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Geochemical characteristics of pore water in shallow sediments from north continental slope of South China Sea and their significance for natural gas hydrate occurrence *

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Abstract

Northern slope of the South China Sea is a potential area of gas hydrates and research focus areas. Analyzed geochemical parameters about pore water of the anions and cations of major components and $\delta^{13}C_{DIC}$ in the sediments from Shenhu sea area, Dongsha sea area and Southwest Taiwan Basin and collected by gravity piston. The results showed that Cl^- concentration were no significant changes with depth at the three stations and their values were consistent with the normal sea water, SO_4^{2-}concentration showed significant changes in gradient descent from core top to bottom at three stations and Ca^{2+}, Mg^{2+}, Ca^{2+}/Mg^{2+} showed a similar downward trend with SO_4^{2-} concentration, but the amplitude is inconsistent. The SMI of Shenhu sea area, Dongsha sea area, Southwest Taiwan Basin were separately 11m, 8m, 6m and $\delta^{13}C_{DIC}$ of pore water in the sediments range from -10 ‰ to -27 ‰, which were similar with geochemistry characteristics of pore water in the sediments at other international regions of being found gas hydrate, such as Blake Ridge and Mexico Gulf. These geochemistry characteristics may suggest that natural gas hydrate reservoir released methane in deep sediments and methane was mixture gas as main causes of pyrolysis. Summary a series anomaly indicators and identification methods that use these geochemical anomalies characteristics about pore water of shallow sediments to trace gas hydrate in deep stratum.

Keywords :Northern of South China Sea, pore water of sediments, geochemical characteristics, natural gas hydrate

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1.Introduction

Currently, in the international geochemical anomalies research of gas hydrate is focused on hydrocarbon gases (C_1-C_6) abnormal concentrations of bottom seawater, sediments and pore water, isotopic composition of carbon, oxygen and other elements and the Cl^-, SO_4^{2-}content changes of pore water and relations with gas hydrates. Geochemistry of pore water is a main component of gas hydrate research which played an important role at natural gas hydrate research in China. Predecessors have found pore water geochemical anomalies that maybe related with gas hydrate in Xisha trough, Shenhu area and Dongsha area [1-3]. On the whole, these studies are still very preliminary. Some indicators correctly indicate whether the presence of gas hydrates also need to be further verified. Analysis geochemistry characteristics of pore water of shallow sediment at Shenhu area, Dongsha area and Southwest Taiwan Basin on the northern slope of South China Sea. Further interpret hydrate state in these regions. Support science and valid data to gas hydrate exploration in the area.

2.Geological setting

The north continental slope of South China Sea ranges from continental shelf front to southern deep water region of Dongsha uplift and Shenhu uplift. The overall distribution is the NE and 900 km of total length, the width gradually narrows from west to east, covering an area about 21×10^4 km^2. The general trend of topography sloping ground northwest to southeast, is a large sloping, the isobath approximately parallel to the coastline, water depth range from 200 to 3 000m (*Fig.*1). Sedimentary basin is more developed in the northern continental slope of South China Sea, such as the Southwest Taiwan Basin, Pearl River Mouth Basin, Sea Trough Basin, Southeast Qiong Basin and Yingge Sea Basin. The maximum sediment thickness is more than 10 km. Since 1999, we carry out natural gas hydrate resources investigation in the deep continental slope of northern South China Sea. Use high resolution multi-channel seismic exploration technology find clear BSR in Xisha Sea Trough, Shenhu area, southwestern Taiwan and East Sand Islands, which shows that there is likely huge potential of gas hydrate resources in the northern of South China Sea. Shenhu area locates in the middle of the northern slope of the South China Sea and near the southeast of Shenhu shoal [4-5]. Dongsha area is in the west of Shenhu area. These two areas are a transition area of the northern slope of South China Sea and Central Basin. Southwest Taiwan Basin locates in the east of northern slope of South China Sea. These areas are in tectonic subsidence since Miocene period. Form a good geological condition of gas hydrates reservoir. Regional flow is relatively active, faults develop, temperature gradient is low (40-67 ℃/km), favorable gas hydrate development [6].

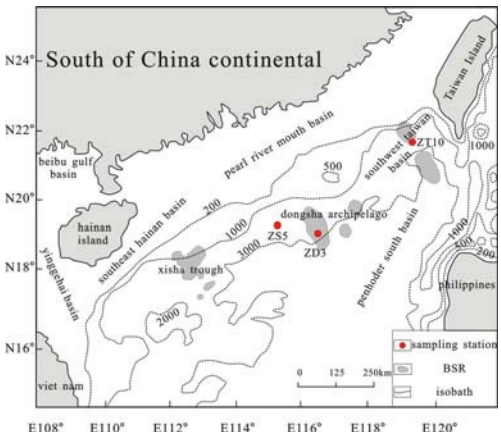

Fig. 1 the location of the core in the northern slope of South China Sea

3.Material and method

3.1.Sample

Samples are mainly from national 973 project team investigating the South China Sea voyage in 2009 and geological survey of the South China Sea cruise of National Science Foundation of China in 2010. Collected three core samples at ZS5、ZD3、ZT10 stations by gravity piston tube in Shenhu area, Dongsha area and Southwest Taiwan Basin. Sample lengths of ZS5、ZD3、ZT10 stations are respectively 8.06m, 7.82m, 4.21m. Pore water samples are obtained on the board. Remove 2cm sample at the top and bottom of gravity piston tube, the remaining samples were intercepted 10 ~ 20 cm each 50 cm interval from the top to the end, then extract pore water using centrifuge. Obtain 40 pore water samples at three stations. Pore water is sealed with PTFE bottles, storage temperature is 4℃.

