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Carbon Geochemistry of Gas Hydrate-associated Sediments in the Southwestern Taiwan Basin

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Abstract: Marine gas hydrates, one of the largest methane reservoirs on Earth, may greatly affect the deep sea sedimentary environment and biogeochemistry; however, the carbon geochemistry in gas hydrate-bearing sediments is poorly understood. In this study, we investigated the carbon variables in sediment core 973-3 from the southwestern Taiwan Basin in the South China Sea to understand the effect of environmental factors and archaeal communities on carbon geochemistry. The carbon profiles suggest the methanogenesis with the incerase of dissolved inorganic carbon (DIC) and high total organic carbon (TOC) (mean = 0.46%) originated from terrigenous organic matter (mean $\delta^{13}C_{TOC}$ value of −23.6‰) driven by the abundant methanogen '*Methanosaeta* and *Methanomicrobiales*'. The active anaerobic oxidation of methane is characterized by the increase of DIC and inorganic carbon (IC), and the depleted $\delta^{13}C_{IC}$, coupled with the increase of TOC and the decrease of $\delta^{13}C_{TOC}$ values owing to the methanotroph '*Methanosarcinales/*ANME' in 430–840 cm. Environmental factors and archaeal communities in core 973-3 are significantly correlated to carbon variables owing to methane production and oxidation. Our results indicate that the carbon geochemical characteristics are obviously responding to the formation and decomposition of gas hydrates. Furthermore, pH, Eh and grain size, and *Methanosaeta* greatly affect the carbon geochemistry in gas hydrate-associated sediments.

Key words: southwestern Taiwan Basin, carbon geochemistry, environmental conditions, archaea, gas hydrate

1 Introduction

Marine gas hydrates are potential huge methane reservoirs (Milkov, 2004). Methanogenesis and anaerobic oxidation of methane (AOM) mediated by microorganisms affect the formation and decomposition of gas hydrates (Boetius et al., 2000). Therefore, many studies have focused on the microbial diversity in hydrate-related sediments (Bidle et al., 1999; Niemann et al., 2006; Lösekann et al., 2007). Lee et al. (2013) suggested the dominance of marine benthic group-B (MBG-B) in archaeal communities and JS1 in bacterial communities in hydrate-bearing sediments of the Ulleung Basin, East Sea of Korea. Furthermore, Yanagawa et al. (2014) proposed that microbial communities in marine sediments associated with gas hydrate were distinct from that in continental margin sediments in the eastern Japan Sea. Lin et al. (2014) suggested that in South China Sea (SCS), major microbial groups in core MD-178-3280, such as *Chloroflexi*, *Planctomycetes*, MBG-B and ANME-1, were involved in the cycling of methane and organic carbon. Subsequently, Jiao et al. (2015) reported the dominance of *δ-Proteobacteria* and miscellaneous crenarchaeotic group (MCG) in gas hydrate-containing sediments from the Shenhu area of SCS; whereas *Planctomycetes* and MBG-D were predominant in hydrate-free sediments. Microbial community structures vary greatly in different gas hydrate-related sediments. Hence, it is essential to study the microbial niche, environmental conditions (Kruger et al., 2005; Nauhaus et al., 2005) and carbon geochemical characteristics (Lin et al., 2014; Yanagawa et al., 2014; Jiao et al., 2015) affecting the microbial diversity.

Most gas hydrates are formed from microbial methane generated by the microbial degradation of organic carbon

