

Dissolved Inorganic Carbon (DIC) and Its Carbon Isotopic Composition in Sediment Pore Waters from the Shenhu Area, Northern South China Sea

TAO YANG^{1,2}, SHAO-YONG JIANG^{1,2*}, JING-HONG YANG^{1,2}, GE LU^{1,2}, NENG-YOU WU³,
JIAN LIU³ and DAO-HUA CHEN³

¹State Key Laboratory for Mineral Deposits Research, Department of Earth Sciences,
Nanjing University, Nanjing 210093, China

²Center for Marine Geochemistry Research, Nanjing University, Nanjing 210093, China

³Guangzhou Marine Geological Survey, China Geological Survey, Guangzhou 510760, China

(Received 27 April 2007; in revised form 16 September 2007; accepted 20 October 2007)

The Shenhu area is one of the most favorable places for the occurrence of gas hydrates in the northern continental slope of the South China Sea. Pore water samples were collected in two piston cores (SH-A and SH-B) from this area, and the concentrations of sulfate and dissolved inorganic carbon (DIC) and its carbon isotopic composition were measured. The data revealed large DIC variations and very negative $\delta^{13}\text{C}$ -DIC values. Two reaction zones, 0–3 mbsf and below 3 mbsf, are identified in the sediment system. At site SH-A, the upper zone (0–3 mbsf) shows relatively constant sulfate and DIC concentrations and $\delta^{13}\text{C}$ -DIC values, possibly due to bioturbation and fluid advection. The lower zone (below 3 mbsf) displays good linear gradients for sulfate and DIC concentrations, and $\delta^{13}\text{C}$ -DIC values. At site SH-B, both zones show linear gradients, but the decreasing gradients for $\delta^{13}\text{C}$ -DIC and SO_4^{2-} in the lower zone below 3 mbsf are greater than those from the upper zone, 0–3 mbsf. The calculated sulfate-methane interface (SMI) depths of the two cores are 10.0 m and 11.1 m, respectively. The depth profiles of both DIC and $\delta^{13}\text{C}$ -DIC showed similar characteristics as those in other gas hydrate locations in the world oceans, such as the Blake Ridge. Overall, our results indicate an anaerobic methane oxidation (AMO) process in the sediments with large methane flux from depth in the studied area, which might be linked to the formation of gas hydrates in this area.

Keywords:

- Dissolved inorganic carbon (DIC),
- $\delta^{13}\text{C}$ -DIC,
- sulfate gradient,
- gas hydrate,
- South China Sea.

1. Introduction

Gas hydrate is a potential new energy source and has shown potential economic and environmental significance (Milkov and Sassen, 2002; Lu *et al.*, 2007; Tomaru *et al.*, 2007), and is increasingly attracting worldwide attention. At the time of writing, gas hydrates have been found or inferred in more than 60 locations in the world oceans. An approximate estimate of the resources points to $10^{15}\sim 10^{18}$ m³ methane (Miller *et al.*, 1991; Kvenvolden, 1993; Borowski, 2006). Gas hydrates commonly occur in sandy marine sediments as massive, nodular, disseminated forms filling sediment pores (Trehu *et al.*, 2004; Uchida *et al.*, 2004). Gas hydrates are generally identified by bottom simulating reflectors (BSR), indicating the

lower boundary between gas hydrate and free gas layers. In gas hydrate fields, a large amount of methane may be released into the overlying sediment and water column and thus affect the shallow carbon cycle (Tomaru *et al.*, 2007).

DIC is the major inorganic carbon form in most natural waters and is comprised of three principal species, i.e., H_2CO_3 , HCO_3^- and CO_3^{2-} , their relative abundance being mainly a function of pH. DIC is related to many biogeochemical processes, such as biogenic CO_2 uptake (e.g. photosynthesis) and release (e.g. respiration), methanic fermentation, methane oxidation, exchange with atmospheric CO_2 (degassing or dissolution), carbonate precipitation or dissolution, and CO_2 generated by metamorphic reactions or magmatic degassing (Assayag *et al.*, 2006). In recent years, DIC concentrations and $\delta^{13}\text{C}$ -DIC in pore waters of marine sediments have been employed to study marine gas hydrates. It is suggested that very

* Corresponding author. E-mail: shyjiang@nju.edu.cn

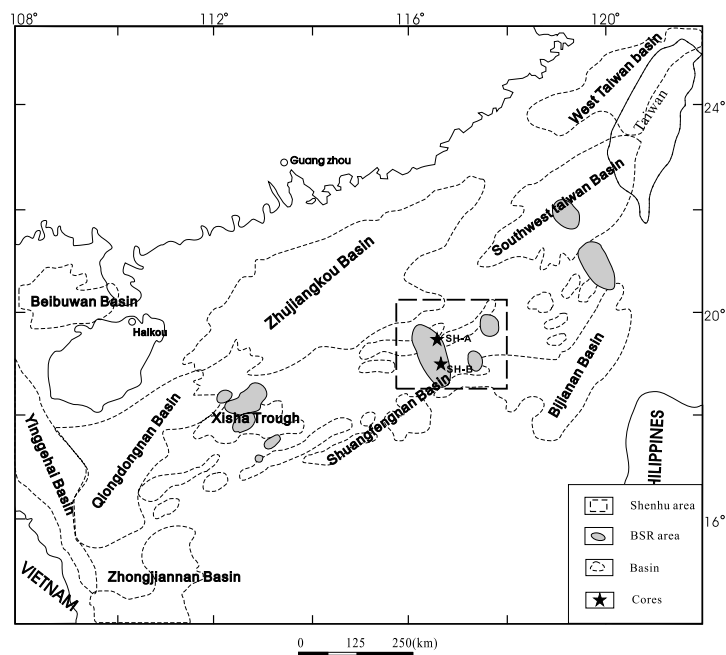


Fig. 1. Location of the studied area in the South China Sea.

low $\delta^{13}\text{C}$ -DIC and high DIC concentrations in sediment pore waters may have an intrinsic link to gas hydrate formation, such as those revealed at ODP cores from many gas hydrate locations, including the Hydrate Ridge (Suess *et al.*, 1999; Torres *et al.*, 2002; Gieskes *et al.*, 2005) and the Blake Ridge (Borowski *et al.*, 1997, 2000). Therefore, DIC can be used as a geochemical tracer during exploration for gas hydrate.

