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COMPARISON OF CARBON ISOTOPIC COMPOSITIONS OF DISSOLVED INORGANIC CARBON (DIC) IN PORE WATERS IN TWO SITES OF THE SOUTH CHINA SEA AND SIGNIFICANCES FOR GAS HYDRATE OCCURRENCE

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ABSTRACT
The northern margin of South China Sea contains several favorable areas for occurrence of gas hydrate. In this study, we collected pore water samples in two piston cores (X-01 and D-01) from Xisha Trough and Dongsha area, respectively, and the concentrations of sulfate and carbon isotopic compositions of dissolved inorganic carbon (DIC) were measured. The results showed different geochemical characteristics in these two sites. The X-01 core shows relatively constant δ^{13}C-DIC values and sulfate concentrations, which suggest that anaerobic methane oxidation (AMO) processes did not occur in this site. In contrast, very large variation in δ^{13}C-DIC values and sulfate concentrations are revealed in D-01 core, and good linear correlations for sulfate gradients and δ^{13}C-DIC values are observed. The calculated sulfate-methane interface (SMI) depth is 9.6 mbsf. These data indicate that an AMO process occurred in sediments with large methane flux from depth in the Dongsha area, which are comparable to other gas hydrate locations in the world oceans such as the Blake Ridge. We suggest that the Dongsha area is one of the most favorable targets for future gas hydrate exploration.

Keywords: gas hydrates; sulfate; δ^{13}C-DIC; Dongsha area; Xisha Trough

INTRODUCTION
Gas hydrates occur world-wide and are restricted to two regions, the polar region and deep-water continental slope *[1]*. Until recently, over 220 gas hydrate deposits have been found *[2]*.

The South China Sea has favorable geologic and tectonic settings, suitable temperature and pressure conditions, and thick organic-rich sediments that are all favorable for the formation of gas hydrate *[3,4,5]*. In recent years, we have conducted gas hydrate exploration in the South China Sea. As a result, geological, geophysical, and geochemical

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evidence, such as bottom-simulating reflector (BSR), cold seep carbonates, etc., have been found to support the presence of gas hydrates in the Xisha Trough, Shenhu and Dongsha areas which are along the northern continental margin of the South China Sea*[3,4,5,6,7,8]*. In this paper, we report geochemical and isotopic data obtained in two sites from Xisha Trough and Dongsha area, respectively, and discuss their implications for occurrence of gas hydrate in the northern South China Sea.

GEOLOGICAL SETTING

The northern continental margin of the South China Sea deposited thick sediments of 1000-7000 m, had a high sedimentation rate, and has an organic matter content of 0.46-1.9% *[9,10]*. This region not only contains a large source of oil and natural gas, but also is a favorable place for the formation of gas hydrate *[3,4,5,6,8,9]*.

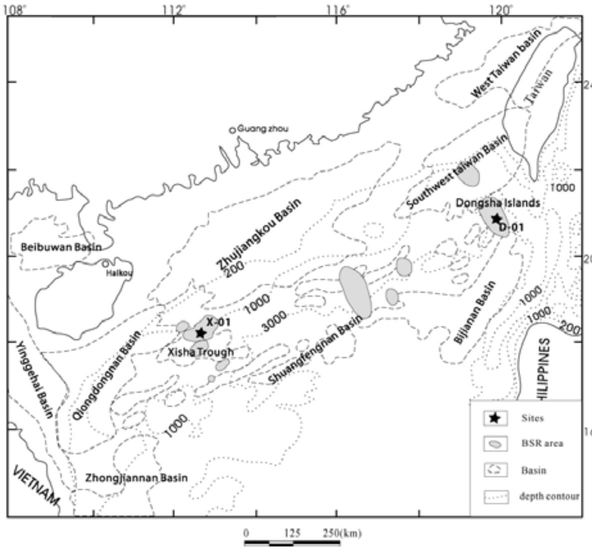

Figure 1 Location of the studied two pistol cores in the Xisha Trough and Dongsha area in the northern South China Sea

The Xisha Trough is a modern E-W-trending trough, which located between the Dongsha islands and the Xisha islands in the northern margin of the South China Sea, and is adjacent to several large oil and gas fields. The Xisha Trough extends 420 km long with water depths of 1500 m in the west part and 3400 m in the east part of the trough. A large amount of biogenic or thermogenic gas have been produced in this and adjacent areas.

