Research Article

Early Diagenesis Records and Pore Water Composition of Methane-Seep Sediments from the Southeast Hainan Basin, South China Sea

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Several authigenic minerals were identified by XRD and SEM analyses in shallow sediments from the Southeast Hainan Basin, on the northern slope of South China Sea. These minerals include miscellaneous carbonates, sulphates, and framboidal pyrite, and this mineral assemblage indicates the existence of gas hydrates and a methane seep. The assemblage and fabric features of the minerals are similar to those identified in cold-seep sediments, which are thought to be related to microorganisms fostered by dissolved methane. Chemical composition of pore water shows that the concentrations of SO_4^{2-} , Ca^{2+} , Mg^{2+} , and Sr^{2+} decrease clearly, and the ratios of Mg^{2+} to Ca^{2+} and Sr^{2+} to Ca^{2+} increase sharply with depth. These geochemical properties are similar to those where gas hydrates occur in the world. All results seem to indicate clearly the presence of gas hydrates or deep water oil (gas) reservoirs underneath the seafloor.

1. Introduction

Methane is a major component of cold fluids on the continental shelf and slope [1, 2]. It is also a major hydrocarbon gas source of deep oilgas and gas hydrates. Hydrocarbon gas can escape through the overlying marine sediment column, enter the water column, and form a coldseep [1, 3, 4]. Most of the hydrocarbon gas can generate authigenic carbonates at or under the seafloor via a series of biogeochemical reactions, and a small amount may even be transported into the water column or enter the atmosphere [5, 6]. Hydrocarbon gas seep provides nourishment for Archaea and sulfate-reducing bacteria (SRB) found in benthic sediments. These microorganisms consume sulfate and oxydize methane into HCO_3^- . This process causes changes of pore water chemical composition and results in the precipitation of carbonate [7, 8]. Methane seeps are an important geological phenomenon in marine sediment, and methane-rich cold

seeps are assumed to be the preferential outcrop of oilgas and gas hydrate on the seafloor. Therefore, the knowledge of methane seeps is significant for oil-gas exploration. Furthermore, the greenhouse potential of methane is 24 times of carbon dioxide. Compared to the artificial carbon dioxide, the greenhouse effect of methane discharged by geodynamic and tectonic processes plays a primary role on the global change in the natural environment [9]. Therefore, there has been an increasing interest in methane seepage (gas hydrate) during the past several years.

Southeast Hainan Basin on the northern slope of South China Sea is a potential gas hydrate deposit. 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 all over the world. For example, the occurrence of gas hydrate is inferred from seismic profiles, especially the bottom simulating reflector (BSR), although

gas hydrates are also known to occur in the areas without BSR in many locations. In Southeast Hainan Basin, the high-resolution multichannel seismic profiles were collected, and BSR and other seismic indications, such as blanking zone and velocity amplitude anomaly inversions, for gas hydrate occurrences, were observed. However, geochemical studies have been of great help for identification of the occurrence of gas hydrates.

The goal of this research is to study the early diagenesis records and geochemistry of pore waters of shallow sediments from Southeast Hainan Basin. The evidences for gas hydrates or deep water oil (gas) reservoirs and the relationship between authigenic mineral, geochemistry of pore waters, and methane seep in shallow sediments were discussed here.

2. Geological Setting and Sampling

A 4.9 m long sediment core was taken in August 2005 from 1508 m depth in the Southeast Basin (Figure 1) by a gravity piston corer, during the HY4-2005-5 Cruise of R/V Haiyang-4 (Guangzhou Marine Geological Survey, Ministry of Land and Natural Resources). The cored sediment is silty clay with a few foraminifera, yielding strong odor of hydrogen sulfide. The sediment core was stored on board at 4°C. The sampling site T1 (111°4' E, 18°2' N) is located in a flat continental slope, 150 km southeast of Sanya, Hainan Province, China. The geological structural unit belongs to the Songxi Depression Belt, Southeast Hainan Basin.