China has an oceanic area of $300 \times 10^4 \text{ km}^2$ with a large number of sedimentary basins (Fig. 1). The northern continental margin of the South China Sea has geologic and tectonic settings, suitable temperature and pressure conditions, and thick, organic-rich sediments, all of which favor the formation of gas hydrates (McDonnell *et al.*, 2000; Chen *et al.*, 2001; Wu *et al.*, 2006a; Yang *et al.*, 2006a). In recent years we have conducted exploration for gas hydrates in the South China Sea and observed bottom-simulating reflectors (BSR) on seismic-reflection profiles in many parts of that region (Fig. 1). In this paper we present sulfate and DIC concentrations and $\delta^{13}\text{C}$ -DIC for the sediment pore waters from the Shenhu area and discuss their implications for carbon cycling and gas hydrate occurrence.

2. Geological Setting

The northern continental margin of the South China Sea has a high sedimentation rate and has deposited thick sediments of 1000–7000 m with an organic matter content of 0.46–1.9% (McDonnell *et al.*, 2000; Wang *et al.*, 2000; Wu *et al.*, 2003). This region has already become a

large source of oil and natural gas. Geological, geophysical, and geochemical investigations have suggested that the northern margin of the South China Sea is a favorable place for the formation of gas hydrates (Shyu *et al.*, 1998; McDonnell *et al.*, 2000; Chen *et al.*, 2001, 2004; Jin and Wang, 2002; Jiang *et al.*, 2004, 2006). Our study area is located in the Shenhu area in the northern margin of the South China Sea, adjacent to several large oil and gas fields, such as Zhujiangkou and Beibuwan basins (Fig. 1). A Chinese-German cooperative project on the distribution, formation and effect of methane and gas hydrate on the environment in the area was conducted in early 2004 and the joint cruise SO-177 of R/V SONNE carried out in June–July 2004 found cold seep carbonates in this area (Wu *et al.*, 2006a) with an unusually high concentration of methane below about 3000 m water depth (Wu *et al.*, 2006b).

3. Method

The core samples were collected from sites SH-A and SH-B in the Shenhu area during a cruise of the onboard R/V “Haiyangsihao” in 2006 using a Gravity Plunger. The lengths of the cores were 8.52 and 8.75 m, respectively. Pore water samples were obtained on board at room temperature by a vacuum apparatus (Fig. 2) from 15-cm long, whole-round subcores collected at intervals of 70 cm and were directly saved in sealed plastic bottles at $\sim 4^\circ\text{C}$. DIC and anion concentrations, as well as carbon isotopic compositions were determined within two months after the end of the cruise.

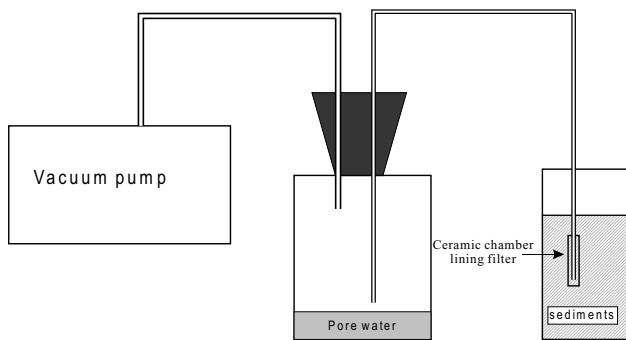


Fig. 2. Diagram showing vacuum apparatus for extracting pore water.

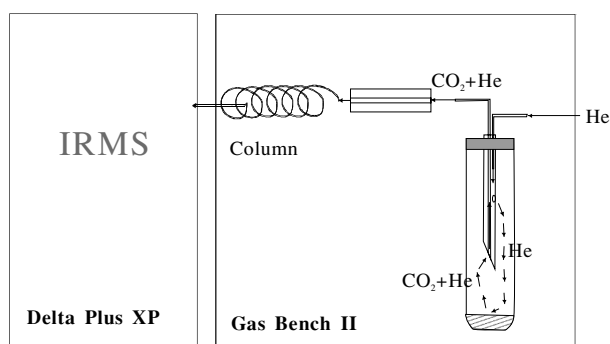


Fig. 3. Diagram showing continuous flow analysis of carbon isotopic composition of dissolved inorganic carbon (DIC).