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(Claypool and Kvenvolden, 1983). Kvenvolden (1985) suggested that gas hydrate-bearing sediments on the Atlantic passive margin and Pacific active accretionary margin contained >0.5 wt.% of total organic carbon (TOC). Based on the pore-water and box model data, Hong et al. (2013) identified 25%–35% of dissolved inorganic carbon (DIC) produced by AOM was consumed by CO_2 reduction; furthermore, the fraction of sulfate consumed by AOM ranged from 70 to 90%, and thus, the estimation of methane flux solely based on sulfate data may be in error by as much as 30%. By monitoring the stable isotopic composition of methane and DIC pools over time during incubation experiments, Yoshinaga et al. (2014) found that residual methane became progressively enriched in ^{13}C at sulfate concentrations above 0.5 mM and progressively depleted in ^{13}C below the threshold during AOM. They attributed this to microbially mediated carbon isotope equilibration between methane and carbon dioxide. Hiruta et al. (2015) suggested that the concentration of $\delta^{13}C_{DIC}$ at the sulfate–methane transition zone (SMTZ) correlated with methane $\delta^{13}C$; however, the rapid SO_4^{2-} consumption did not reduce $\delta^{13}C_{DIC}$. Collectively, the response of carbon geochemical characteristics to the accumulation of gas hydrates is a topic of debate.

The southwestern Taiwan Basin is the best gas hydrate prospect area of SCS (Lu Hongfeng et al., 2005; Su Ming et al., 2014; Fu Piaoer et al., 2016; Jia et al., 2016; Hao et al., 2017). Lin (2011) estimated approximately 2.7 × 10^{12} m^3 marine gas hydrate reserves in this basin, accounting for 84% of SCS (Wang et al., 2006). In the last ten years, several studies have covered the genesis of gas hydrates, the carbon isotopic composition of authigenic carbonates (Lu Hongfeng et al., 2005), the interface between sulfate and methane in the subsurface (Zhang Jie et al., 2014) and the coexistence of the elemental sulfur (ES) and authigenic pyrites (Lin et al., 2015). Besides, Lin et al. (2014) and Yang et al. (2015) suggested that the distribution of microbial communities was closely related to the evolution of gas hydrates in the southwestern Taiwan Basin. In this study, we analyzed the geochemical characteristics of carbon and environmental conditions in sediments of core 973-3 from the southwestern Taiwan Basin. Moreover, we displayed the relations among environmental factors, archaeal communities and carbon geochemistry.

2 Materials and Methods

2.1 Regional settings and sample collection

The geological settings of the southwestern Taiwan Basin in SCS are favorable for a widespread distribution of gas hydrates as described by Lin et al. (2014) and Su et al. (2017). The sediment core was recovered at the site of 973-3 (22°00.8421′N, 118°47.4159′E, 1026m below sea level) from the potential gas hydrate-bearing area during the leg HY6-2011-1 in 2011 (Fig. 1). The core location is adjacent to the Jiulong methane reef, which is an area of methane seepage (Han et al., 2008). Core 973-3 was cut into 25 cm-long sections immediately after the retrieval. Sediment samples for geochemical analysis were refrigerated at 4° C to prevent organic material decomposition. Subsamples for the microbiological study were taken in sterile centrifuge tubes and stored at −20 °C for on-shore laboratory analysis. Pore water was extracted using the procedure described by Lin et al. (2014).

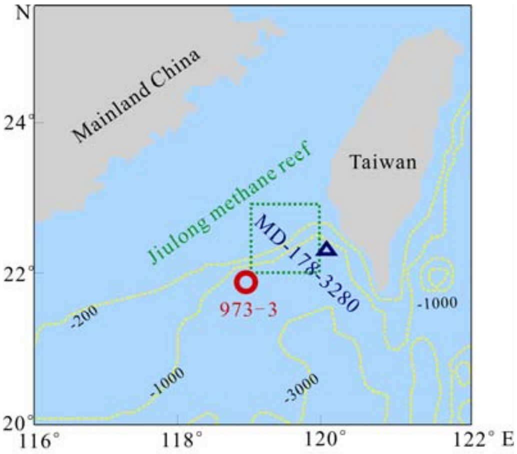

Fig. 1. Regional map showing the study area in the southwestern Taiwan Basin.
The red circle denotes the location of core 973-3. The purple box marks the Jiulong methane reef (Han et al., 2008). The blue triangle shows the location of core MD-178-3280 investigated by Lin et al. (2014).