The Xisha Trough is a Cenozoic sedimentary basin with high sedimentation rate and a thick sediment pile. The sediments contain high organic matters with TOC contents of 0.41%~1.02%*[11]*.

The Dongsha area is located in the southeast quadrant of the northern margin of the South China Sea close to the Southwest Taiwan Basin. This region and adjacent area have favorable condition for gas hydrate formation as they have large water depth, large sediment thickness, high organic matter contents, and the highest sedimentation rate in the northern margin of the South China Sea*[12，13]*. The tectonic settings of Dongsha area are complex due to its Cenozoic rifting and drifting tectonic history *[8]*.

METHODS

Pore water samples were collected from two piston cores (X-01 and D-01) from Xisha Trough and Dongsha area during a cruise of the onboard R/V “Haiyangsihao” in 2005 using a Gravity Plunger. The lengths of the X-01 and D-01 are 11.5 and 7.1 m, respectively. Pore water samples were obtained on board at room temperature using a vacuum apparatus from 15-cm long, whole-round subcores that were collected at intervals of 70 cm and directly saved in sealed plastic bottles at ~4°C. Carbon isotopic compositions of DIC and anion concentrations were determined within two months after the end of the cruise in the State Key Laboratory for Mineral Deposits Research of Nanjing University.

The $\delta^{13}C$-DIC in pore waters were analyzed using a continuous flow isotope ratio mass spectrometer (CF-IRMS)*[14]*. The instrument we used was a Delta Plus XP coupled with an on-line Gas Bench II device. 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 $\delta^{13}C$ values were measured. The analytical precision of $\delta^{13}C$ values for pore water samples is <0.1‰.

Sulfate concentrations were measured by ion chromatography (Metrohm IC 790). A Metrosep A Supp4-250 type chromatographic column and 1.8 mmol/L Na_2CO_3 + 1.7 mmol/L $NaHCO_3$ mixed solution in the anion system were used during the analyses with an analytical precision estimated to be <1% *[15]*.

RESULTS AND DISSCUSION

The results show different geochemical characteristics in the two sites (Figs. 2, 3).