DIC concentrations and $\delta^{13}\text{C}$ -DIC in pore waters were analyzed using a continuous flow isotope ratio mass spectrometer (CF-IRMS) in the State Key Laboratory for Mineral Deposits Research of Nanjing University. We used a new method to obtain simultaneously the DIC concentration and $\delta^{13}\text{C}$ -DIC in pore waters as reported by Assayag *et al.* (2006) and Yang *et al.* (2006b). The instrument we used was a Delta Plus XP continuous flow isotope ratio mass spectrometer coupled with an on-line GasBench II device (Fig. 3). In brief, 0.5 ml of water sample was taken and treated with pure H_3PO_4 in a glass vial at 25°C , the CO_2 produced was stripped with He, transferred into the mass spectrometer and $\delta^{13}\text{C}$ values were measured. We carried out experiments for different reaction durations, but the results showed no statistically significant change in $\delta^{13}\text{C}$ -DIC after 4 hours of reaction (Yang *et al.*, 2006b). The analytical precision of $\delta^{13}\text{C}$ values for pore water samples is $<0.1\text{‰}$. Four in-house water standards were prepared for DIC concentration determination with concentrations of NaHCO_3 of 0, 1.18, 2.35 and 4.69 mM, respectively (Yang *et al.*, 2006b). The intensity of produced CO_2 gas showed an excellent linear correlation ($R^2 = 0.998$) with the DIC concentration

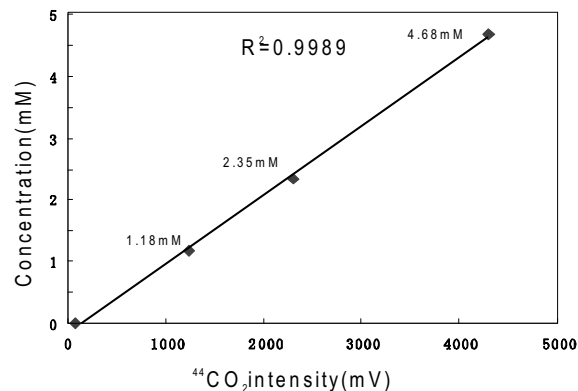


Fig. 4. Correlation of $^{44}\text{CO}_2$ intensity and DIC-concentration of DIC water standards.

Table 1. Analytical results of pore waters from the SH-A and SH-B cores.

Core	Depth (m)	$\delta^{13}\text{C}_{\text{VPDB-DIC}}$ (‰)	DIC (mM)	SO_4^{2-} (mM)
SH-A	0.13	-13.8	8.8	22.9
	0.88	-14.6	8.2	21.7
	1.63	-15.4	14.4	20.9
	2.38	-14.5	9.8	21.2
	3.13	-13.6	6.8	23.3
	3.88	-15.1	11.7	20.9
	4.63	-17.9	13.1	16.7
	5.38	-16.3	11.9	18.6
	6.13	-17.1	16.6	14.5
	6.88	-18.7	22.1	10.6
SH-B	7.63	-20.0	24.9	7.5
	8.75	-19.7	28.9	5.5
	0.10	-9.1	4.4	28.4
	0.80	-14.5	5.4	23.9
	1.50	-16.7	7.7	22.1
	2.67	-19.9	10.4	18.5
	3.37	-15.6	12.5	20.1
	4.07	-15.7	15.2	18.5
	4.77	-16.6	16.5	16.7
	5.47	-17.1	26.9	15.5
6.17	-17.7	23.8	12.2	
6.87	-17.4	21.5	11.9	
7.57	-17.7	25.3	9.6	
8.52	-19.7	29.4	6.4	

(Fig. 4), which allowed us to construct a standard curve based on this correlation for each day and to calculate the DIC concentration in the water samples; the analytical precision of this method was estimated to be $<5\%$.

Sulfate concentrations were measured by ion chromatography (Metrohm IC 790). A Metrosep A Supp4-250

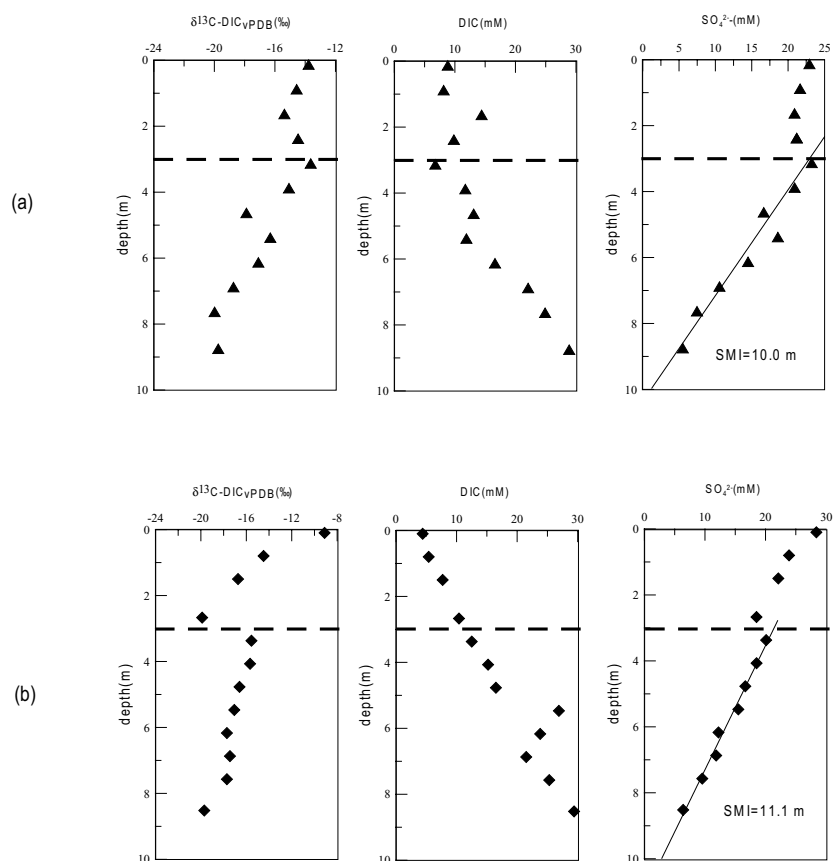


Fig. 5. Depth profiles of DIC, SO₄²⁻, and δ¹³C-DIC in core SH-A (a) and core SH-B (b).

type chromatographic column and 1.8 mmol/L Na₂CO₃ + 1.7 mmol/L NaHCO₃ mixed solution in the anion system were used during the analyses with an analytical precision estimated to be <1% (Ge *et al.*, 2006).