Oil- and gas-bearing depositional basins on the northern continental slope of the South China Sea were developed during the late Cenozoic [10–12], when a strong extrusion phase followed a period of rift extension and sea-floor spreading 30–24 Ma ago. The area (Figure 1) is characterized by frequent tectonic and magmatic episodes, slope slumps, high heat flux (average about 75 mW/m²), abundant thermogenic gas and biogas in shallow sediments, carbon dioxide and nitrogen-rich gas. Four subareas, including Southwest Taiwan, Northeast Dongsha, Baiyun Sag of Pearl River Mouth Basin, and Southeast Hainan Basin, were identified to be the most favorable for gas seep or gas hydrate presence, showing geological, geochemical, and biological evidences for cold seeps [13–21]. The sediment thickness is reported to be about 12000 m [22], whereas 5000 m thick organic-rich sediments have been accumulated since the Cenozoic [23].

The thick Quaternary organic-rich sediments in Southeast Hainan Basin provide enough sources for hydrocarbons [24]. High geothermal gradient [25] and abnormal high pressure [26] are fitted for hydrocarbons formation, diffusion, and transportation. Methane-rich gas is categorized into three groups: bio-low mature transient gas, normal mature thermogenic gas, and super mature thermogenic gas [23], and the conditions for gas hydrate accumulation were confirmed in previous studies [27]. Some methane-seep-related features, such as mud volcanoes, mud diapirs, and gas chimneys, were discovered in the basin [24, 28]. Unfortunately, there is no similar report at the sampling site, even if the existence of gas hydrates in the Southeast Hainan

Basin has been confirmed by geophysical evidences [24, 28–30]. The existence of gas hydrate in the same site (T1) has also been proved by microbial evidence [31].

3. Materials and Methods

The sediment cores within PVC liners were immediately cut into 80 cm sections after its recovery on deck. The core sections were airtight sealed with plastic cap, gummed typed and stored on board at 4°C. The sealed sections were further splitted longitudinally in a flow-through (N₂) anaerobic chamber at Guangzhou Marine Geological Survey, China. One half of each section was described and archived, while the other half was sampled for pore water and sediment. The external rim of each subsection was removed using sterile tools to avoid contamination. Subsections of freshly cored sediments were removed and placed into special sealed glass bottles. The samples were stored at 4°C for X-ray diffraction (XRD), scanning electron microscope (SEM), and pore water analysis. All analyses were carried out at the Department of Geological Sciences and the Department of Biology, University of Miami.

XRD was employed to analyze mineralogy in the sediments. Samples were oven heated at 60°C for 12 hrs, pestled into less than 200 μ mesh, and X-rayed with a Scintag XGEN-4000 X-ray diffraction system, using Cu radiation in a graphite monochromator, a scintillation counter, with 0.02 two-theta steps from 5 to 70 degrees, for 2 seconds per step, with 0.15406 nm wavelength, 40 kV tube voltage, and 34 mA tube current. Mineral identification was done by a combination of search-match software and comparison with the JCPDS card files.

A Zeiss Supra 35 VP-FEG SEM equipped with EDAX Energy Dispersive X-ray microanalysis system was used to identify minerals and to image their morphologies. In preparation for SEM observations, selected samples were vacuum dried and gold coated. The working distance is 10.3 mm, and voltage is 5 kV.

Sediment pore water samples were collected after centrifugation of about 50 g sediment subsamples (5000 g for 10 minutes). Each sediment subsample could obtain about 13–20 mL water. To measure anions and cations, aliquots of pore water were mixed with 0.1 HCl solutions. The diluted (pore water samples) solutions were then analyzed by high-performance liquid chromatography (HPLC) for anions (IonPacAS14 column 4 $\times$ 250 mm) and direct current plasma emission spectrometry (DCP) for cations.

4. Results and Discussions

4.1. Authigenic Minerals and Microstructures of Sediments.

XRD results (Figure 2) show that the sediments contain land-derived detrital minerals, that is, quartz, illite, kaolinite, albite, calcite, and a complex suite of authigenic minerals, that is, miscellaneous carbonates, sulphates, and pyrite. Major mineral components and their semiquantification are listed in Table 1. Abundant microstructures were observed by SEM (Figure 3), and the whole crystal form, surface,

FIGURE 1: Position of the sampling site, Southeast Hainan Sea, South China Sea.

FIGURE 2: XRD pattern of mineral components in sample T1-12 from the Southeast Hainan Basin. Clay, clay minerals; Q, quartz; Anh, anhydrite; Ill, illite; Ab, albite; Cc, calcite; Mg-Cc, Mg-calcite; H, halite; Py, pyrite; Kao, kaolinite.

angle, and crystallographic elements are kept intact during the observations. These characters confirm that the minerals are authigenic in situ, without transport and erosion.