2.2 Geochemical analysis of carbon

Sediments for geochemical analysis were freeze-dried and ground. Prior to TOC analysis, inorganic carbon (IC) was removed with 1 N HCl. Total carbon (TC) and TOC and their isotopic compositions ($\delta^{13}C_{TC}$ and $\delta^{13}C_{TOC}$) were determined using a Carlo Erba NC 2500 elemental analyzer interfaced with a Thermo Finnegan Delta^{plus} XP isotope ratio mass spectrometer (EA-IRMS), as described by Selvaraj et al. (2015). IC was calculated from the difference between wt.% TC and TOC (IC = TC − TOC). Furthermore, we measured the carbon isotopic composition of inorganic carbon ($\delta^{13}C_{IC}$) using IRMS, detailed in Pohlman et al. (2013).

The isotopic ratios ($^{13}C/^{12}C$) are expressed in the δ-notation relative to the VPDB standard. DIC was determined using a dissolved inorganic carbon analyzer (AS-C3, Apollo Scitech). The uncertainty associated with TC, TOC and DIC was ±5%, whereas the uncertainty for $\delta^{13}C$ was ±0.5‰.

2.3 Environmental factors analysis

Pore-water pH and Eh were measured using a water quality analyzer (Multi 3430, WTW), and the salinity was analyzed using a master refractometer. Sediment grain size was determined using a Mastersizer Hydro 2000M/MU (Malvern) after removing carbonates and organic matter (OM) with 1 N HCl and 30% H_2O_2, respectively (Chen and Selvaraj, 2008).

For the bivariate correlation analyses of the archaeal communities (Yang Yufeng et al., 2016), environmental factors and carbon geochemistry, we used the IBM SPSS Statistics 22 software package.

3 Results

3.1 Carbon variation

In core 973-3, TC is dominated by IC. The most prominent aspect of the down-core variation is the broad increase and decrease of IC in the entire core (Fig. 2a). IC is high and variable (mean = 1.97%) from 500 to 850 cm, moderate from 40 to 430 cm (mean = 1.94%) and low and less variable below 900 cm (mean = 1.07%). TOC ranges from 0.36% to 0.71% (mean = 0.46%). The mean DIC increases with depth, e.g. 8.55 mM in 0–430 cm, 15.68 mM in 550–840 cm and 17.79 mM in 900–1200 cm (Fig. 2b). The $\delta^{13}C_{TOC}$ values generally fall between −24.8‰ and −22.1‰ VPDB (mean = −23.6‰) and reach a minimum at 630 cm (Fig. 2c). The $\delta^{13}C_{IC}$ values range between −2.3‰ and −1.0‰ VPDB in the entire core 973-3, with $\delta^{13}C_{IC}$ decreasing at 210 cm and below 800 cm (Fig. 2c).

3.2 Environmental factors

Figure 3 shows the variations of pH, Eh, salinity and grain size with depth in core 973-3. The pH in pore water increases with depth, ranging from 8.40 to 9.18 (Fig. 3). In contrast, Eh values in pore water are high (−103.20 to −80.00 mV) above 500 cm, but low (−126.00 to −113.30 mV) below 500 cm. Salinity in pore water ranges from 19.04‰ to 46.27‰, with a sharp increase between 550 and 840 cm. The grain size of the sediments in core 973-3 varies from 6.64 to 10.64 μm, suggesting mostly fine silty sediments.

3.3 Correlation analysis

The Pearson's correlation coefficients of environmental factors, archaeal communities (Fig. 4; Yang Yufeng et al., 2016) and geochemical parameters of carbon are listed in Table 1. The pH correlates positively with DIC ($r = 0.56$, $P < 0.05$) and negatively with $\delta^{13}C_{IC}$ ($r = -0.57$, $P < 0.05$). In contrast, Eh correlates negatively with DIC ($r = -0.57$, $P < 0.05$) and positively with $\delta^{13}C_{IC}$ ($r = 0.56$, $P < 0.05$). Grain size is positively correlated with TC, IC and $\delta^{13}C_{IC}$ ($P < 0.05$). *Methanosaeta* is positively correlated with $\delta^{13}C_{IC}$ ($r = 0.79$, $P < 0.01$). Other archaea are negatively correlated with $\delta^{13}C_{IC}$ ($r = -0.69$, $P < 0.05$).