4. Results

Analytical results are listed in Table 1. The pore water samples show a DIC concentration from 4.4 to 29.4 mM, and a δ¹³C-DIC variation from -9.1 to -20.0‰. The sulfate (SO₄²⁻) concentrations also show large variations from 5.5 to 28.4 mM.

The depth profiles of pore water DIC, SO₄²⁻, and δ¹³C-DIC in cores SH-A and SH-B are illustrated in Fig. 5. At core SH-A, the downward patterns display two distinctly different zones of 0–3 mbsf and from 3 mbsf to the bottom of the core. From 0 to 3 mbsf the concentrations of DIC and SO₄²⁻ and the δ¹³C-DIC values are relatively constant. In contrast, below 3 mbsf these parameters show good linear gradients with decreases in δ¹³C-DIC and SO₄²⁻ and an increase in DIC, respectively (Fig. 5(a)). The sulfate gradient and sulfate-methane interface (SMI) calculated by least-squares linear regression using the data below 3 mbsf are 3.12 mM·m⁻¹ and 10.0 m, re-

spectively.

At core SH-B, the two zones in the depth profile can also be distinguished, although they are less clear compared to core SH-A. It appears that both zones at core SH-B show linear gradients, but the gradients for δ¹³C-DIC and SO₄²⁻ in the lower zone of >3 mbsf are greater than those from the upper zone of 0–3 mbsf (Fig. 5(b)). However, no significant difference in DIC concentrations occurs between the zones, although two DIC data at 5–6 mbsf show a slight offset from the main linear trends (Fig. 5(b)). The sulfate gradient and sulfate-methane interface (SMI) at core SH-B calculated by least-square linear regression using the data below 3 mbsf are 2.38 mM·m⁻¹ and 11.1 m, respectively.

5. Discussion

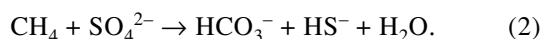
5.1 SOM vs. AMO process

In organic-rich marine sediments, sulfate reduction is generally the most important remineralization process, with the net reaction adding DIC and H₂S to pore waters (Reeburgh, 1983). It is well-known that sulfate depletion in marine sediments is usually controlled by the amount

and quality of organic matter deposited within sediments; thus, the oxidation of sedimentary organic matter (SOM) through sulfate reduction (Eq. (1)) is considered to be one of the prime sulfate reduction pathways (Westrich and Berner, 1984; Canfield, 1991):



A secondary mechanism of sulfate depletion in sediment pore waters is through anaerobic methane oxidation (AMO) (Eq. (2)) near the base of the sulfate reduction zone, or the so-called sulfate-methane interface (SMI) (Reeburgh, 1976):



In general, SOM (Eq. (1)) is the dominant reaction that controls interstitial sulfate concentrations and gradients in marine sediments. AMO (Eq. (2)) becomes an important process that affects interstitial sulfate concentration gradients in methane-charged sediments, like those overlying gas hydrate deposits in the world oceans, such as the Blake Ridge and Hydrate Ridge (Borowski *et al.*, 2000; Borowski, 2006).

According to Eqs. (1) and (2), the ratios (α) of DIC production to sulfate consumption are 2:1 and 1:1, by SOM and AMO processes, respectively. Therefore, a simple stoichiometry can be estimated for sulfate and DIC using the following equation:

$$\alpha = (D_C * dC_C) / (D_S * dC_S) \quad (3)$$

where D is free-solution diffusion coefficient (D is $6.1 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ and $5.8 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ for the bicarbonate radical and sulfate, respectively, at temperature of $\sim 4^\circ\text{C}$ in near-surface marine sediments (Li and Gregory, 1974), α is the atomic ratio of C:S, and C is concentration of sulfate and DIC.

We did not consider the effect of carbonate mineral formation from the pore water system in the above stoichiometry because we did not observe evidence for the formation of authigenic carbonates from the pore waters we studied. If this process occurred, it would have caused a significant decrease of DIC concentrations, and large losses of DIC from pore waters may cause the data to deviate from linear gradients in plots of sulfate versus DIC concentrations. This was not the case for our data, however (Fig. 6).

From the empirical equation derived from Fig. 6, we obtain $\alpha = 1.98$ and $\alpha = 1.18$ for the upper and lower zones at site SH-A. At site SH-B, the upper zone has $\alpha = 0.62$ and the lower zone has $\alpha = 1.21$. Except for the upper zone of site SH-A, where α is close to 2, but with a weak linear relationship ($R^2 = 0.39$), the data are close to

