

GEOCHEMICAL ANOMALY OF PORE WATERS AND IMPLICATIONS FOR GAS HYDRATE OCCURRENCE IN THE SOUTH CHINA SEA

Shao-Yong Jiang* , Tao Yang, Lu Ge, Jing-Hong Yang
State Key Laboratory for Mineral Deposits Research and Center for Marine Geochemistry
Research, Department of Earth Sciences, Nanjing University
22 Hankou Road, Nanjing 210093
CHINA

Neng-You Wu, Jian Liu, Guang-Xue Zhang, Dao-Hua Chen
Guangzhou Marine Geological Survey, China Geological Survey
Guangzhou 510760
CHINA

ABSTRACT

Except for direct drilling and sampling of marine gas hydrates, the occurrence of gas hydrates has been identified generally by inference from indirect evidence, derived from geological, geophysical, and geochemical data. In this paper, we intend to discuss the geochemical anomalies of pore waters and their implications for gas hydrate occurrence in the northern continental slope of the South China Sea. The molecular concentration and isotopic composition of methane in sediments can provide clues to gas sources, whereas ionic and isotopic compositions of pore waters, such as steep SO_4^{2-} gradients, shallow SMI (sulfate-methane interface) depths; decreasing pore water chlorinity, and heavy oxygen isotopic compositions, are used to identify gas hydrate occurrence and the distribution and thickness of sediment layers containing gas hydrates. Other good geochemical indicators include anions and cations concentrations such as Br^- , I^- , PO_4^{3-} , NH_4^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , B^{3+} , Li^+ , and Ba^{2+} in pore waters. We also found that the very negative carbon isotopic compositions of dissolve inorganic carbon (DIC) in pore waters can serve as good indicators for gas hydrate occurrence. In the South China Sea, three most promising target areas for gas hydrates include the Dongsha, Shenhu, and Xisha Trough.

Keywords: gas hydrates; isotopic; geochemical indicators; South China Sea

INTRODUCTION

Gas hydrate is an ice-like solid substance predominantly composed of water and methane, which commonly occurs in deep-water (700-2500m) marine sediments under appropriate pressure, temperature, and salinity conditions. In the world oceans, >220 gas hydrate deposits have been found, >100 wells drilled and kilometers of hydrated cores studies [1]. In the northern continental slope of the South China Sea, we have started to explore and study gas hydrates using

combined geological, geophysical, and geochemical methods since 1999. In 2004, a joint Sino-Germany cruise SO-177 of R/V SONNE found one of the largest areas of cold seep carbonates in the world oceans at the Shenhu area [2]. In 2007, gas hydrate cores were drilled out and sampled in the Shenhu area of the South China Sea during a cruise organized by China Geological Survey. In the exploration and investigation of marine gas hydrates, geochemical methods have played an important role, and this paper discusses

* Corresponding author: Phone: +86 25 83596832 Fax +86 25 83592393 E-mail: shyjiang@nju.edu.cn

the geochemical anomalies of pore waters in marine sediments and their implications for gas hydrates in the South China Sea.

THE NORTHERN CONTINENTAL SLOPE OF THE SOUTH CHINA SEA

The northern continental slope of the South China Sea contains many sedimentary basins with large source of oil and natural gas (Fig. 1). In recent years, increasing evidence has shown that this region is a favorable place for the formation of gas hydrates [2-9]. Three prospecting target areas for occurrence of gas hydrates have been indicated in the South China Sea, namely, the Xisha Trough, the Shenhu and Dongsha areas (Fig.1).

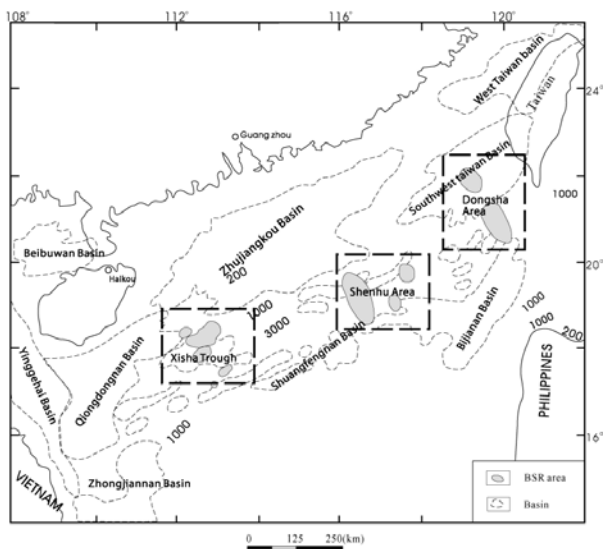


Figure 1: Three prospecting target areas for gas hydrate occurrence in the northern continental slope of the South China Sea