4. Discussion

4.1 Carbon geochemical characteristics and gas hydrates

The formation of gas hydrates primarily depends on the accumulation of particulate organic carbon on the seafloor (Kvenvolden, 1985; Wallmann et al., 2012). The mean TOC of core 973-3 is 0.46 wt.%, which is above the threshold TOC of 0.4% −0.5% for significant methanogenesis in situ and gas hydrate formation (Waseda, 1998; Klauda and Sandler, 2005). Based on the $\delta^{13}C$ of −22‰ to −20‰ for marine OM and −27‰ for

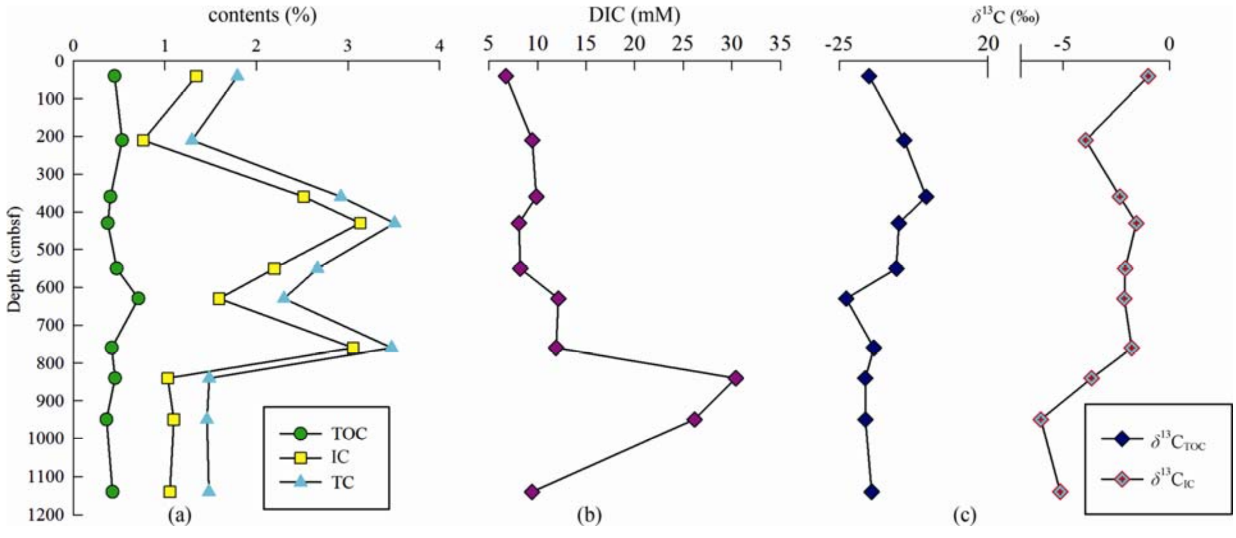

Fig. 2. Carbon parameters vs depth in core 973-3.
(a), TC, TOC and IC; (b), DIC; (c), $\delta^{13}C_{TOC}$ and $\delta^{13}C_{IC}$

