



# Pore-Water Geochemical Gradients of Sulfate, Calcium, Magnesium, and Iodide Correlated With Underlying Gas Hydrate Potential: A Case Study of the Shenhu Area, South China Sea

Xinyu Ai<sup>1</sup>, Rihuan Zha<sup>1</sup>, Yijun Lai<sup>1</sup>, Tao Yang<sup>1\*</sup> and Pibo Su<sup>2</sup>

<sup>1</sup>School of Earth Sciences and Engineering, Nanjing University, Nanjing, China, <sup>2</sup>Guangzhou Marine Geological Survey Guangzhou, China

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### \*Correspondence:

Tao Yang  
yangtao@nju.edu.cn

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Geochemical profiles in pore water of marine sediments have been considered as important indicators of gas hydrate occurrence. In the gas hydrate area around the world, the decrease of sulfate, calcium, and magnesium concentrations with depth mainly results directly or indirectly from the anaerobic oxidation of methane (AOM). The ubiquitous abnormally high concentration gradients of iodide in the research area reflect the large methane-generating potential of the area. Thus, we explore the feasibility of using gradients of sulfate, iodide, and authigenic carbonate precipitation as indicators for gas hydrate in the regional exploration of gas hydrate formation. We test the criterion in the gas hydrate zone in the South China Sea (SCS) for the recognition of gas hydrate by using the gradients of sulfate, calcium plus magnesium, and iodide. Contour maps of pore-water gradients from expeditions in the study area are used to correlate the key gradients to underlying gas hydrate occurrence. The results show that the largest potential gas hydrate indicated by the contour maps of the indicators are well consistent with the discovery of GMGS1 and GMGS3 expedition. It implies the possible applicability of this geochemical method in gas hydrate exploration. Also, we identify a promising area in the South China Sea for future gas hydrate investigations. It is the first collective application of the gradients of sulfate, calcium plus magnesium, and iodide to a gas hydrate terrane, especially to a large area of the SCS. We believe that the result of this research will benefit the future exploration of gas hydrate and will arouse a lot of interest from other researchers.

**Keywords:** Pore water, gas hydrate, geochemistry, South China Sea, sulfate, calcium, magnesium, iodide

## HIGHLIGHTS

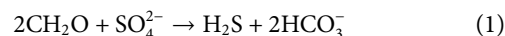
1. We link sulfate, calcium, magnesium, and iodide pore-water gradients to the occurrence of underlying gas hydrates.
2. We support this hypothesis using data from recognized gas hydrate occurrences globally.
3. We identify a promising area in the South China Sea for future gas hydrate investigations.

## 1 INTRODUCTION

The gas hydrate is an ice-like substance consisting of water and gas (most is CH<sub>4</sub>) that forms under conditions of low temperature, high pressure, and adequate gas concentration (Sloan, 1990). An accepted estimation of gas hydrate resources is about 3,000 trillion cubic meters (TCM), which is enormous when compared with the conventional gas resources (~404 TCM) and shale gas (204-456 TCM) (Chong et al., 2016). Due to its considerable reserves and clean combustion products, gas hydrate may become a promising energy resource (Collett, 2002; Hesse, 2003; Makogon et al., 2007; Boswell and Collett, 2011; Chong et al., 2016). The methane contained within gas hydrates is a kind of potential greenhouse gas, 20 times more effective as a greenhouse gas than carbon dioxide (CO<sub>2</sub>) (Mitchell, 1989; Ruppel, 2011). Therefore, any release of methane from gas hydrate decomposing due to temperature or pressure changes can cause a positive feedback cycle for atmospheric warming, thus impacting climate change (Borowski et al., 1996; Haq, 2000; Wallmann et al., 2014; Brown et al., 2016; Reay et al., 2018). Accordingly, the abundance, nature, and distribution of gas hydrate are of great importance and have been arousing a lot of research interests of many researchers.