Main identified miscellaneous carbonates are calcite, Mg-calcite, nesquehonite, magnesite, siderite, and so forth.

Calcite is one of the major components in the sediment samples, and most part of it is foraminifera shell. Mg-calcite and nesquehonite are common in XRD patterns, but magnesite and siderite are only identified in few subsamples. Part of calcite is aragonite pseudomorph, which looks like an assemblage with acicular, filiform, and ball-shaped carbonates under SEM. The assemblage is identified with calcite by energy dispersive X-ray spectra. However, the crystal form and habit are similar to aragonite (Figures 3(c), 3(d)). There is no identified aragonite peaks in the XRD pattern, which suggests that aragonite was replaced by calcite, and the pseudomorph of aragonite is observed. It evinces that phase transformation of aragonite into calcite has occurred in sediments. The factor leading to formation of acicular, filiform, and ball-shaped aragonite is metabolism of methane-related microorganisms. Sassen et al. found that acicular aragonite, framboidal pyrites, mycelium, and asphalt have symbiotic relationship in cold seep carbonates [5], and the bacterium activity boosting precipitation of authigenic carbonates has been discovered by lab work [32, 33]. Ehrlich observed successfully ball-shaped and dumbbell assemblage of acicular aragonite by bacilli culture in laboratory [34]. Ball-shaped

TABLE 1: Major mineral components and their semi-quantification results in sediments from the Southeast Hainan Basin (%).

No.	Depth (cm)	Illite	Gypsum	Kaolinite	Brucite	Witherite	Barite	Anhydrite	Quartz	Microcline	Albite	Ba-calcite	Calcite	Mg-calcite	Siderite	Magnesite	Vaterite	Pyrite	Maghemite
T1-44	20	24.2		11.9			22.3		13.1		2.3		7.9			3.5	3.4	11.5	
T1-46	35	25.4		13.4	7.0	1.3	22.5	3.5	12.0		2.7		8.9			3.5			
T1-36	85	28.7		14.2			25.9		13.8		2.6	5.8	6.0			3.0			
T1-38	100	25.2		9.1			30.2		14.6		2.5		8.7		1.9	3.3		4.5	
T1-28	200	30.3		11.7	9.6		25.0		10.4			4.4	3.7					4.9	
T1-30	216	20.8		13.4	3.8		28.0		10.7			5.4	5.9			3.7		8.3	
T1-32	230	26.4		13.4	10.0		28.9		9.1			3.0	5.3					3.9	
T1-20	320	27.4		16.2			28.2		14.5		4.0		9.6						
T1-22	336	24.5		10.7	11.6		27.1		10.5		2.3		3.7			4.6		5.1	
T1-24	355	19.7		11.1	10.4	16.0		2.5	13.4		1.6		11.7	2.3		3.1	3.3	5.0	
T1-12	380	24.41	3.08	11.37				2.94	26.50		3.27		25.16	2.51				0.76	
T1-14	395	43.1		16.7	7.1		15.3		6.4		2.3		3.3	1.8				4.0	
T1-16	415			16.6			37.8	6.6	13.5		6.2		7.6	2.7				9.0	
T1-2	440	20.8		17.9				2.8	29.4		3.4		19.9	3.1		2.7			
T1-4	450	26.1	4.3	15.0					26.4		3.6		19.0	2.9		2.6			
T1-6	465	20.3		14.8			1.7		30.0	9.9	3.3		18.2					1.8	
T1-8	475	22.1		11.3				3.2	29.8	8.0	3.8		15.1	2.3		2.6		1.7

(a) Authigenic carbonates, T1-4

(b) Authigenic dolomite (euhedral rhombus crystal), T1-38

(c) Aragonite assemblage, clay minerals with mycelium, T1-2

(d) Ball-shaped aragonite assemblage, T1-22

(e) Tabular Ca sulphate (authigenic), T1-30

(f) Authigenic Barite, T1-20

(g) Authigenic pyrite, T1-28

(h) Authigenic framboidal pyrite, T1-16

FIGURE 3: SEM images of authigenic minerals in sediments from the Southeast Hainan Basin.

carbonates cemented by mycelium were observed under SEM (Figure 3(d)), which further confirmed that there was some cause-effect relationship between carbonates assemblage and microorganism. Mg-calcite and Nesquehonite are authigenic rhombohedral crystals, and usually coat the surface of microorganism shells like coccoliths, diatoms, and so on [5].