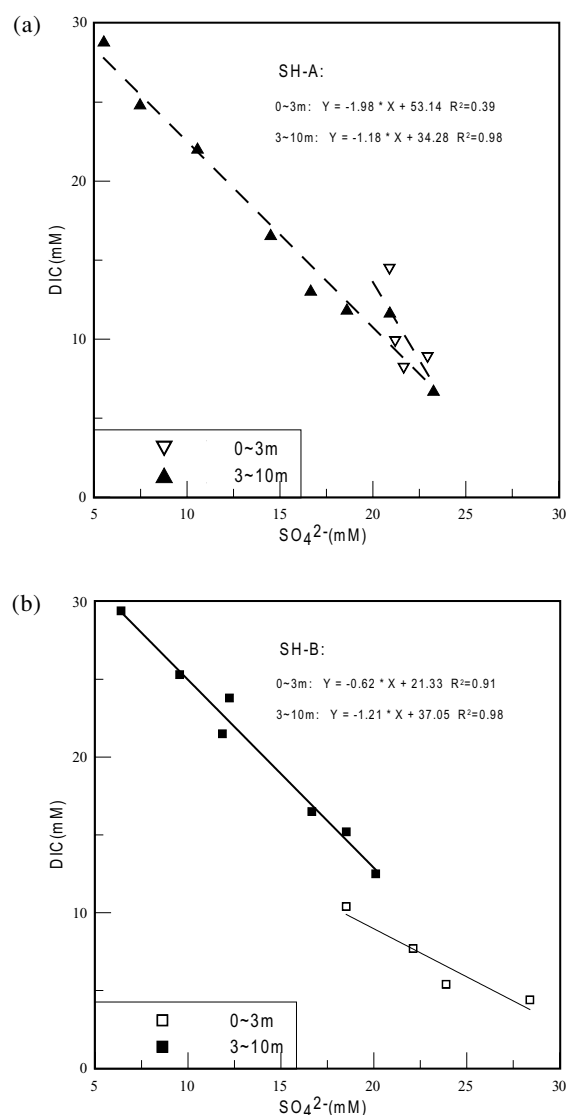


Fig. 6. DIC concentration vs. sulfate concentration diagram of the porewater samples in core SH-A (a) and core SH-B (b).

$\alpha = 1$, suggesting that AMO is the dominant process for sulfate reduction in the Shenhu area.

5.2 Significance of sulfate gradient and flux

A number of studies have demonstrated that steep sulfate gradients and shallow SMI (sulfate-methane interface) depths are a consequence of the increased influence of AMO within organic-rich marine sediments (Borowski *et al.*, 1999). Thus, steep, linear sulfate gradients may be an excellent geochemical indicator of methane-charged sediments, and may also be an indicator of the existence of gas hydrates in marine sediments, as long as P-T conditions are suitable for gas hydrate formation. The SMI values at sites SH-A and SH-B are 10.0 m and

11.1 m, respectively, which are quite similar to the SMI depths in gas hydrate locations such as the Blake Ridge (9.8–14.4 m, Claypool and Threlkeld, 1983; Borowski *et al.*, 2000).

Using Fick's First Law, we can calculate the flux of sulfate into the sediment from overlying seawater by the linear sulfate gradients:

$$J = D_o \phi^3 \frac{\partial C}{\partial x}. \quad (4)$$

Here J is the flux, D_o is free-solution diffusion coefficient, ϕ is porosity, and $\partial C/\partial x$ is the concentration gradient (Borowski *et al.*, 2000). Assuming that the mean sediment porosity is approximately 75% for the near-surface sediments of the northern South China Sea (Wang *et al.*, 2000), we can estimate sulfate fluxes of 18×10^{-4} and 24×10^{-4} mmol cm⁻²yr⁻¹ from SH-A and SH-B in the Shenhu area, respectively. These fluxes are quite similar to or even greater than those reported by Borowski *et al.* (2000) for Blake Ridge, which has a sulfate flux of 8.2×10^{-4} to 18×10^{-4} mmol cm⁻²yr⁻¹. Since the underlying methane concentrations regulate the upward methane flux and thus control the rate of AMO, the sulfate flux is inversely proportional to the methane flux and the underlying methane concentrations. As a result, the high sulfate flux predicted in the Shenhu area may indicate a high methane flux and high methane concentration underlying the Shenhu area.

A high-resolution seismic reflection profile in the deep sediment within the Shenhu area has revealed a large BSR (Fig. 1), which is a widely recognized geophysical indication of gas hydrate occurrence (Kvenvolden, 1993). Hence, we suggest that the high methane concentrations and high methane flux in this area may have a genetic link to gas hydrates at depth in the sediment columns. In May–June 2007, deep drilling conducted by China Geological Survey has obtained genuine gas hydrate samples in 10–25 m intervals at 183–225 mbsf depth in this area (http://www.chinadaily.com.cn/china/2007-06/06/content_887844.htm).

5.3 Implications of carbon isotopic composition of DIC

The carbon isotopic composition of DIC is a key parameter in assessing the relative significance of sulfate depletion mechanism in marine sediments. It is suggested that very negative $\delta^{13}\text{C}$ -DIC values may indicate a significant contribution of carbon from methane through the AMO process (Reeburgh, 1982; Borowski *et al.*, 1999). At site 995 of the Blake Ridge, $\delta^{13}\text{C}$ -DIC values as negative as -37.7‰ have been reported at the sulfate-methane interface (Borowski *et al.*, 2000), which reflect a dominant contribution of light carbon from methane.