Geophysical methods are widely applied to the study of gas hydrate distribution and abundance. Bottom-simulating reflectors (BSRs) are often coincident with gas hydrate occurrences at depth because dissociating gas hydrate produces in situ gaseous methane that causes an acoustic impedance contrast that generates its strong seismic reflector (Miller et al., 1991; Hornbach et al., 2012). However, a BSR is not necessarily associated with, or completely consistent with, the presence of gas hydrate (Kvenvolden et al., 1993; Le et al., 2015; Dumke et al., 2016). Thus, we try to improve the setup of regional gas hydrate exploration by employing some geochemical indicators. Geochemical methods have already

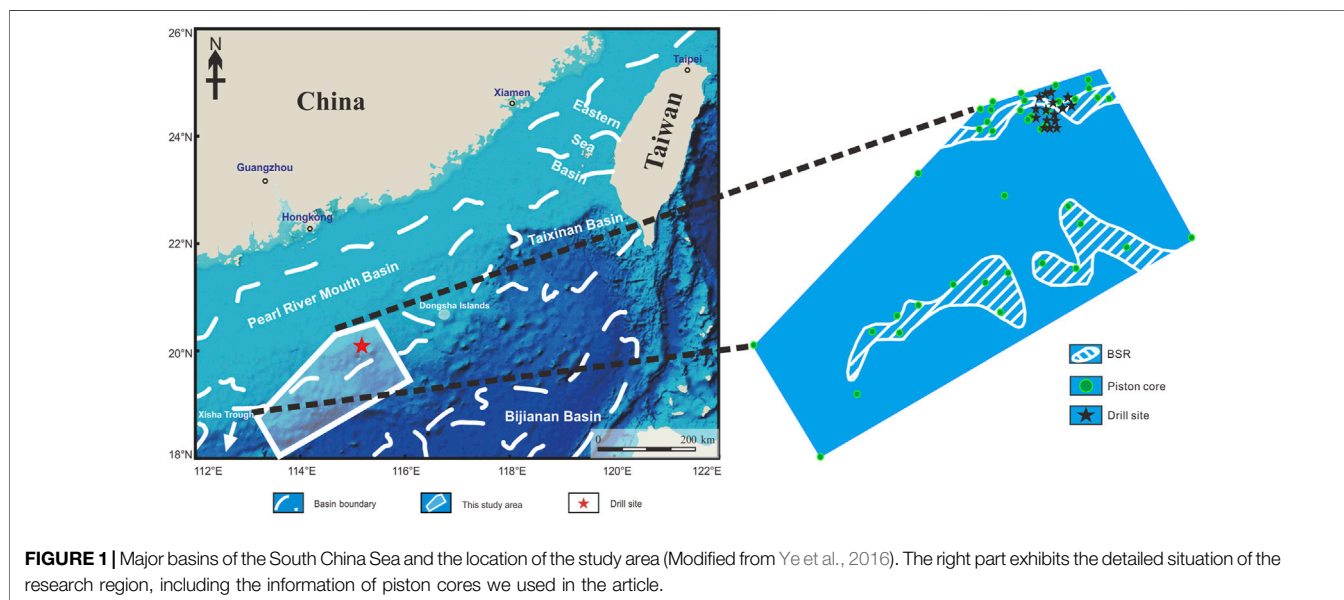
been tried to confirm potential gas hydrate-bearing areas through the geochemical studies of pore water in sediment (Borowski et al., 1996; Dickens, 2001; Bhatnagar et al., 2008; Wu et al., 2013; Pogodaeva et al., 2020). One of the most commonly used geochemical tools for hydrate recognition in drill cores is the presence of freshening chloride anomalies coupled with δ<sup>18</sup>O increase in pore water (Hesse, 2003; Luo et al., 2014). Nevertheless, the cores need to penetrate through the hydrate occurrence zone (often hundreds of meters below the seafloor) for the recognition of these anomalies, which is an economic disadvantage for large-scale exploration projects. Alternatively, the profiles of other pore water species (e.g., SO<sub>4</sub><sup>2-</sup>, Γ<sup>-</sup>) that record early diagenetic reactions in shallow sediments can serve as a powerful tool in gas hydrate exploration (Schulz, 2006). Some reactions associated with methane could be employed to indicate the existence of gas hydrate because a large amount of methane may occur in the gas hydrate occurrence zone. Within the sulfate reduction zone, normally, sulfate is consumed by organoclastic sulfate reduction (OSR) (Berner, 1980; Gieskes et al., 1981):