Authigenic carbonates deposits have been documented in area near methane seep in both the active and passive continental margin [5, 6]. The carbonates formation relates closely to methane seep or gas hydrate decomposition because of their special microstructure [2, 35]. The Southeast Hainan Basin in South China Sea is a potential area for gas hydrate reservoirs. Methane microseep and its oxidation drive the bicarbonate deposited associating with the available research data although there are no large methane seep found at the sampling site.

Main sulphate minerals identified in the sediments are barite, anhydrite, and gypsum. Gypsum and anhydrite appear as tabular and panidiomorphic textures (Figure 3(e)). The occurrence of authigenic gypsum and anhydrite indicates high concentration of sulphate ion in the pore water. Sulfate reduction is the main pathway of CH_4 oxidation in CH_4 -riched anoxic sediments. Although the CH_4 - SO_4^{2-} redox cell will decompose and consume sulphate in the sediments, that does not mean there is no SO_4^{2-} . On the contrary, SO_4^{2-} originates from the decomposition of organic-rich sediments, and there must be abundant organic matter in gas hydrate reservoirs [36], whereas Ca^{2+} may originate from the decomposition of calcilith or fluids with Ca^{2+} from the gas hydrate present underneath [37]. Therefore, the supersaturated concentration of Ca^{2+} , and SO_4^{2-} in pore water drives authigenic gypsum precipitation. Authigenic gypsum has been identified in the sediments from Hydrate Ridge in the northeast Pacific Ocean. That indicates gypsum should be one of the authigenic minerals which have close relation with methane hydrate reservoir [38]. In conclusion, gypsum is one of the markers for hydrate presence similar to other authigenic minerals, carbonates, and barite.

Barite shows a short prismatic and euhedral crystal structure under SEM (Figure 3(f)). Authigenic barite micro-crystals had been identified in sediments from the Peru continental margin (site 684) and Japan Sea (site 799) by the Ocean Drilling Program (ODP), and they contain more ^{34}S than that in the sea water with a $\delta^{34}\text{S}$ of +84‰. The widespread occurrence of barite indicates high concentration of Ba in pore water. Barite is the major mineral in the cold-seep sediments in Peru and Russian Okhotsk [39, 40]. The source of Ba in the cold seep is assumed to be the barite solution as a result of the sulphate deoxidization at depth [41].

Pyrite was identified in most samples by XRD analysis, and the representative diffraction peaks are 2.709×10^{-10} and 2.423×10^{-10} m. Pyrite is distributed as single granules (Figure 3(g)) or framboidal assemblages (Figure 3(h)); $\delta^{34}\text{S}$ value of the framboidal pyrite is greatly negative in cold-seep sediments and low-temperature hydrothermal fluid sediments. This indicates that the sulphur of pyrite originates from bacterial reduction of sulphate in sea water [42–44].

Sulphate bacteria mainly depend on sulphate decomposition in the anoxic environment by activity of sulphate redox cell. Meanwhile, the HCO_3^- concentration increases in the pore water with decomposition of organic matter. Sulphide forms with free HS^- and low-valence iron, and finally sulphide transforms into pyrite [45, 46]. Sassen et al. found many framboidal pyrites, and pyrite granules in sediments from a gas hydrate area in the Gulf of Mexico and suggested that the strong anaerobic methane oxidation (AOM) contributes to pyrite formation in sediments [5]. Liu et al. also believed that AOM is the main reason for sulphide increase in the sediments from the northeastern South China Sea [47]. Therefore, authigenic pyrite is also the major product of AOM process in sediments from a gas hydrate (methane seep) area. High concentration of pyrite in anoxic sediments can indicate the methane abnormality [48] and the occurrence of methane-rich fluids and further show the shallow SMI to a certain degree.