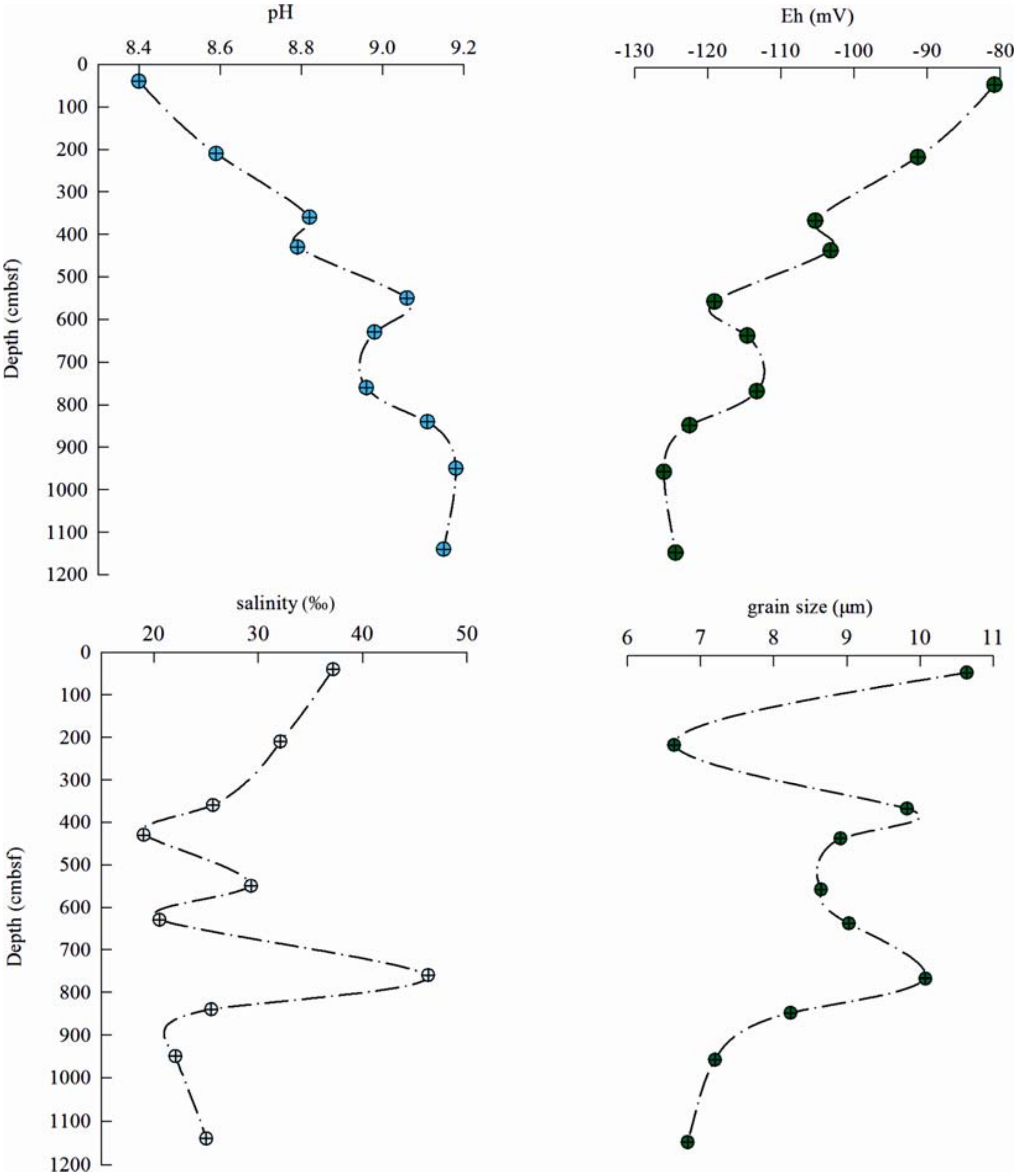

Fig. 3. pH, Eh, salinity and grain size vs depth in core 973-3

terrigenous OM (Meyers, 1997; Mckay et al., 2004; Kaneko et al., 2010), the mean $\delta^{13}C_{TOC}$ of −23.6 ± 0.8‰, which is consistent with the mean $\delta^{13}C_{TOC}$ of −24.9 ± 0.9‰ (Kao et al., 2014) of particulate organic carbon in suspended sediments from major rivers in Taiwan, suggests that the OM in core 973-3 is mostly derived from terrigenous sources, such as episodic, huge riverine sediment transport from the high mountains in Taiwan (Selvaraj et al., 2015). Although the terrestrial OM in core 973-3 is potentially less liable to decomposition (Kastner, 2001), the high sedimentation rates greatly reduce the amount of time that TOC spends in the sulfate reduction zone and thus enhance the delivery of labile TOC to the methanogenic zone (Chen Fang et al., 2014; Solomon et al., 2014). Therefore, the abundant methanogen communities in core 973-3 (Fig. 4; Yang Yufeng et al., 2016) could utilize the products of OM fermentation and decomposition to produce sufficient methane up to 6.2 mmol/L below 800 cm (Zhang Bidong et al., 2015).