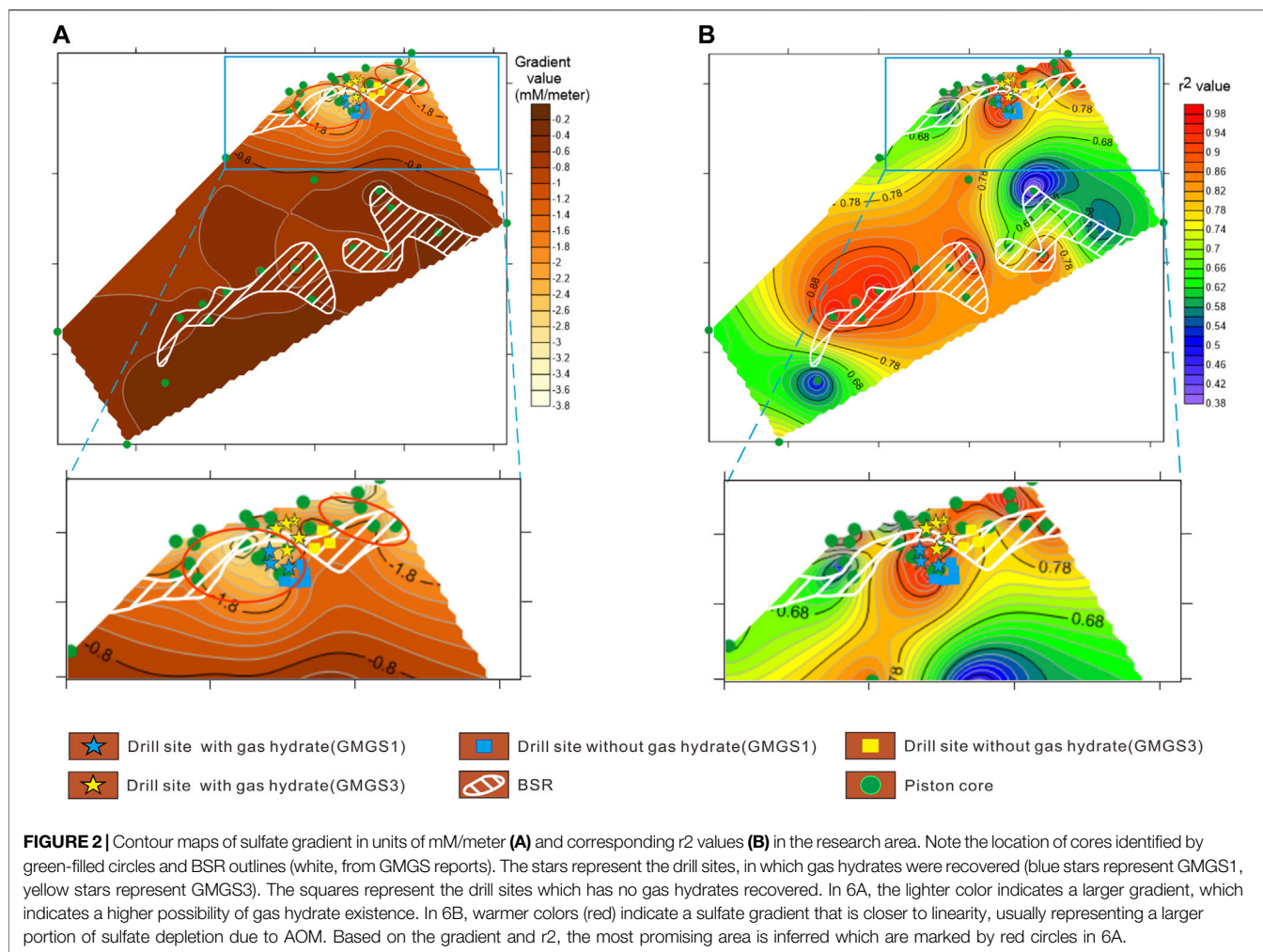


However, in the sulfate-methane transition zone (SMTZ, or SMI for sulfate-methane interface) where methane upwells from deep sediments, sulfate supplied from seawater will be exhausted by the anaerobic oxidation of methane (AOM) reaction (Barnes and Goldberg, 1976),



Substantial depletion of sulfate through AOM causes the SMTZ to become shallower (Blair and Aller, 1995; Borowski et al., 1996; Dickens, 2001). Some researchers accordingly proposed that the linearity of sulfate gradients and the shallow depth of SMTZ could be used to indicate the existence of gas hydrate-bearing areas (Borowski et al., 1999;