In summary, AOM in the methane seep area results in alkalinity increase in both pore water and sea water [49, 50]. Methane is oxidized to HCO_3^- by SO_4^{2-} , a process in favor of CO_3^{2-} accumulation. Furthermore, AOM changes the geochemical conditions and results in the rapid deposition of miscellaneous carbonates including aragonite, Mg-calcite, and dolomite [51]. Meanwhile, pyrite formation results from the reaction of H_2S , derived from bacterial sulphate reduction, with reactive iron [45, 46]. Precipitation of aragonite, Mg-calcite, and pyrite is the result of processes related to the presence of methane seep in the northern Black sea [1, 8]. Abundant cold-seep-related minerals, Mg-calcite, dolomite, and framboidal pyrite, precipitate in Monterey Gulf, California [52]. Authigenic minerals including miscellaneous carbonates, sulphate, and sulphide form in gas hydrate-bearing and hydrocarbon seepage in Gulf of Mexico [5]. All these records of authigenic mineral assemblages and fabric features are geological evidences for cool-seep activities, hydrocarbon seeps, and gas hydrate dissociation. The widespread occurrence of authigenic carbonates, pyrite, and sulphate in the sediments of Southeast Hainan Basin, South China Sea is completely similar to reported cases in a typical gas hydrate area. This aspect further indicates gas hydrate existence in the study area.

4.2. Chemical Composition of Pore Waters. Anomalies in the chemical composition of pore water indicating the occurrence of gas hydrates, such as anomalous concentrations of Br, Cl, CH_4 , and K, are known in the literature [53, 54].

In pore waters from the Southeast Hainan Basin, NH_4^+ concentration is close to zero within the upper 320 cm section and increases with depth in lower section (Table 2, Figure 4). That may be due to the zymosis of organic matter via bacteria during gas hydrate formation and dissociation [55]. The concentration of Mg^{2+} decreases slightly with depth, and the Ca^{2+} concentration falls slightly (Table 2, Figure 4). The solubility product of calcium carbonate is less than magnesium, and calcium carbonate deposits easily from the solution. Therefore, Ca^{2+} deposits faster than Mg^{2+} from

TABLE 2: Pore water chemical composition for the analysed core from the Southeast Hainan Basin (mg/dm³).

Depth (cm)	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Mn ²⁺	Fe ²⁺	F ⁻	Br ⁻	SO ₄ ²⁻
20	0.0	585.1	1465.9	510.1	17.7	28.8	3.0	71.4	2559.5
35	0.0	561.4	1421.1	529.1	17.2	19.9	2.7	69.3	2496.8
85	0.0	588.1	1448.6	487.3	16.8	45.6	3.0	70.8	2447.2
100	0.0	571.2	1393.3	466.7	15.8	36.6	4.4	69.7	2308.3
200	0.0	592.1	1446.4	469.2	9.0	35.7	4.2	79.1	2423.1
216	0.0	558.9	1342.0	429.9	8.5	30.5	3.2	65.3	2199.2
230	0.0	592.8	1412.7	461.5	8.8	48.7	3.0	68.1	2323.2
320	0.0	674.6	1521.3	431.2	7.5	18.1	4.1	71.5	2014.3
336	10.7	558.5	1412.9	439.9	8.0	27.0	3.5	75.4	2175.8
355	0.0	565.9	1460.6	466.5	8.8	46.9	3.1	78.5	2199.9
380	26.4	552.7	1424.1	429.8	7.8	18.0	3.0	67.8	2170.3
395	22.8	595.4	1415.8	423.2	7.9	28.6	3.2	76.0	2173.7
415	15.7	546.4	1406.7	439.1	8.9	53.2	3.7	71.8	2074.6
440	44.7	537.8	1375.7	412.3	12.0	22.2	3.0	72.7	2085.0
450	55.5	579.6	1421.8	412.7	7.6	9.0	3.8	77.6	2163.3
465	53.6	550.5	1434.4	425.2	8.0	14.4	4.7	79.2	2078.0
475	61.3	595.2	1407.1	363.0	7.3	25.2	4.1	72.6	2153.7

FIGURE 4: Geochemistry of pore waters versus depth of sediments from the Southeast Hainan Basin.

pore water into solid phase. Furthermore, the Mg^{2+}/Ca^{2+} ratio increases sharply with depth (Figure 4). The concentrations of Sr^{2+} , and Mn^{2+} go down sharply with depth in the shallow sediments (Table 2). This suggests that Sr^{2+} and Mn^{2+} are removed into the same authigenic phase(s). Also the ratio of Sr^{2+} to Ca^{2+} increases sharply with depth (Figure 4), and the cause may be that Ca^{2+} , Mg^{2+} , Sr^{2+} , and Mn^{2+} cations are easily incorporated within carbonates

deposited at the expense of dissolved carbon dioxide. The consumption of Ca^{2+} , Mg^{2+} , Sr^{2+} , and Mn^{2+} cations in pore water, combined with the authigenic carbonates like calcite (aragonite pseudomorphous), Mg-calcite, and magnesite, indicates that there is supplement of dissolved CO_2 likely originated from AOM in depth during the diagenesis process, then diagenesis is a process affecting AOM and providing cations and dissolved species to pore water for further

reactions. Previous research showed that carbon dioxide could form during gas hydrate decomposition and upper migration in gas hydrate-bearing areas, leading to formation of authigenic carbonates, syngenetic to gas hydrate [56, 57].

