMGS2-16 were 0.45% and 0.63%, respectively. They could meet the threshold for *in situ* gas hydrate formation, but were not available for the formation of high-saturation gas hydrates. The dominant members of Bacteria at the class taxonomic level were Alphaproteobacteria, Bacilli, Bacteroidia, Epsilonproteobacteria and Gammaproteobacteria, and those in Archaea were Marine_Benthic_Group_B (MBGB), Miscellaneous_Crenarchaeotic_Group (MCG), Group C3, Methanomicrobia and Methanobacteria. Indicators of microbes associated with thermogenic organic matter were measured. These include: (1) most of the dominant microbes had been found dominant in other gas hydrates bearing sediments, mud volcanos as well as oil/coal deposits; (2) hydrogenotrophic methanogens and an oilfield-origin thermophilic, methylotrophic methanogen were found dominant the methanogen community; (3) hydrocarbon-assimilating bacteria and other hyperthermophiles were frequently detected. Therefore, thermogenic signatures were inferred existed in the sediments. This deduction is consistent with the interpretation from the seismic reflection profiles. Owing to the inconsistency between low TOC content and gas hydrates with high saturation, secondary microbial methane generated from the bioconversion of thermogenic organic matters (oil or coal) was speculated to serve as enhanced gas flux for the formation of high-saturation gas hydrates. A preliminary formation model of high-saturation biogenic gas hydrates was proposed, in which diagenesis processes, tectonic movements and microbial activities were all emphasized regarding to their contribution to gas hydrates formation. In short, this research helps explain how microbial act and what kind of organic matter they use in forming biogenic gas hydrates with high saturations.

1. Introduction

Gas hydrates are crystalline deposits consisting of water and gas molecules, which are typically found in circumpolar permafrost regions or in offshore marine sediments on continental margins (MacDonald et al., 1994; Reed et al., 2002; Sassen et al., 1999). Large amounts of carbon are stored in these deposits: the global

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inventory estimates range from 500 to 2500 Gt (Milkov, 2004) and 1600–2000 Gt (Archer et al., 2008) of carbon. Gas hydrates that have been sampled and/or inferred in all of the global oceans are most commonly formed from microbial methane (Collett et al., 2009). Three kinds of gas hydrate structures, namely, I, II, and H, have been recognized (Ripmeester et al., 1987). Gas hydrates that have been sampled and/or inferred in all of the global oceans are commonly expected to be structure I, which is considered of microbial origin according to the criteria of Bernard et al. (1976) (Bernard et al., 1976; Collett et al., 2009).

Previous studies suggest that biogenic methane occurred in gas hydrate was generated by methanogenesis from sedimentary organic carbon (Kvenvolden, 1993), and the threshold of the total organic carbon (TOC) for *in situ* gas hydrate formation had been estimated. For example, Waseda (1988) suggested that a minimum of 0.5 wt. % TOC is required to fuel methanogenesis sufficiently to produce methane in excess of saturation and precipitate gas hydrate; Klauda and Sandler (2005) proposed that the minimum TOC content for *in situ* gas hydrates forming is 0.4 wt. %. However, Wallmann et al. (2012) pointed that methanogenesis from *in situ* TOC content is not enough for generating gas hydrate saturations greater than 3%, and that an advective delivery of methane from depth is needed. Xu and Ruppel (1999) and Wang et al. (2011) also suggested that establishing a gas hydrate saturation up to ~ 45% by *in situ* microbial methane alone is difficult, and an enhanced gas flux is needed. Therefore, there is still no unanimous consensus yet on how and what kind of organic matters get involved in forming high saturation biogenic gas hydrates.

To date, investigations of the microbial communities in gas hydrate-bearing sediments have been conducted in many places. These include the Gulf of Mexico (Mills et al., 2003; Yan et al., 2006), the Hydrate Ridge (Boetius and Suess, 2004), the Cascadian Margin (Bidle et al., 1999; Lanoil et al., 2005; Marchesi et al., 2001), the Nankai Trough (Arakawa et al., 2006; Colwell et al., 2004; Nunoura et al., 2012; Reed et al., 2002), the Ulleung Basin (Briggs et al., 2013; Lee et al., 2013), the Pacific Ocean Margin (Inagaki et al., 2006), the Andaman Sea (Briggs et al., 2012), the South China Sea (SCS) (Jiao et al., 2015; Zhang et al., 2012). These studies mainly focused on the distribution of extremophiles in deep-sea methane containing environment, or the anaerobic oxidation of methane process which is ubiquitous in methane-rich environment. Although, through comparison studies, researchers have summarized that the dominance of JS1 and MBGB phyla were significant correlated with the existence of gas hydrates (Parkes et al., 2014), their specific roles in the biogeochemistry process for gas hydrate formation were rarely discussed.