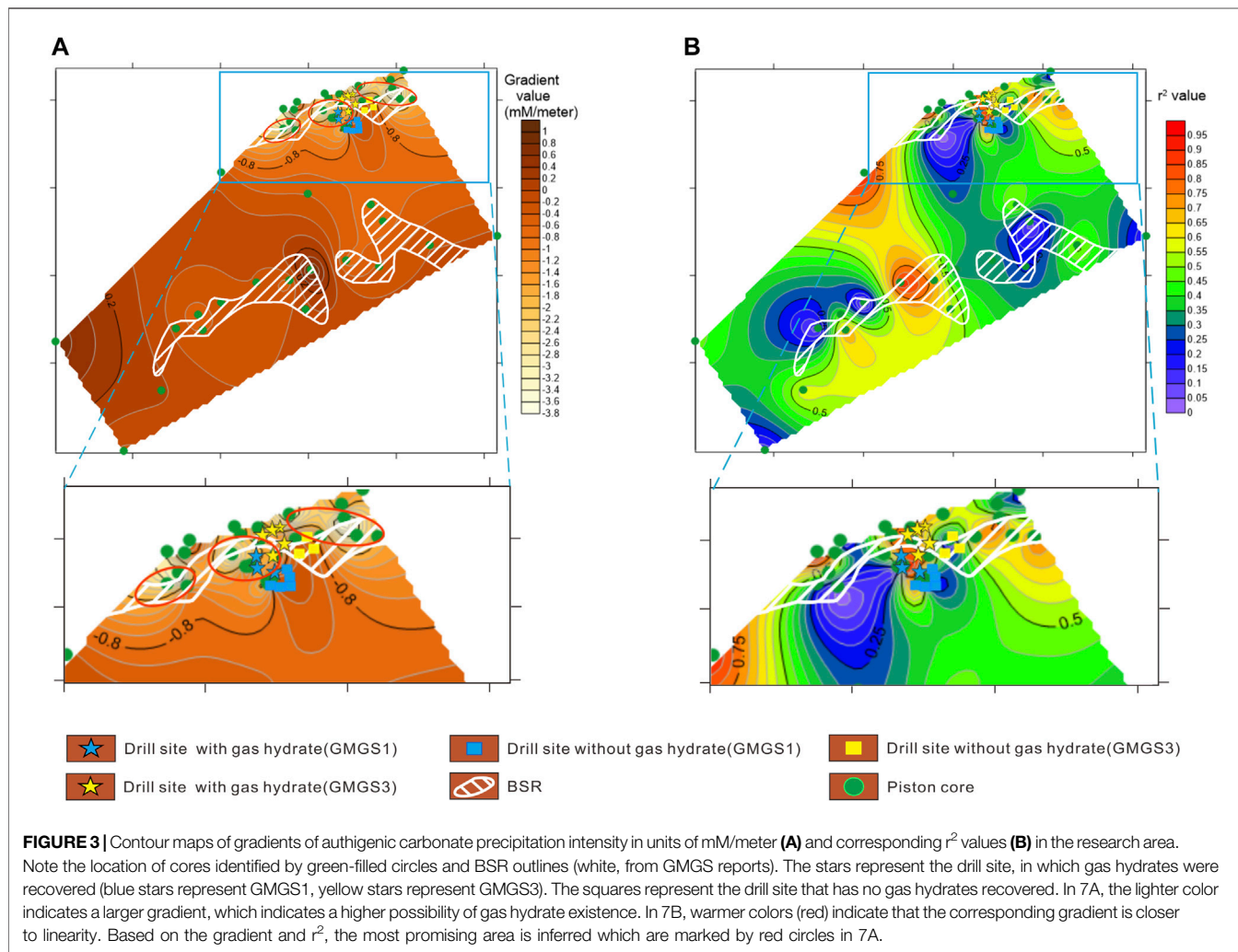




Kim et al., 2020). What's more, the calcium concentration of pore water is also sensitive to the AOM process (Rodriguez et al., 2000). It declines with depth due to the enhanced authigenic carbonate precipitation. At the SMTZ where intense AOM reactions occur, the sharp increase in pore water alkalinity may cause the rapid decrease in calcium concentration (Raiswell, 1988; Boetius et al., 2000; Rodriguez et al., 2000). Besides, concentrated iodine anomaly is also commonly observed in gas hydrate-bearing areas (Fehn et al., 2003; Fehn et al., 2006; Muramatsu et al., 2007). The abnormally high concentration of iodide in pore water is related to the decomposition of massive sedimentary organic matter, which represents a large potential gas source. As a result, the concentrated iodide concentration of pore water could also reflect the possible occurrence of gas hydrate. Based on previous research we mentioned above, we try to explore the feasibility of using gradients of sulfate, iodide, and authigenic carbonate precipitation as indicators for gas hydrate in the regional exploration of gas hydrate formation.