Based on the high pyrite content of up to 17% and most depleted $\delta^{13}C$ of −2.03‰ in foraminifera, Chen et al. (2014) suggested that AOM was active at 550−820 cm depth in core 973-3. Lin et al. (2015) also came to the same conclusion based on ES in SMTZ as the obvious evidence of AOM owing to cold seep activities. Consistent with these interpretations, the $\delta^{13}C_{IC}$ of −6.1‰ to −1.0‰ in core 973-3 are substantially more $\delta^{13}C$-depleted than the regional range for biogenic carbonate (−1‰ to −0.4‰) (Zhang Bidong et al., 2015), indicating the high authigenic carbonate content attributed to AOM. The gradually

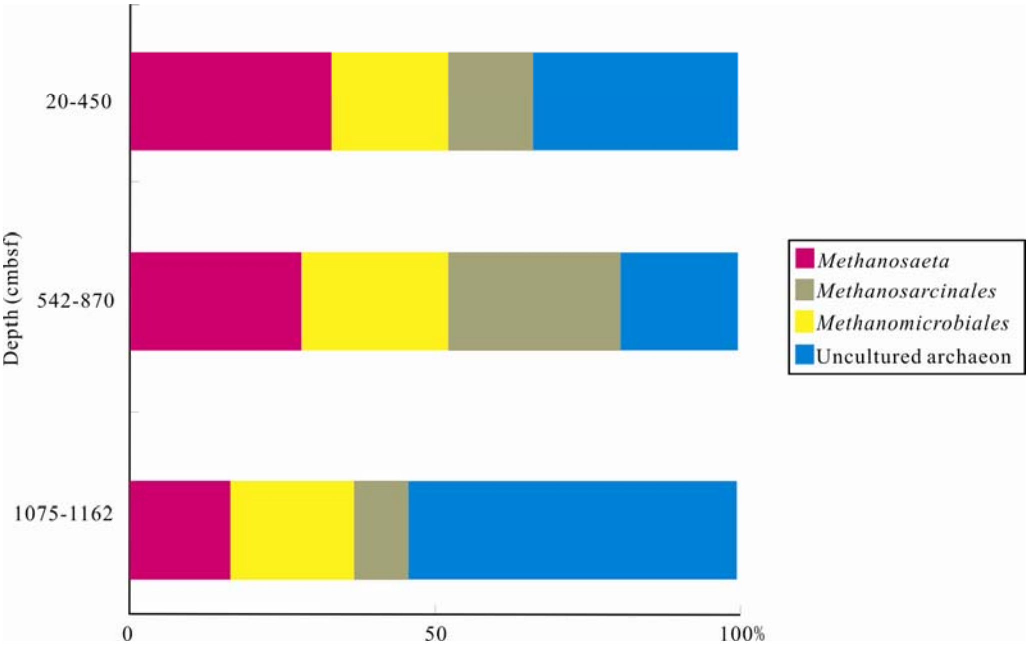

Fig. 4. Archaeal community structure in core 973-3 (modified from Yang Yufeng et al., 2016).
Yang et al. (2016) investigated the archaeal diversity in 20, 243, 455, 542, 630, 870, 1075 and 1162 cm of core 973-3, using the Power Soil DNA Isolation Kit for DNA extraction, and 355F/1068R as the primer for PCR amplification.