3.2.Analysis

Samples were carried out a detailed geochemical analysis at Mineral Deposits of the State Key Laboratory of Nanjing University after transporting to the laboratory. Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+} concentration of pore water is analyzed by ion chromatography with Metrohm 790IC.The standard deviation is less than 2%. The $\delta^{13}C_{DIC}$ of sediment pore water were measured by the Finnigan MAT252. The sample and 100% phosphoric acid react at 25 ℃ with some time, and then take CO_2 that released from reaction into the mass spectrometer for stable carbon isotope analysis and precision is less than 0.1%.

4.Results and discussion

4.1.Result

Pore water test results is seen Table 1. Cl^- concentration is from 491.63mmol / L to 632.85mmol / L. They are no significant changes in ZS5, ZD3, ZT10 stations with the depth and are broadly consistent with the normal sea water. The other elements showed a downward trend at three stations with the depth in addition Cl^-. SO_4^{2-}content of the three stations showed a clear gradient change from 28.64mmol / L at the top to 2.87mmol / L at the bottom. At the same time, Ca^{2+}, Mg^{2+} and SO_4^{2-} showed a similar downward trend, but increasing of the changing trends in the three stations is not the same. The carbon isotope of total dissolved inorganic carbon (DIC) is -10.14 ‰ to -27.17 ‰, emerged a negative bias phenomenon at three stations.

TABLE 1 ION CHARACTERISTIC AND δ13CDIC COMPONENT OF PORE WATER IN NORTH CONTINENTAL SLOPE OF SOUTH CHINA SEA

Unit of depth is cm, unit of Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} is mmol/L, unit of$\delta^{13}C_{DIC}$ is ‰.

ID	Depth	Ca^{2+}	Mg^{2+}	Mg^{2+}/Ca^{2+}	Cl^-	SO_4^{2-}	$\delta^{13}C_{DIC}$
ZT10-1	10	18.25	51.50	0.35	558.46	28.64	-21.80
ZT10-2	110	6.70	45.20	2.82	556.67	22.36	-18.30
ZT10-3	210	6.49	45.98	7.09	551.72	17.65	-23.58
ZT10-4	310	5.04	46.32	9.19	566.94	13.79	-20.34
ZT10-5	405	3.63	43.42	11. 96	558.97	6.18	-13.18
ZD3-1	50	10.28	53.64	5.22	559.34	25.30	-27.17
ZD3-2	150	5.58	48.61	8.71	573.25	21.96	-20.34
ZD3-3	250	4.99	46.26	9.28	603.47	17.06	-13.18
ZD3-4	350	4.65	48.04	10.33	544.60	15.96	-16.02
ZD3-5	450	2.08	43.99	21.20	491.63	10.49	-10.14
ZD3-6	550	2.46	45.36	18.45	500.46	5.80	-18.31
ZD3-7	650	1.46	42.33	29.03	493.28	2.87	-11.58
ZS5-1	40	12.25	48.57	3.97	632.85	27.66	-17.22
ZS5-2	150	7.01	40.28	5.75	611.47	22.17	-20.19
ZS5-3	250	4.22	41.57	9.85	631.06	23.76	-15.47
ZS5-4	350	3.70	40.44	10.94	613.13	9.50	-15.64
ZS5-5	450	3.59	40.16	11.19	593.45	13.94	-12.34
ZS5-6	550	2.78	38.45	13.82	579.26	11.63	-14.26
ZS5-7	650	2.19	36.45	16.66	534.49	8.17	-10.99
ZS5-8	750	1.90	36.53	19.21	532.13	5.01	-10.51

4.2.Analysis

Salinity anomaly is the most important geochemical exploration of gas hydrate identification signs [7-8]. In the hydrate formation process, because of its rejection of salt ions into the crystal structure and to absorb a large amount of fresh water, result in fluid salinity increase. Sediment is compressed to reduce the gap with increasing of the depth of sediment burial. Solids and fluids began initial separation occur including natural gas hydrate, the fluid rose up the row, the high chlorine values gradual spread decrease. While the underlying gas hydrate decomposition in fresh water would dilute the remaining liquid chlorine in there we see the negative anomalies. We found similar abnormalities in the other gas hydrate region that has been the core samples. But they are taken from sea bottom 100 ~ 250 m at the core with gas hydrate sediments, do not hydrate the display at shallow layer [9-11]. Cl^-did not show significant anomalies in the pore water of shallow sediment at ZS5, ZD3, ZT10 stations in this region(*Fig.* 2), which shows there is no gas hydrate occurrence at shallow stratum and deep salinity change do not affected shallow pore water.