Many gas hydrate-bearing areas around the world have been identified and investigated including the Blake Ridge (Paull et al., 1996; Paull and Matsumoto, 2000), Hydrate Ridge (Milkov et al.,

2003; Torres et al., 2004), Gulf of Mexico (Boswell et al., 2009), Nankai Trough (Kastner et al., 1993) and Ulleung Basin (Park et al., 2008). In China, several geophysical and geochemical explorations of gas hydrate have been carried out on the northern slope of the South China Sea (SCS) since the 1990s (Zhang et al., 2002; Wu et al., 2004; Jiang et al., 2008; Wu et al., 2011; Zhang et al., 2012; Zhang et al., 2015; Jin et al., 2020; Wang et al., 2021). Numerous data from piston cores and drill sites have been accumulated, which allows us to make a regional comparison of hydrate distribution. The existence of gas hydrate in the northern SCS has been confirmed by geological, geophysical, and geochemical evidence including the occurrence of well-developed BSRs, methane-derived carbonate and shallow SMTZ depth (Liu et al., 2006; Song et al., 2007; Wang et al., 2011; Wu et al., 2011; Li et al., 2012; Li et al., 2015; Zhang et al., 2015; Chen et al., 2016; Jin et al., 2020). During the Sino-German Cooperative Project in early 2004, methane seepages in the SCS were verified for the first time by the discovery of Jiulong Methane Reef (Han et al., 2008). Three years later, natural gas hydrate samples were first recovered in a gas hydrate drilling expedition (GMGS1) which was initiated by Guangzhou Marine Geological Survey in the Shenhu area, northern SCS (Zhang et al., 2007; Wu



et al., 2011). In 2013, GMGS2 was conducted in the east of Pearl River Mouth Basin of SCS, and massive gas hydrates were successfully recovered (Zhang et al., 2015). Recently, several visible gas hydrates were recovered in the Shenhu area again during the expedition GMGS3, which further constrain the gas hydrate reserves of the SCS (Yang et al., 2015). In 2016, GMGS4 was conducted in Shenhu area, and the new gas hydrates were found (Yang et al., 2017). In 2018, GMGS5 was conducted in Qiongdongnan area of SCS, and massive gas hydrates were sampled (Ye et al., 2019).