The concentration and isotopic composition of DIC

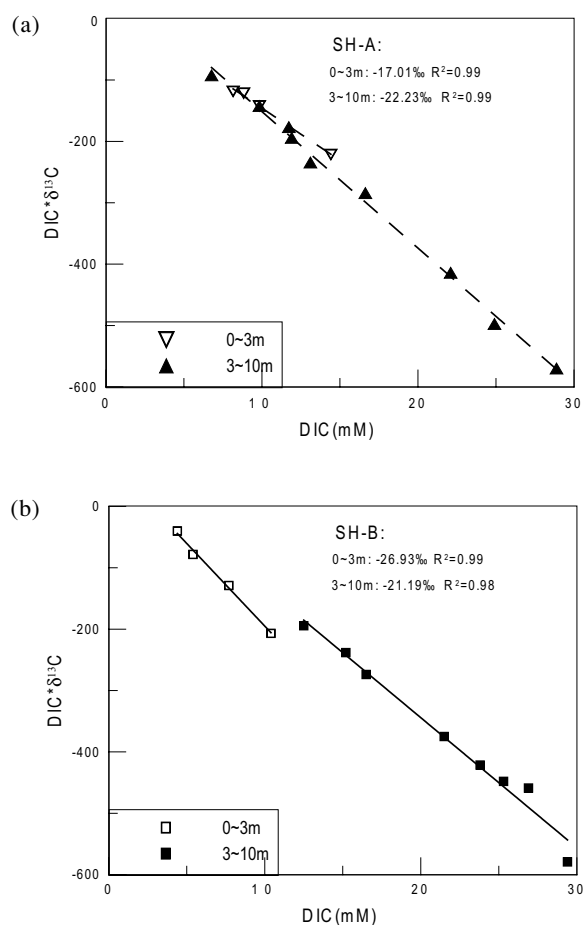


Fig. 7. DIC concentration vs. $\delta^{13}\text{C}$ *DIC diagram of the porewater samples in core SH-A (a) and core SH-B (b).

in pore waters have been used to characterize the DIC source at depth in the sediment column (Borowski *et al.*, 1999, 2000; Thomas *et al.*, 2002). In Fig. 7, we used $\delta^{13}\text{C}$ *DIC vs. DIC plots to determine the $\delta^{13}\text{C}$ of the carbon added to pore water DIC pool in the sediments (Martin *et al.*, 2000; Thomas *et al.*, 2002). The slope of a line fitted to the plot gives the isotopic composition of the DIC added to pore water (Martin *et al.*, 2000). At site SH-A, the $\delta^{13}\text{C}_{\text{add}}$ in the upper zone is -17.0‰ , whereas this value is -22.2‰ in the lower zone (Fig. 7(a)). At site SH-B, the $\delta^{13}\text{C}_{\text{add}}$ in the upper zone is -26.9‰ , whereas this value is -21.2‰ in the lower zone (Fig. 7(b)). The different $\delta^{13}\text{C}_{\text{add}}$ in the upper zone of the two sites may suggest that they have different carbon sources, and the more depleted $\delta^{13}\text{C}_{\text{add}}$ data in site SH-B reflect a major methane source for the added fluid. In site SH-A, bioturbation and fluid advection may have occurred in the upper zone, causing homogeneity of the sulfate and DIC data. Because sulfate reduction also occurs in the bioturbation zone, oxidation of sedimentary organic mat-

ter is quite likely and SOM may have different and generally less depleted carbon isotopic compositions than methane from deeper sediments. In contrast to the differences in $\delta^{13}\text{C}_{\text{add}}$ in the upper zones, the $\delta^{13}\text{C}_{\text{add}}$ data in the lower zones of both sites are quite similar (-22.2 and -21.2%), suggesting a uniform deep carbon source at both sites. These results are higher than the -37.7% reported at site 995 at Blake Ridge, but are similar to those of many methane-charged marine sediment locations (Orphan *et al.*, 2005). We suggest that both methane and CO_2 may have diffused upward from the methanogenesis zone to shallow depths and contributed to the carbon isotopic compositions of DIC. Previous studies have found large carbon isotope fractionations accompanying the biological production of methane in the methanogenesis zone, where the preferential removal of ^{12}C from CO_2 to CH_4 leaves the residual CO_2 increasingly enriched in ^{13}C (Boehme *et al.*, 1996; Thomas *et al.*, 2002). Hence, both the methane with light carbon and the CO_2 with relatively heavier carbon that diffused upward contributed to the overall isotopic composition of DIC added to pore water.

In Fig. 7, the steep isotope gradients of DIC highly depleted in ^{13}C are consistent with the production of DIC by the AMO process. The steep sulfate gradients, high DIC concentrations and light $\delta^{13}\text{C}$ -DIC indicate that fluids with abundant methane diffused upward and may define the processes that account for gas hydrate formation at this location.

6. Conclusions

The pore waters from cores SH-A and SH-B in the Shenhu area show large variations in DIC concentrations and $\delta^{13}\text{C}$ -DIC values. The very negative $\delta^{13}\text{C}$ -DIC and steep sulfate gradients may indicate derivation of DIC from abundant methane upwelling and oxidation in the sulfate reduction zone by the AMO process. The high DIC concentration and sulfate flux also suggest that deep fluids below the SMI include abundant methane, probably produced by the dissolution of gas hydrates in the deep sediment layers of the Shenhu area.

Acknowledgements

This study was financially supported by grants from National Science Foundation of China (40773029) and a Key Scientific Project of Investigation and Evaluation of Marine Gas Hydrate in China Seas (GZHZ200203-04-02) organized by China Geological Survey. Profs. Minhan Dai, Udo Fehn, Jing Zhang, Weijun Cai, and an anonymous reviewer are thanked for their valuable comments and suggestions, which significantly improved the manuscript.