The concentrations of Cl^- and Br^- are relatively constant, whereas SO_4^{2-} decreases clearly with depth (Figure 4). These trends, combined with the presence of authigenic carbonates, barite, gypsum, anhydrite, and pyrite, indicate AOM and sulphate reduction

The reaction has affected the shallow sediments at the site T1 of the Southeast Hainan Basin, South China Sea, or the sulphate-methane interface (SMI) has been lifted up to the shallow layer. It means that there is abundance of gas hydrate or gas-oil resource underneath the sampling site. Compared to other methane seep area, the concentration gradient of sulphate in core T1 is smaller. That means sulfate in pore water is not exhausted in sampling depth. So, the depth of SMI should be deeper than the sampling's. Therefore, it is clear that there is a hypogenetic fluid, related to gas hydrate occurrence under the sampling site.

The results of microbial colony research at same site [31] demonstrated that physiological functions of these relatives include Fe(III) and Mn(IV) reduction (*Pelobacter*), sulfate reduction (H_2S production) (*S. kaireitica*), decomposition of complex aromatic hydrocarbons and denitrification (*P. stutzeri*), hydrocarbon degradation (*A. jadensis*), and thio-sulfate/sulfite oxidation (*Sulfitobacter* spp.) in the sediments, similarly to observations of gas hydrate-bearing sediments in the Sea of Okhotsk [58]. The occurrence of microbe suggests hydrocarbon oxidation coupled with sulphate, and Fe (III) reduction is an important process during the early diagenesis in the Southeast Hainan Basin, South China Sea. Oxidation of hydrocarbons may contribute to the increasing alkalinity and carbonate precipitation. The metabolic processes are consistent with the decreasing Mg^{2+} , Ca^{2+} , Sr^{2+} and SO_4^{2-} concentrations in pore water, the precipitation of authigenic carbonates and pyrite in the shallow sediments. These results strongly suggest that there should be gas hydrate reservoirs in the sampling area.

5. Conclusions

Taking together all available mineralogical and geochemical data from the Southeast Hainan Basin, South China Sea, we can draw the following conclusions.

- (1) The shallow sediments from the Southeast Hainan Basin are of a complex suite of authigenic minerals, such as carbonates, sulphates, and framboidal pyrite, indicating clearly the existence of gas hydrates or deep water oil (gas) reservoirs. The assemblage and fabric features of aragonite and mg-calcite could be a result of the activity of microorganisms, which consumes dissolved methane. The miscellaneous authigenic carbonates are the result of abundant HCO_3^- in the pore water, whose source should be related to AOM by microorganisms. Reduction of

sulphate and iron may be coupled with oxidation of methane and hydrocarbons, which causes decreased SO_4^{2-} concentration in pore water and precipitation of authigenic pyrite and carbonates in the sediments.

- (2) Chemical composition of pore waters shows that the concentrations of SO_4^{2-} , Mg^{2+} , Ca^{2+} , Sr^{2+} and Mn^{2+} decrease, and the concentration of NH_4^+ increases with depth. The ratios of $\text{Mg}^{2+}/\text{Ca}^{2+}$, $\text{Sr}^{2+}/\text{Ca}^{2+}$ increase sharply with depth. These geochemical data indicate strongly the presence of gas hydrates or deep water oil (gas) reservoirs beneath the seafloor.

In summary, mineralogical and geochemical data in the shallow sediments and pore waters suggest to us that the Southeast Hainan Basin is one of the promising targets on the northern margin of the South China Sea for further gas hydrate or deep water oil (gas) reservoir exploration. The data allow us to better understand the influence on the methane seep and geochemistry of fluids in shallow sediments exerted by gas hydrates or deep water oil (gas) reservoirs, whose presence could not be determined with certainty until there is further evidence, and the presence of methane seeps on the seafloor needs to be evidenced by swath bathymetry, shallow seismic data, or direct evidence on seafloor images in the future.

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