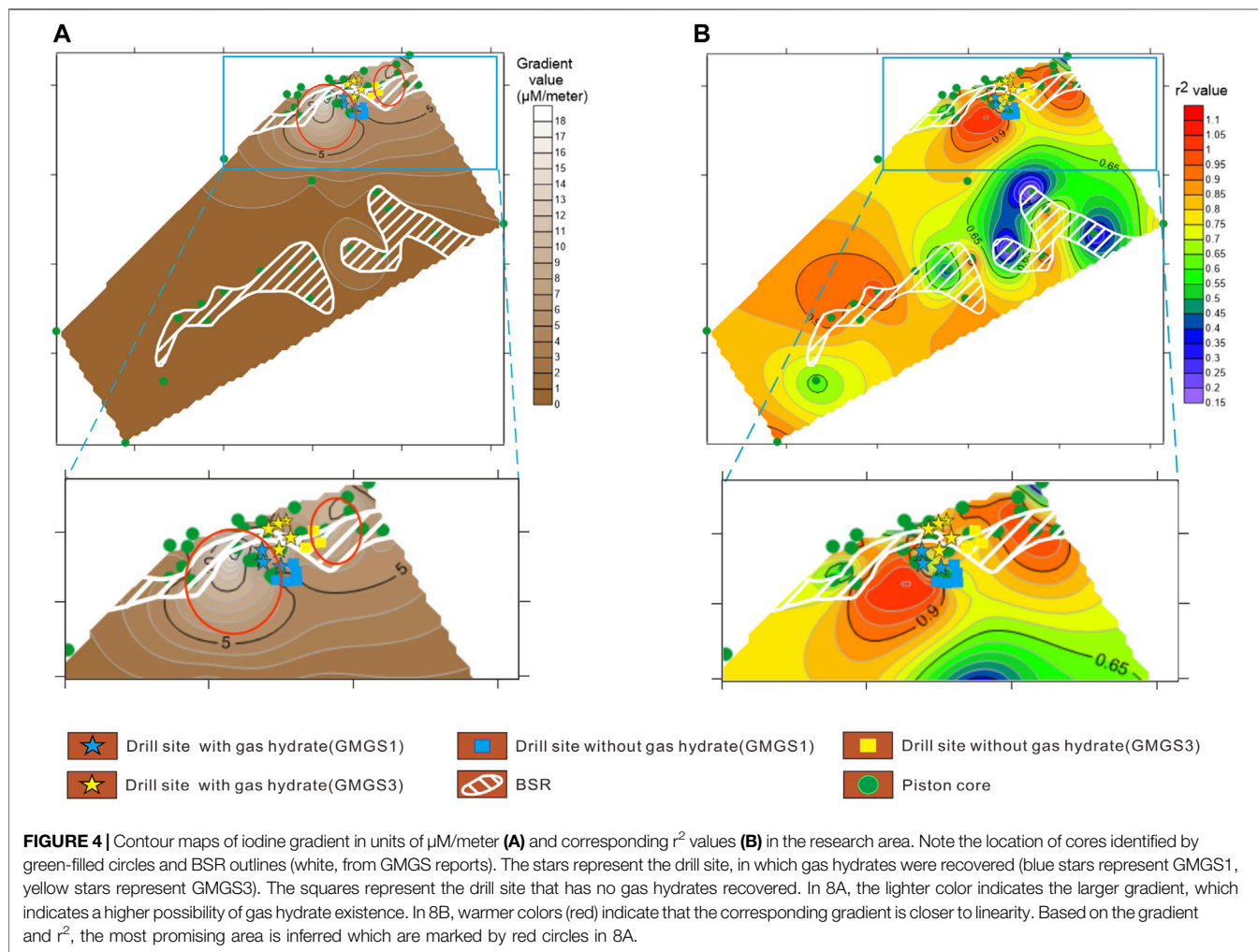
Based on previous gas hydrate research, we correlate comprehensive geochemical indicators, the gradients of sulfate, calcium plus magnesium, and iodide, to the occurrence of underlying gas hydrate in marine sediments. The approach is based on the influence of the occurrence of gas hydrate on the geochemical characteristics of shallow pore water and was tested by correlating the collective gradients to known areas of gas hydrate. This result is compared with the hydrate detection results of GMGS1 and GMGS3. Based on this geochemical criterion, we also predict another promising area for future gas hydrate exploration in the northern SCS through the geographic information system. We believe that this research will benefit the

future exploration of gas hydrate and will arouse a lot of interest from other researchers.

## 2 GEOLOGICAL SETTING AND METHODS

The South China Sea, tectonically controlled by interactions of Eurasian Plate, Pacific Plate, and Indo-Australian Plate, is one of the largest marginal basins in the western Pacific Ocean (Li, et al., 2012; Wang et al., 2013). A series of sedimentary basins (e.g., the Taixinan Basin, the Pearl River Mouth Basin, and the Qiongdongnan Basin) in the northern SCS are filled with Mesozoic and Cenozoic sediments, whose largest thickness is over 10 km. The thick sediments provide ideal methane sources for gas hydrate formation (Lüdmann and Wong, 1999). Moreover, the northern slope of the SCS has a water depth of 200~3400 m and a bottom water temperature of 2~5 °C, these temperature and pressure conditions are suitable for gas hydrate formation (Yao, 2001).

The study region, the Shenhu area, is situated in the middle of the northern slope of SCS (between the Xisha Trough and the Dongsha Islands) (Figure 1). In this area, quantities of



deepwater sedimentary fan have developed since Neogene, with average sedimentation rates of 110, 38, 27  $\text{m Ma}^{-1}$  for Pleistocene, Pliocene, Miocene respectively (Wu et al., 2011). A series of high-angle faults and vertical fracture systems cut the sedimentary section since Pliocene. A series of central diapiric areas such as gas chimneys are well developed in the Shenhu area, providing favorable geological environments and structures for gas hydrate formation (Lüdmann et al., 2001; Wu et al., 2004). High-resolution seismic investigations show that most of BSRs are 150-350 m below the seafloor (Wu et al., 2013). In order to detect the occurrences and determine the distribution of gas hydrates, some surveys have been carried out by Guangzhou Marine Geological Survey since the 1990s. Hundreds of piston cores were recovered by research vessels of the Guangzhou Marine Geological Survey in recent years.