Yao [9] found BSRs for the first time in the northern margin of the South China Sea after a 100,000 Km seismic profile survey, and suggested that gas hydrates might occur both within the Xisha Trough and in the south of the Dongsha area according to the BSRs and the temperature- pressure regimes there. In the following years, other researchers also reported BSRs and other geophysical indicators such as blanking and wipe-out below the BSR in the South China Sea [6, 10-11]. They suggested a link of these BSRs to the potential occurrence of gas hydrates in the region.

Gas hydrates occur either in the accretionary prism of active continental margin or in the crest and trough in passive continental margin. In South

China Sea occur these two tectonic settings. The northwestern of the South China Sea is a passive tectonic margin, whereas the eastern margin is an actively collisional margin. Typical tectonic and sediment structures related to gas hydrates are found in South China Sea, such as accretionary prism, mud diapirs, slumps, cold seep venting and fluid-induced structures [6, 12]. In the South China Sea, the sediment thickness can reach up to several thousand meters and the sedimentation rates range from 33 to 1400 m/Ma, which are similar to the sedimentation rates at Blake Ridge [13].

GAS COMPOSITIONS

Elevated downward hydrocarbon gas concentrations in headspace gas samples and sediments are good indicators for gas hydrates. In the South China Sea, the ODP drilling and the pistol cores both show an increase in methane concentration. In the ODP 184 Hole 1146 in the Dongsha area, head space methane concentration as high as 85,000 ppmv has been determined at 563.2 mbsf. High head space ethane concentration of 155 ppmv has also determined at 572.8 mbsf in this drill core [14-15]. Wang JQ et al [16] reported methane concentrations in sediments from the ODP 184 Hole 1146 in the range of 15.7 to 394.1 $\mu\text{l/kg}$, which show a similar increasing trend with depth to those headspace values reported by Zhu et al [15]. These authors have suggested that the high methane concentrations at the deep sections of the ODP 184 holes likely indicate decomposition of gas hydrates nearby, which migrated laterally to site 1146 through faults or bedded planes.

In the gas hydrate occurrences, methane venting or high methane anomaly may be observed in the water column (e.g., Blake Ridge, Gulf of Mexico, and Arabian Sea etc.). Active methane venting has not been found in the South China Sea, but the discovery of large area of cold seep carbonates suggests to us that gas seeping may have occurred in this region, and high methane content anomaly in bottom seawater has also been determined in several areas in the South China Sea.

SULFATE GRADIENTS AND SMI DEPTHS

Steep, linear sulfate gradients and shallow SMI depths are excellent geochemical indicators for gas hydrate occurrence [17]. In the Xisha Trough, the SO_4^{2-} concentrations of pore waters vary from 19.9

to 36.8 mM, with a downhole decreasing trend for most of the cores, and the calculated SMI (sulfate-methane interfaces) depths and sulfate gradients using least-square linear regression are between 21 and 47 mbsf, and between -0.7 and -1.7 mM/m, respectively [13]. In the Dongsha area, the SMI depths at ODP 184 Sites 1144 and 1146 are 11 and 65 mbsf, respectively [14-15]. The piston cores in the Dongsha area show very shallow SMI values of 7.5 to 14.2 mbsf [18]. These values are quite similar to those at gas hydrate locations in the world oceans [17].

CHLORINITY

Significant decrease of chlorinity in pore waters in gas hydrate bearing zone sediments was first found in DSDP Leg 67 [19]. Now, pore water chlorinity has become one of the most important evidence for gas hydrate existence. Two trends for chlorinity may relate to gas hydrate. One is decreasing chlorinity due to the dissociation of gas hydrate during core recovery. Another is roof chlorinity increase due to salt exclusion effect during the formation of gas hydrate [20].