increasing TOC from 0.37% to 0.71% in 430–630 cm, coupled with the depletion in $\delta^{13}C_{TOC}$ values in this interval (Fig. 2a and 2c), is consistent with the TOC and $\delta^{13}C_{TOC}$ variations in Hyrate Ridge (Valentine et al., 2005) and Dongsha area of SCS (Yu Xiaoguo et al., 2013). This suggests the active methane oxidation driven by the upward diffusion of deep methane and is consistent with the predominance of *Methanosarcinales/*ANME in 542–870 cm (Fig. 4). Moreover, there is a significant negative correlation between DIC and $\delta^{13}C_{IC}$ values (Table 1; $P< 0.05$) (Figures 2b and 2c). Even though the classic mechanism for generating the observed DIC and $\delta^{13}C_{IC}$ values in methane-rich marine sediments is the oxidation of ^{13}C-depleted methane by AOM (Malinverno and Pohlman, 2011; Pohlman et al., 2013), TC and IC are positively correlated with $\delta^{13}C_{IC}$ (Table 1; $P< 0.05$). This suggests that microbial communities mediate methanogenesis by CO_2 reduction and internal carbon cycling in SMTZ in the study site (Hong et al., 2013; Yoshinaga et al., 2014). IC is positively correlated with TC (Table 1; $P< 0.01$), which is consistent with the study of Johnson et al. (2014) in the Kerala-Konkan Basin, suggesting IC affects TC but not TOC.

4.2 The effect of environmental factors

Environmental traits are important for methane production and oxidation (Wang et al., 1993; Chmura et al., 2011; Ramírez-Pérez et al., 2015; Wilson et al., 2015). The significant correlations among pH, DIC and $\delta^{13}C_{IC}$ suggest that DIC comprising mass HCO_3^- may increase the pH, whereas $\delta^{13}C_{IC}$ decreases owing to the hydrolysis and fermentation of OM (Froelich et al., 1979), together with microbial methane oxidation (Boetius et al., 2000). This agrees with the positive correlation between DIC and

Alk in sediments (Solomon et al., 2014). However, the details are complicated owing to the various DIC sources (Hong et al., 2013; Hiruta et al., 2015). Eh values suggest the anoxic and anerobic conditions, and the effect of Eh on DIC and $\delta^{13}C_{IC}$ is opposite to that of pH (Table 1).

The sharp increase of salinity from 19.04‰ at 430 cm to 46.27‰ at 760 cm in core 973-3 agrees with the salinity anomalies at Sites 1249 and 1250 of Hydrate Ridge (Torres et al., 2004) and Qiongdongnan Basin of SCS (Yang Tao et al., 2013), suggesting the brine intrusion during gas hydrate formation. There is no correlation between salinity and carbon parameters in the present study (Table 1). This is consistent with the study of Jiao et al. (2015) of hydrate-bearing sediments in the Shenhu area of SCS that found no correlation between salinity and the carbon metabolism of microbial communities in methane-rich sediments (Wilson et al., 2015).

In contrast to pH and Eh, there is a positive correlation between grain size and IC (Table 1). Furthermore, the profile of grain size is similar to that of IC (Figures 2a and 3). These results are consistent with the study of Chen et al. (2015) in the Shenhu area of SCS. Thus, we infer that the silty sediments contribute to the formation of IC. The best explanation for it is that the IC fractions comprise abundant authigenic carbonates (from 8 to 10 μm) owning to AOM (Chen Fang et al., 2014; Chen et al., 2015). Furthermore, the correlation coefficient of grain size and $\delta^{13}C_{IC}$ ($r = 0.86$) is much larger than that of grain size and IC ($r = 0.62$) in Table 1, with a positive correlation between IC and $^{13}C_{IC}$. This suggests the coarser sediments contain ^{13}C-enriched carbonate (Valentine, 2001).