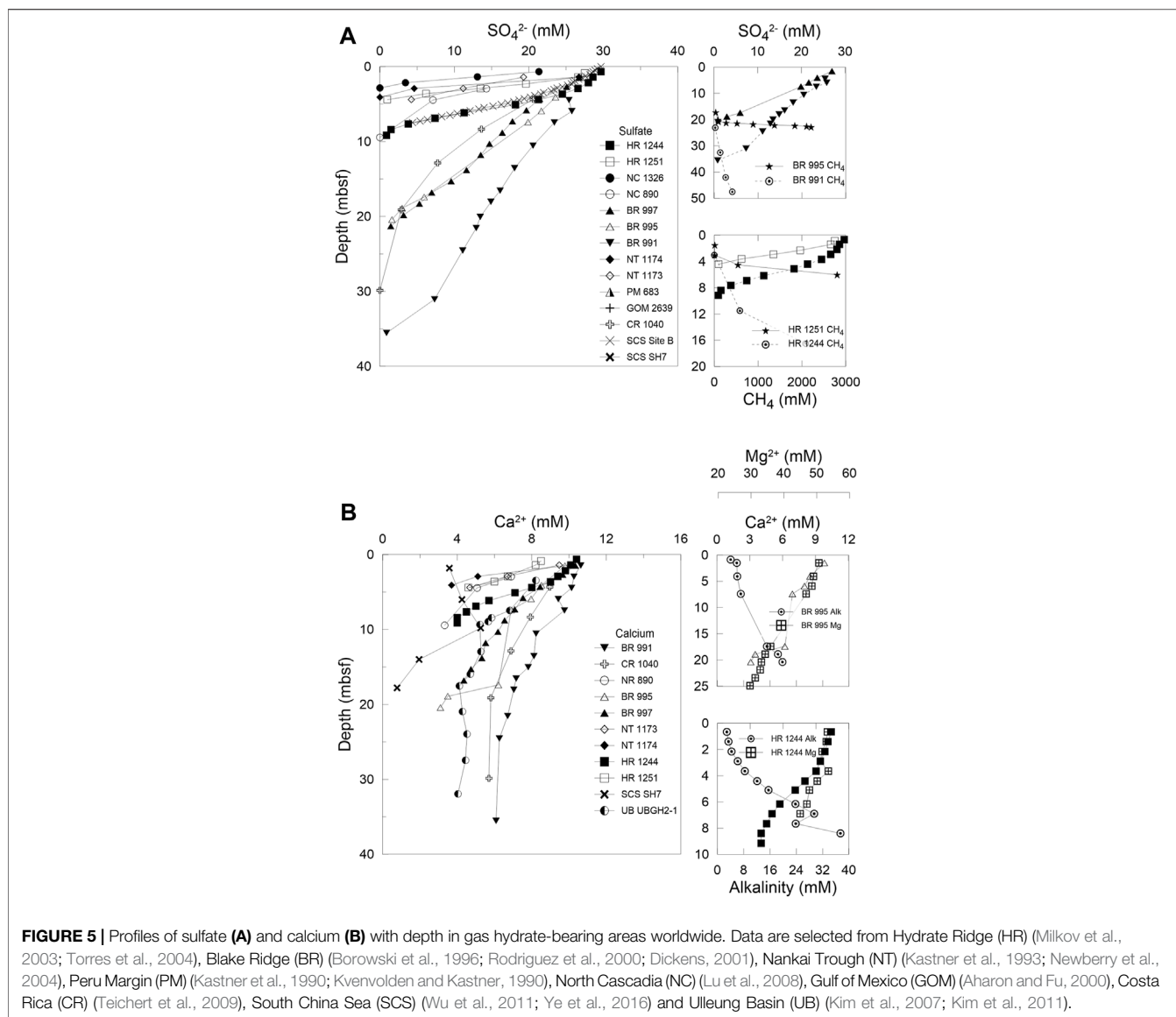
All the geochemical data were measured at the state key laboratory for mineral deposits research, Nanjing University. The anions and cations of pore water except iodide were measured by an ion chromatography (Metrohm 790-1, Metrosep A Supp 4-250/Metrosep C 2-150). Anions were eluted by 1.8  $\text{mM Na}_2\text{CO}_3$  + 1.7  $\text{mM NaHCO}_3$ . For cation

system, ions were eluted by 4  $\text{mM}$  dihydroxysuccinic acid + 0.75  $\text{mM}$  pyridinedicarboxylic acid. In both systems, the flow rate of eluent was set at 1.0  $\text{mL}/\text{min}$ , and the relative standard deviation of the measurement results was less than 3%. Iodide was measured using an inductive couple plasma mass spectrometry (ICP-MS) (Element II, ThermoFisher), and the analytical precisions were estimated to be <2%. Samples for iodide measurement was prepared by diluting in 1% aqua ammonia with 10 ppb of Rh as an internal standard.