In the South China Sea, ODP 184 Hole 1146 shows a decrease in Cl^- concentrations with depth [15]. Below 540.4 mbsf, Cl^- shows a significant decrease, with values of 547 mM at 559.7 and 579.0 mbsf and a minimum value of 536 mM at 598.2 mbsf, which were probably produced by decomposition of gas hydrate nearby and migrated to site 1146 along faults or bedded planes [15]. In the Shenhu area, the gas hydrate drill cores recovered in 2007 also show low chlorinity (333.2 mM in core SH-2, 418.1 mM in core SH-3, and 337.4 mM in core SH-7) in the gas hydrate bearing zones.

Pore water samples with Cl^- concentrations significantly higher than normal seawater are also found in shallow marine sediments in the South China Sea [13]. But these samples may not relate to the roof effect of chlorinity as reported at sites with shallow gas hydrate occurrence elsewhere since a general linear correlation between Cl^- and Br^- (and Na^+ , K^+ , Mg^{2+}) are observed and a mixing between normal seawater and a saline brine is the simplest explanation [13].

Br^- AND I^-

In the gas hydrate locations, pore water Br^- and I^- concentrations show a large increase over seawater

values. For example, in ODP 164 site 997, below ~400 mbsf Br^- contents are about three times of seawater and I^- contents are three orders of magnitude of seawater values [20]. In this study, we found high Br^- concentrations (up to 278 ppm) in pore water samples in several piston cores in the Dongsha area. High I^- concentrations are both found in the Dongsha and Shenhu areas. In particular, pore water samples from the BSR fields in the Shenhu area show significantly higher I^- contents (4997-5878 ppm) than those from the non-BSR fields (147-1103 ppm).

PO_4^{2-} AND NH_4^+

In the gas hydrate occurrence area, the pore water show significantly higher ammonia and phosphate concentrations in shallow marine sediments [21]. An increasing trend of pore water phosphate concentrations with depths is also observed, which match the SMI curve of SO_4^{2-} gradients in pore water. We suggest that the anomalies of ammonia and phosphate concentrations in pore water may be used as new geochemical tracers to prospect marine gas hydrate [21].

CATIONS

Cations, such as K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Li^+ , B^{3+} , Sr^{2+} , and Ba^{2+} , in pore waters may be useful indicators for gas hydrate existence. In ODP 164 sites 994, 995, and 997, pore water Ca^{2+} and Mg^{2+} concentrations decrease dramatically and Mg/Ca and Sr/Ca ratios increase significantly in the shallow depths of <40 mbsf, whereas Sr^{2+} concentrations and Sr/Cl ratios fall below seawater values between 100 and 450 mbsf corresponding to the gas hydrate bearing zones at these sites [22]. Mazurenko et al. [23] used pore water Mg/Cl ratios to identify mixing of various fluids in the gas hydrate deposits in the Ginsburg and Yuma mud volcano sediments, Moroccan Margin.

In the Xisha Trough, pore-water Mg/Ca and Sr/Ca ratios increase with depths in piston cores HX-17 and HX-21 [13]. These trends are probably caused by precipitation of carbonates due to AMO (anaerobic methane oxidation) or SOM (oxidation of sedimentary organic matter through sulfate reduction) processes, which produce CO_3^{2-} [17, 20, 24]. In the Dongsha area, pore waters from ODP 184 show a sharp increase in Li^+ concentration at depth up to 1337 μM at the base of the hole, whereas Ca concentrations decrease quickly from 16.7 mM at surface to a minimum value of 2.6

mM at 65.35 mbsf, corresponding to sulfate reduction zone [15].

OXYGEN AND HYDROGEN ISOTOPES

A sharp increase in pore water $\delta^{18}\text{O}$ values has been used as good indicator for the gas hydrate bearing zones, because heavy isotope ^{18}O is preferentially incorporated in the solid phases of gas hydrate. When gas hydrate dissociated, isotopically heavy water is released to cause the ^{18}O enrichment in the pore waters [19-20]. Hydrogen isotopes behave essentially the same as that for oxygen.

In the Dongsha area, pore waters from ODP 184 cores did not show any systematically significant shift in both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ from typical seawater stored in sediments, except for several samples with anomalously lower values of oxygen (-3.7‰) and hydrogen (-14‰) [15]. In the Xisha Trough, pore water samples also show similar $\delta^{18}\text{O}$ (0.0 to 5.0‰) and $\delta^2\text{H}$ values (-5 to -39‰) to seawater, but in core A-14 a slightly increasing trend with depth in both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ is observed, and Yang et al. [25] suggest a possible indication for gas hydrate occurrence in this site, although further work is needed to test it.