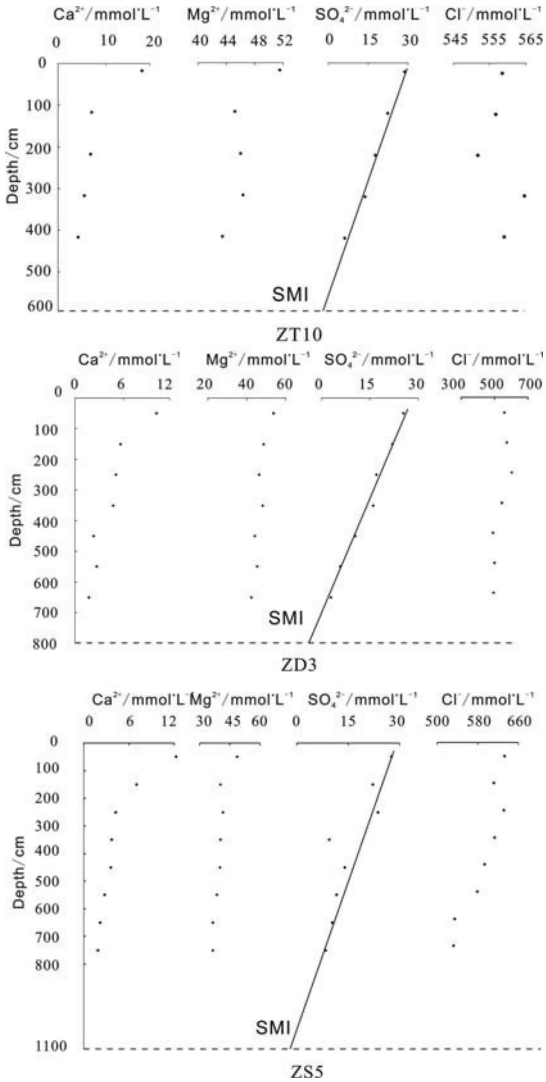

Fig. 2 ION CHARACTERISTIC OF PORE WATER IN NORTH CONTINENTAL SLOPE OF SOUTH CHINA SEA

Sulfate concentration in pore water is also one important of geochemical exploration indicators of gas hydrate [12-16]. In anaerobic marine sediments, sulfate as the oxidant reacts with organic matter by the action of microorganisms in the sediments of its oxidationb[17]: 2 (CH_2O) + $SO_4^{2-} \rightarrow$ $2HCO_3^-$ + H_2S (reaction 1). Generally speaking, in most of the sediments, organic matter oxidation is caused mainly due to changes in sulfate concentration gradient, but is often accompanied by anoxic oxidation of methane (anaerobic methane oxidation, AMO) at gas hydrate zone, the reaction from the Methane and sulfate as reducing agent instead of organic reaction [18-19]: CH_4+$SO_4^{2-} \rightarrow$ HCO_3-+HS^-+H_2O (reaction 2), due to reaction (2) than reaction (1) consume less energy, AMO process is a dominant status in natural gas hydrate zone. Sulfate-methane is the interface to the line from the seabed at the gradual loss of pore water sulfate concentration to the lowest value and the concentration of methane under the limit increased [20-22]. Methane content of deep sediment stratum decides upward flux of methane, but also indirectly controls the rate of AMO and the depth of SMI and sulfate fluxes. It can be seen from Figure 2, ZS5, ZD3, ZT10 stations of the SMI were 11m, 8m, 6m, shows the shallow SMI, suggesting that the more strongly the role of AOM, which under the cover of methane gas content in sediment large, may be the release of methane gas hydrate. Total dissolved carbon dioxide, carbon isotopic composition also shows pyrolysis of methane is a gas consisting mainly of mixed origin, usually pyrolysis $\delta^{13}C > -25$ ‰, biogas $\delta^{13}C < -45$ ‰, carbon isotopic mixing between the two causes [23]. Study area, a number of deep faults from deep stratum to provide a favorable channel migration for pyrolysis transporting, sediment thick for gas gathering provides a good storage environment.

5.Conclussion

Shenhu area, Dongsha area, Southwest Taiwan Basin of Northern slope of the South China Sea in the shallow pore water did not show significant changes in salinity, which is relationship with a larger burial depth of gas hydrate. But as gas hydrate potential area, study area, microbial activity and relatively flow of deep penetration are strong upward in shallow sediments. Specific performance is that SMI is shallower depth and the sulfate flux is relatively high in this region, which suggests that there is a lot of methane released from deep sediment stratum. Provide sufficient gas source to gas hydrate reservoir. While may be shown a significant authigenic carbonate precipitation at the shallow surface layer. In short, the shallow SMI, authigenic carbonate minerals and sulfate of high flux can be react surge composition from deep stratum and effectively trace the presence of gas hydrates.

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