References

Assayag, N., K. Rive, M. Ader, D. Jezequel and P. Agrinier (2006): Improved method for isotopic and quantitative

- analysis of dissolved inorganic carbon in natural water samples. *Rap. Commu. Mass Spectro.*, **20**, 2243–2251.
- Boehme, S. E., N. E. Blair, J. P. Chanton and C. S. Martens (1996): A mass balance of ^{13}C and ^{12}C in an organic-rich methane-producing marine sediment. *Geochim. Cosmochim. Acta*, **60**, 3835–3848.
- Borowski, W. S. (2006): Data report: Dissolved sulfide concentration and sulfur isotopic composition of sulfide and sulfate in pore waters, ODP Leg 204, Hydrate Ridge and vicinity, Cascadia Margin, offshore Oregon, **204**. p. 1–13. In *Proceeding of the Ocean Drilling Program, Scientific Results*, ed. by A. M. Tréhu, G. Bohrmann, M. E. Torres and F. S. Colwell, Ocean Drilling Program, College Station, TX.
- Borowski, W. S., C. K. Paull and W. Ussler (1997): Carbon cycling within the upper methanogenic zone of continental rise sediments: An example from the methane-rich sediments overlying the Blake Ridge gas hydrate deposits. *Mar. Chem.*, **57**, 299–311.
- Borowski, W. S., C. K. Paull and W. Ussler (1999): Global and local variations of interstitial sulfate gradients in deep-water, continental margin sediments: sensitivity to underlying methane and gas hydrates. *Mar. Geol.*, **159**, 131–154.
- Borowski, W. S., T. M. Hoehler, M. J. Alperin, N. M. Rodriguez and C. K. Paull (2000): Significance of anaerobic methane oxidation in methane-rich sediments overlying the Blake Ridge gas hydrates, **164**. p. 87–99. In *Proceeding of the Ocean Drilling Program, Scientific Results*, ed. by C. K. Paull, R. Matsumoto, P. J. Wallace and W. P. Dillon, Ocean Drilling Program, College Station, TX.
- Canfield, D. E. (1991): Sulfate reduction in deep-sea sediments. *Am. J. Sci.*, **291**, 177–188.
- Chen, D., Z. Zhao and B. Yao (2001): Predicted pressure-temperature and thickness below seafloor of gas hydrate formation of natural gases from Ya-13 gas field in Qiangdongnan basin in the northern margin of South China Sea. *Geochemica*, **30**, 585–591 (in Chinese with English abstract).
- Chen, D., L. M. Cathles and H. H. Roberts (2004): The geochemical signatures of variable gas venting at gas hydrate sites. *Mar. Petr. Geol.*, **21**, 317–326.
- Claypool, G. E. and C. N. Threlkeld (1983): Anoxic diagenesis and methane generation in sediments of the Blake Outer Ridge, Deep Sea Drilling Project Site 533, **76**. p. 391–402. In *Initial Reports of the Deep Sea Drilling Project (DSDP)*, ed. by S. Orlofsky, U.S. Govt. Printing Office, Washington, D.C.
- Ge, L., T. Yang, S. Y. Jiang and J. H. Yang (2006): Ion chromatogram method for analysing anions and cations in pore water from marine sediments. *Mar. Geol. Quarter. Geol.*, **26**, 125–130 (in Chinese with English abstract).
- Gieskes, J., C. Mahn, S. Day, J. B. Martin, J. Greinert, T. Rathburn and B. McAdoo (2005): A study of the chemistry of pore fluids and authigenic carbonates in methane seep environments: Kodiak Trench, Hydrate Ridge, Monterey Bay, and Eel River Basin. *Chem. Geol.*, **220**, 329–345.
- Jiang, S. Y., J. H. Yang, H. F. Ling, T. Yang, D. H. Chen, Z. C. Xue, J. F. Ji and P. Ni (2004): Search for gas hydrates in the South China Sea: A geochemical approach. *Mar. Geol. Quar-*