SEEP CARBONATES AND THEIR CARBON AND OXYGEN ISOTOPES

Due to high carbonate activity in pore waters related to methane oxidation reactions, authigenic carbonates may precipitate at gas hydrate deposits. These carbonates usually preserve a very negative carbon isotopic signature, indicating a gas hydrate related origin. In the northern continental slope of the South China Sea, cold seep authigenic carbonates have been found in all the three prospecting target areas (Xisha Trough, Shenhu, Dongsha). For example, authigenic carbonate crust and chimneys are found in the southeast Dongsha, offshore southwest Taiwan, with very negative $\delta^{13}\text{C}$ values of -56.9 to -32.8‰, and $\delta^{18}\text{O}$ values of 2.2 to 5.0‰ PDB [26]. In the southwest Dongsha area, dolomite and siderite nodules are found with $\delta^{13}\text{C}$ values of -18.2 to -36.1‰, and $\delta^{18}\text{O}$ values of 0.4 to 2.8‰ PDB [27]. Chimney-like carbonates dredged from the Dongsha area show the most negative $\delta^{13}\text{C}$ values of -51.25 to -51.76‰ and highest $\delta^{18}\text{O}$ values of 4.76 to 5.11‰ PDB [3]. In the Xisha Trough, seep carbonate crust composed mainly of aragonite show $\delta^{13}\text{C}$ values of -13.3 to -

29.1‰, and $\delta^{18}\text{O}$ values of 2.3 to 3.7‰ PDB [28]. These data suggest that the carbon in seep carbonates was derived from oxidation of methane of thermogenic or microbial origin that may relate to gas hydrates.

DIC AND CARBON ISOTOPES

Dissolved inorganic carbon (DIC) is a major carbon component in pore waters and its contents mainly depend on the fluid pH and are related to biogeochemical processes. The concentration and carbon isotopic composition of DIC have been used as good tracers for gas hydrate study in recent years [5,20,24,29]. For example, at Blake Ridge, very negative $\delta^{13}\text{C}$ -DIC of -39‰ has been suggested to be related to strong sulfate reduction by anaerobic methane oxidation related to gas hydrate formation [20]. In the Shenhu area, carbon isotopic compositions of DIC are reported for two pistol cores with $\delta^{13}\text{C}$ -DIC values of -9.1 to -20.0‰, a general downhole decrease of $\delta^{13}\text{C}$ -DIC and increase of DIC concentrations are observed in the deeper sediment column of the cores. It is suggested that an anaerobic methane oxidation (AMO) process occurred in the sediments with large methane flux from depth in this area [5]. In the Xisha Trough, pore-waters from a pistol core (X-01) show rather constant $\delta^{13}\text{C}$ -DIC value around -8.0‰ [29]. In contrast, pore-waters from a pistol core (D-01) at Dongsha area show very large variations in $\delta^{13}\text{C}$ -DIC values from -3.7 to -28.8‰ and display good linear correlations between sulfate gradients and $\delta^{13}\text{C}$ -DIC values, suggesting a genetic link to strong AMO process in this site [29].

CONCLUSIONS

Geochemical methods are useful tools to study gas hydrate formation. In recent years, we conduct a detailed geochemical investigation of pore waters in the northern continent slope of the South China Sea, including anions (Cl^- , Br^- , I^- , SO_4^{2-}), cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , B^{3+} , Li^+ , Ba^{2+} , and NH_4^+), and isotopes ($\delta^{18}\text{O}$ - and $\delta^2\text{H}$ - pore water, $\delta^{13}\text{C}$ -DIC, $\delta^{13}\text{C}$ - and $\delta^{18}\text{O}$ - Carbonate). The results show that geochemical anomalies occurred in three prospecting target areas including the Xisha Trough, Shenhu and Dongsha areas. In 2007, first deep drilling program for gas hydrate organized by China Geological Survey already found gas hydrates in the Shenhu area. The geochemical evidence indicates that the Dongsha area is also

one of the most promising target areas for gas hydrate occurrence in the South China Sea.

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