4.3 The effect of archaeal communities

The distribution of archaeal communities in core 973-3 is closely related to methanogenesis and methane oxidation (Fig. 4), suggesting the presence of gas hydrates in marine sediments (Yang Yufeng et al., 2016). *Methanosaeta* (32.9%) dominates the shallow part of core 973-3 (20−450 cm), and *Methanosarcinales* (28.3%) is dominant in the middle part (542−870 cm) and *Methanomicrobiales* is abundant (20.7%) in 1075–1162 cm (Fig. 4). The archaeal community structure in core 973-3 is obviously distinct from those in gas hydrate-bearing and hydrate-free sediments from the Japan Sea (Yanagawa et al., 2014) or Shenhu area of SCS (Jiao et al., 2015). Lin et al. (2014) suggested that the metabolic capabilities of microbial communities in core MD-178-3280 (Fig. 1) were directly related with the methane cycle. Hence, we analyzed the correlation between archaeal communities and carbon geochemical characteristics.

The distribution of archaeal communities in core 973-3 obviously affects the carbon geochemistry. DIC, IC and $\delta^{13}C_{TOC}$ increase from the sediment surface to 430cm, whereas TOC and $\delta^{13}C_{IC}$ decrease (Fig. 2), and *Methanosaeta* dominates in 20–450 cm (Fig. 4). This suggests OM decomposition, because *Methanosaeta* uses acetate to form methane (Purdy et al., 2003; Banning et al., 2005). Furthermore, the significant correlation between *Methanosaeta* and $\delta^{13}C_{IC}$ ($P < 0.01$; Table 1) suggests that *Methanosaeta* may affect the IC transform.

The levels of DIC in 550–840 cm are much higher, more than twice the DIC concentrations above 500 cm (Fig. 2), whereas *Methanosarcinales*/ANME is predominant in 542–870 cm (Fig. 4). This suggests methane oxidation driven by *Methanosarcinales*/ANME for energy acquisition (Hinrichs et al., 1999; Knittel et al., 2005), which is consistent with the IC increase and $\delta^{13}C_{IC}$ depletion in sediments (Fig. 2). *Methanomicrobiales* uses energy from $CO_2 + H_2$ for methane formation (Dojka et al., 1998; Falz et al., 1999; Purdy et al., 2002). Hence, *Methanomicrobiales* and DIC from OM fermentation are high in 1075–1162 cm (Fig. 4).

Methanomicrobiales and *Methanosarcinales* have no effect on carbon geochemical characteristics (Table 1). This might result from the mismatching of archaeal communities and substrate availability (CO_2 and CH_4) and gene abundance. Although we analyze the DIC concentrations, it is impossible to distinguish the fractions of CO_2 derived from OM mineralization and the DIC produced by CH_4 oxidation (Hong et al., 2013). Therefore, it is necessary to investigate gene abundance because of the additional constraints on the distribution of specific archaeal lineages related to the cycling of organic degradation and methane (Lin et al., 2014).

Interestingly, other archaea are significantly correlated negatively with $\delta^{13}C_{IC}$ ($P < 0.05$; Table 1). However, the physiological characteristics of other archaea are unknown. Hence, the known methanogens and methanotrophs may be a small fraction of the microbial community found in hydrate-bearing conditions (Biddle et al., 2008; Valentine, 2011).

5 Conclusions

Carbon geochemical characteristics in pore water and sediments from core 973-3 suggest gas hydrate formation and decomposition process.

(1) The methanogenesis is characterized by high DIC and TOC originated from terrigenous OM driven by the methanogens.

(2) The carbon geochemical characteristics suggest AOM with increasing DIC and IC and depleted $\delta^{13}C_{IC}$ driven by the methanotrophs in 430–840 cm.

(3) Environmental factors, such as pH, Eh and grain

size, and *Methanosaeta* greatly affect the carbon geochemistry of gas hydrate-associated sediments.

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