- ter. Geol.*, **24**(3), 103–109.
- Jiang, S. Y., T. Yang, L. Ge, J. H. Yang, H. F. Ling, N. W. Wu, J. Liu and D. Chen (2006): Geochemical evidence for gas hydrate occurrence in the northern margin of the South China Sea. *2006 Western Pacific Geophysics Meeting, EOS Trans. AGU Abstract*, **87**, OS44B-01.
- Jin, C. and J. Wang (2002): Preliminary study on the gas hydrates stability zone in the South China Sea. *Acta Geologica Sinica*, **76**, 423–428 (in Chinese with English abstract).
- Kvenvolden, K. A. (1993): Gas hydrates—geological perspective and global change. *Rev. Geophys.*, **37**, 173–187.
- Li, Y. and S. Gregory (1974): Diffusion of ions in sea water and in deep-sea sediments. *Geochim. Cosmochim. Acta*, **38**, 703.
- Lu, H., Y. T. Seo, J. W. Lee, I. Moudrakovski, J. A. Ripmeester, N. R. Chapman, R. B. Coffin, G. Gardner and J. Pohlman (2007): Complex gas hydrate from the Cascadia margin. *Nature*, **445**, 303–306.
- Martin, W. R., A. P. McNichol and D. C. McCorkle (2000): The radiocarbon age of calcite dissolving at the sea floor: Estimates from pore water data. *Geochim. Cosmochim. Acta*, **64**, 1391–1404.
- McDonnell, S. L., M. D. Max, N. Z. Cherkis and M. F. Czarnecki (2000): Tectono-sedimentary controls on the likelihood of gas hydrate occurrence near Taiwan. *Mar. Petr. Geol.*, **17**, 929–936.
- Milkov, A. V. and R. Sassen (2002): Economic geology of offshore gas hydrate accumulations and provinces. *Mar. Petr. Geol.*, **19**, 1–11.
- Miller, J. J., M. W. Lee and R. Von Huene (1991): An analysis of a seismic reflection from the base of a gas hydrate zone, offshore Peru. *AAPG Bulletin*, **75**, 910–921.
- Orphan, V. J., W. Ussler, III, T. H. Naehr, C. H. House, K.-U. Hinrichs and C. K. Paull (2005): Geological, geochemical, and microbiological heterogeneity of the seafloor around methane vents in Eel River Basin, offshore California. *Chem. Geol.*, **205**, 265–289.
- Reeburgh, W. S. (1976): Methane consumption in Cariaco Trench waters and sediments. *Earth Planet. Sci. Lett.*, **28**, 337–344.
- Reeburgh, W. S. (1982): A major sink and flux control for methane in marine sediments: anaerobic consumption. p. 203–217. In *The Dynamic Environment of the Ocean Floor*, ed. by K. A. Fanning and F. T. Manheim, Lexington, MA (D. C. Heath), Lexington.
- Reeburgh, W. S. (1983): Rates of biogeochemical processes in anoxic sediments. *Annu. Rev. Earth Planet. Sci. Lett.*, **11**, 269–298.
- Shyu, C. T., S. K. Hsu and C. S. Liu (1998): Heat flows off southwest Taiwan: Measurements over mud diapirs and estimated from bottom simulating reflectors. *Terr. Atmos. Ocean. Sci.*, **9**, 795–812.
- Suess, E., M. E. Torres, G. Bohrmann, R. W. Collier, J. Greinert, P. Linke, G. Rehder, A. Trehu, K. Wallmann, G. Winckler and E. Zuleger (1999): Gas hydrate destabilization: Enhanced dewatering, benthic material turnover and large methane plumes at the Cascadia convergent margin. *Earth Planet. Sci. Lett.*, **170**, 1–15.
- Thomas, C. J., N. E. Blair, M. J. Alperin, D. J. DeMaster, R. A. Jahnke, C. S. Martens and L. Mayer (2002): Organic carbon deposition on the North Carolina continental slope off Cape Hatteras (USA). *Deep-Sea Res. II*, **49**, 4687–4709.
- Tomaru, H., Z. L. Lu, G. T. Snyder, U. Fehn, A. Hiruta and R. Matsumoto (2007): Origin and age of pore waters in an actively venting gas hydrate field near Sado Island, Japan Sea: Interpretation of halogen and I-129 distributions. *Chem. Geol.*, **236**, 350–366.
- Torres, M. E., J. McManus, D. E. Hammond, M. A. de Angelis, K. U. Heeschen, S. L. Colbert, M. D. Tryon, K. M. Brown and E. Suess (2002): Fluid and chemical fluxes in and out of sediments hosting methane hydrate deposits on Hydrate Ridge, OR, I: Hydrological provinces. *Earth Planet. Sci. Lett.*, **201**, 525–540.
- Trehu, A. M., P. E. Long, M. E. Torres, G. Bohrmann, F. R. Rack, T. S. Collett, D. S. Goldberg, A. V. Milkov, M. Riedel, P. Schultheiss, N. L. Bangs, S. R. Barr, W. S. Borowski, G. E. Claypool, M. E. Delwiche, G. R. Dickens, E. Gracia, G. Guerin, M. Holland, J. E. Johnson, Y. J. Lee, C. S. Liu, X. Su, B. Teichert, H. Tomaru, M. Vanneste, M. Watanabe and J. L. Weinberger (2004): Three-dimensional distribution of gas hydrate beneath southern Hydrate Ridge: constraints from ODP Leg 204. *Earth Planet. Sci. Lett.*, **222**, 845–862.
- Uchida, T., H. L. Lu and H. Tomaru (2004): Subsurface occurrence of natural gas hydrate in the Nankai Trough Area: Implication for gas hydrate concentration. *Resour. Geol.*, **54**, 35–44.
- Wang, P., W. L. Prell and P. Blum (2000): Ocean Drilling Program Leg 184 Scientific Prospectus South China Sea, site 1144, **184**. p. 1–97. In *Proceedings of the Ocean Drilling Program, Initial Reports*, ed. by P. Wang, W. L. Prell and P. Blum, Ocean Drilling Program, College Station, TX.
- Westrich, J. T. and R. A. Berner (1984): The role of sedimentary organic matter in bacterial sulfate reduction: the G model tested. *Limnol. Oceanogr.*, **29**, 236–249.
- Wu, B., G. Zhang, Y. Zhu, Z. Lu and B. Chen (2003): Progress of gas hydrate investigation in China offshore. *Earth Sci. Front.*, **10**, 177–189 (in Chinese with English abstract).
- Wu, N., H. Dong, E. Suess, H. Jiang, Y. Ye, C. Zhang, H. Rowe and Y. Huang (2006a): Carbonate build-up found in the northeastern South China Sea. *2006 Western Pacific Geophysics Meeting, EOS Trans. AGU Abstract*, **87**, OS41F-01.
- Wu, N., E. Suess, S. Fu, B. Domeyer, Y. Huang and Y. Zhu (2006b): Pore-water geochemistry of surface sediments from Haiyang 4 area of the northeastern South China Sea. *2006 Western Pacific Geophysics Meeting, EOS Trans. AGU Abstract*, **87**, OS31A-0098.
- Yang, T., S. Y. Jiang, L. Ge, J. H. Yang, H. F. Ling, N. Y. Wu, G. X. Zhang, J. Liu and D. H. Chen (2006a): Geochemical characteristics of sediment pore water from site XS-01 in the Xisha Trough of South China Sea and their significance for gas hydrate occurrence. *Quat. Sci.*, **26**, 42–48 (in Chinese with English abstract).
- Yang, T., S. Y. Jiang, M. Lai, J. H. Yang, L. Ge and H. F. Ling (2006b): Analytical method for concentration and carbon isotopic composition of dissolved inorganic carbon (DIC) by continuous flow-isotope ratio mass spectrometer. *Geochimica*, **35**, 675–680 (in Chinese with English abstract).