Taixinan basin is located in the northeastern continental slope of SCS (Fig. 1). Geochemical anomalies, bottom simulating reflectors (BSRs) and seismic blanking zones suggested the existence of gas hydrates in this area (McDonnell et al., 2000; Shyu et al., 2006; Song, 2000; Wu et al., 2003, 2005). From June to September in 2013, gas hydrate drilling expedition GMGS2 was carried out in the Taixinan basin, performed by China Geological Survey (CGS) and Guangzhou Marine Geological Survey (GMGS) in cooperation with Fugro N.V. (Netherlands) and GEOTEK (UK) by using the geotechnical drillship M/V REM Etive (Zhang et al., 2014). Structure I gas hydrates with high saturations (40–100%) were obtained during this drilling project (Zhang et al., 2014), though a large number of geophysical data have shown that deep source fluids are related to gas formation (Gong et al., 2008; Li et al., 1999; Zhang et al., 2015; Hui et al., 2016). In the current research, we studied the bulk elemental geochemistry and microbial communities in two hydrate-containing drilling cores (GMGS2-09 and GMGS2-16). The relationship between bulk elemental geochemistry and gas hydrate formation, and the physiological characters of the frequently detected microbial members were discussed. On this basis, we suggest a possible pathway for how microbial acts in the formation of biogenic gas hydrates with high saturation.

2. Sampling and methods

2.1. Sample description and collection

The study area is located in the Taixinan Basin in the northern South China Sea. Here, BSRs, slumps, active faults and diapirs have been widely identified (He and Liu, 2008) (Fig. 1). The drilling area of GMGS2 is near to the deformation front of SW Taiwan, which is a major structural trap that may host a significant amount of gas (Lin et al., 2009). Thirteen sites were drilled during this expedition, including 10 logging-while-drilling (LWD) and 3 downhole wireline logging (DWL) pilot holes (Zhang et al., 2015). Gas hydrates were identified from the LWD and DWL data in 9 cores. Of them, 5 sites were cored for further analysis, including sites GMGS2-05, GMGS-2-07, GMGS2-08, GMGS2-09 and GMGS2-16. The gas hydrates samples recovered were characterized by shallow burying, large thickness, multiple types and high saturations (Zhang et al., 2014).

The sediment samples in this study were recovered from sites GMGS2-09 and GMGS2-16, with the drilling depth of them being 110 m and 235 m, respectively. In core GMGS2-09, carbonate-cemented chemosynthetic bivalve shells of a few centimeters developed at the near surface layers and nodular hydrates (Fig. 2A) were identified at 9–21 m below seafloor (mbsf). Two hydrate-bearing horizons were identified in core GMGS2-16. In the shallow part (15–30 mbsf), a roughly 15 m thick gas hydrates, widely laterally distributed in the form of nodules; while in the deep part (189–226 mbsf), gas hydrates occurred in disseminated type (Fig. 2B) in the silty clay sediments (Zhang et al., 2015). Overall, the dominant lithology of the sediment from the two cores is silty clay, and sand intervals were only identified in the near surface part of core GMGS2-09. The core-derived lithology associated with gas hydrate occurrence is silty clay with some nodular carbonates or fine carbonates partially dispersed (Supp. Fig. 1).

Sediment subsamples were collected from each sediment core. Three samples (09_2, 09_5, 09_16) retrieved respectively from the depth of 3.33 mbsf, 26.48 mbsf and 104.51 mbsf from core GMGS2-09 and four samples from GMGS2-16 (16_1, 16_13, 16_15 and 16_39) retrieved respectively from the depth of 0.15 mbsf, 18.15 mbsf, 24.65 mbsf and 192.35 mbsf were chosen for microbial analyses (the corresponding sampling depth of each sample were marked on Fig. 3 by dash line). These samples generally represent layers of near surface, gas hydrate-containing section and near bottom. Upon retrieving, samples were carefully peeled and the inner part of each sample was frozen at −20 °C until analyses.

2.2. Elemental carbon, nitrogen and sulfur (CNS) bulk content analysis

Total carbon (TC), total nitrogen (TN) and total sulfur (TS) in sediments were determined by combustion of squeezed sediment samples and gas-chromatographic detection of CO_2, N_2 and SO_2 produced during combustion using Carlo-Erba 1500 CNS element analyzer. To determine the contents of total organic carbon (TOC), additional samples (~200 mg) were acidified with 1M HCl (~10 mL) to remove carbonate minerals. The carbonate-free residue was washed thoroughly with deionized distilled water and dried before analyses. The analytical error was <0.2 wt% for TC and TOC, <0.02 wt% for TN, and <0.1 wt% for TS, using $C_6H_7NO_3S$ as standard. In the duplicate analysis, TC, TS and TOC had a reproducibility error of <0.5 wt%, whereas TN had a reproducibility error of <0.05 wt%.