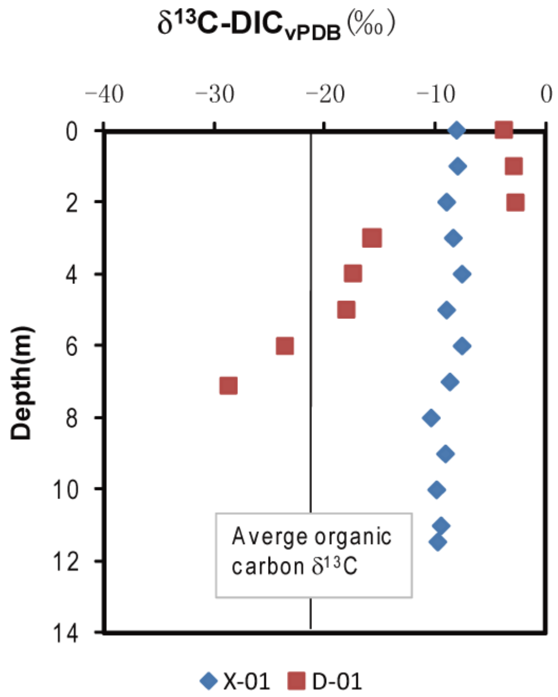

Figure 2. Depth profiles of δ^{13}C-DIC in cores X-01 and D-01

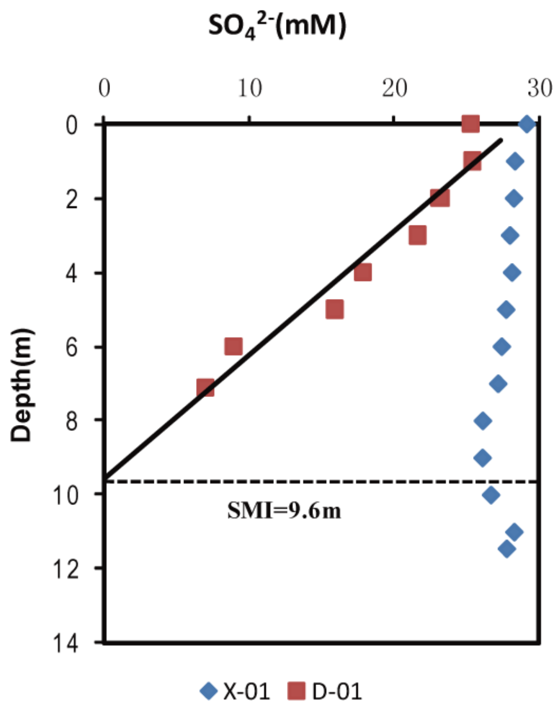

Figure 3. Depth profiles of sulfate in cores X-01 and D-01

The X-01 core shows a very small variation in δ^{13}C-DIC values and sulfate concentrations, with mean δ^{13}C-DIC value of -8.0‰ and close to seawater sulfate values. In contrast, pore water samples from D-01 show very large variations in δ^{13}C-DIC values from -3.7 to -28.8‰ and sulfate concentrations from 25.7 to 6.8 mM. In addition, this core displayed good linear correlations for sulfate gradients and δ^{13}C-DIC values, and the sulfate-methane interface (SMI) depth calculated by least-square linear regression is 9.6 mbsf.

Anaerobic methane oxidation (AMO) is the most important remineralization process in surface sediments of gas hydrate formation area, like those overlying gas hydrate deposits in the Blake Ridge and Hydrate Ridge. (Eq.1)

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \qquad (1)$$

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 negative δ^{13}C-DIC values may indicate a significant contribution of carbon from methane through the AMO process *[7,16,17]*. At site 995 of the Blake Ridge, δ^{13}C-DIC values as negative as -37.7‰ have been reported at the sulfate-methane interface *[16]*, which reflects a dominant contribution of light carbon from methane.

In the X-01 site, pore waters did not show very negative δ^{13}C-DIC values, and the data are higher than the carbon isotopic composition of mean organic carbon. Therefore, we consider the AMO process may have not occurred in this site. In contrast, pore water samples from D-01 show very negative δ^{13}C-DIC values, with two data being obviously lower than the carbon isotopic composition of mean organic carbon. We suggest that they were affected by the carbon from methane through the AMO process. The negative values reflected a dominant contribution of light carbon from methane. Upward diffusion of DIC, which depleted in ^{13}C, is considered to be cause of good linear δ^{13}C-DIC gradients with depth.

The AMO process can produce sulfate gradients in methane-charged sediments, which are inversely related to the depth of sulfate reduction zone in the sediments. Steeper sulfate gradients have been interpreted to reflect a significant downward diffusive flux of sulfate driven by sulfate consumption at the base of the sulfate reduction zone due to AMO process. 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 *[16,18]*. Thus, the sulfate data have been used excellent geochemical indicator for the existence of gas hydrates in marine sediments.

Sulfate concentrations in X-01 core showed no significant gradients which indicated that AMO process did not present in this site. The steep sulfate gradient presented in D-01 core may have related to AMO process in this region. SMI value generally is inversely proportional to the methane flux and the underlying methane concentrations, as a result, the shallow SMI value in D-01 core, which are quite similar to the SMI depths in gas hydrate locations such as the Blake Ridge (9.8-14.4 m *[18,19]*, may indicate a high methane flux and high methane concentration underlying this area.

The steep carbon isotopic gradients of DIC with highly depletion in ^{13}C are consistent with the depletion of sulfate by the AMO process. A high-resolution seismic reflection profile in the deep sediment within the Dongsha area has revealed a large BSR, and the steep sulfate gradients and very negative δ^{13}C-DIC indicate that fluids with abundant methane diffused upward and may define the processes that account for gas hydrate formation in this region.

CONCLUSIONS

The Xisha Trough and Dongsha area are favorable places for occurrence of gas hydrates in the northern continental slope of South China Sea. A comparison of two pistol cores in the two areas suggest to us that the X-01 site in the Xisha Trough did not presented geochemical anomalies associated to gas hydrates, whereas at the D-01 site in the Dongsha area, the very negative δ^{13}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. These characteristics probably were produced by the formation of gas hydrates in the deep sediment layers in the Dongsha area.

In summary, we suggest that the Dongsha area is among the best prospecting targets for gas hydrate on the northern margin of the South China Sea.

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