The gradients of indicators are calculated by least-squares fitting, generating a correlation coefficient ( $r^2$ ) used to assess the linearity of geochemical profiles. Detailed data of core sites are shown in **Table 1**. The  $r^2$  value ranges from 0-1, which represents a strong correlation at value 1, a decoupling correlation at value 0. Both the gradient and corresponding  $r^2$  values are mapped over the study area using Surfer® software.

### 3 RESULTS

We analyzed 246 pore water samples from 23 piston cores in Shenhu area (**Figure 1**). Due to the space limitation and since the



gradient redox is what we mainly discuss, in this paper we only show the gradient and  $r^2$  calculated from sulfate, iodide and calcium plus magnesium concentration profiles (Table 1).

The downward concentration gradients of sulfate, calcium plus magnesium ions and iodide vary from -0.2 to -3.72, from 0.94 to -3.15 and from 0.13 to 11.3, respectively.

HS428PC has the steepest decreasing gradient of sulfate and the steepest increasing gradient of iodide. HS251PC has the lowest sulfate decreasing gradient and HS60PC has the lowest iodide increasing gradient. For calcium plus magnesium, the downward gradient values exhibit both negative and positive. The highest downward increasing gradient of calcium plus magnesium occurs in HS08-6PC and the highest downward decreasing gradient is in HS296PC. Almost all the sites with relatively high absolute gradient values have the  $r^2$  values close to 1.

The absolute values of sulfate and iodide downward gradient have a positive relationship, which means that when sulfate decreasing trend is steeper, the iodide has a steeper increasing trend. The calcium plus magnesium concentration gradient is more complicated, but in general, the absolute values exhibit a positive relationship with sulfate and iodide.

The sites with highest absolute gradient values of sulfate, iodide or authigenic carbonate intensity [i.e., the depletion of  $(Ca^{2+}) + (Mg^{2+})$ ] are invariably distributed in the northeast region of the study area (in red circles from Figure 2A, Figure 3A and Figure 4A) where the  $r^2$  values are also high. The absolute gradient values gradually decrease from the northeast corner to the rest of the study area, with most of study area showing low absolute values except the northeast region. In addition, it has to be noticed that high  $r^2$  values also exist in other regions except for the northeast area.

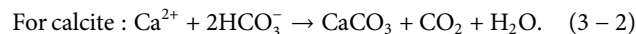
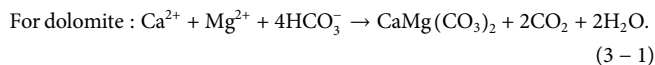
## 4 DISCUSSION

### 4.1 Geochemical Anomalies Associated With Gas Hydrate

#### 4.1.1 AOM Process

In the gas hydrate-bearing areas, AOM is usually strong due to the enrichment of methane. Methane flux from below causes a significant portion of the interstitial sulfate pool to be consumed through AOM and deplete sulfate more rapidly than OSR alone (Borowski et al., 1996; Borowski et al., 2000). Under the correct condition, intense AOM can result in the linear depletion of sulfate, while OSR leads to a convex curve of the sulfate gradient. (Borowski et al., 1996; Niewöhner et al., 1998; Dickens, 2001; Joye et al., 2004). Thus, under the condition where AOM is intense due to the upward methane flux from below in the methane seepage area of the gas hydrate zone, the curve of sulfate gradient is impacted mainly by AOM rather than OSR. As shown in **Figure 5A**, the rapid consumption of sulfate with depth is common in gas hydrate-bearing sites all over the world. Despite the general downtrend, there are some differences in sulfate gradients among different regions due to the various tectonic and sedimentary environments. For the same region, larger methane flux usually leads to steeper sulfate gradients, as clearly shown in **Figure 5A**. For example, in Black Ridge, the methane flux of Site 995 is larger than Site 991, and the sulfate gradient of Site 995 is steeper. A similar situation occurs in Hydrate Ridge where the sulfate gradient of Site 1,251 is steeper than that of Site 1,244 perhaps due to the larger methane flux of Site 1,251.

Increased consumption of sulfate through AOM also can result in increases in alkalinity near the SMTZ, producing a diagenetic environment beneficial to the precipitation of dissolved calcium and magnesium to form authigenic carbonate cement:



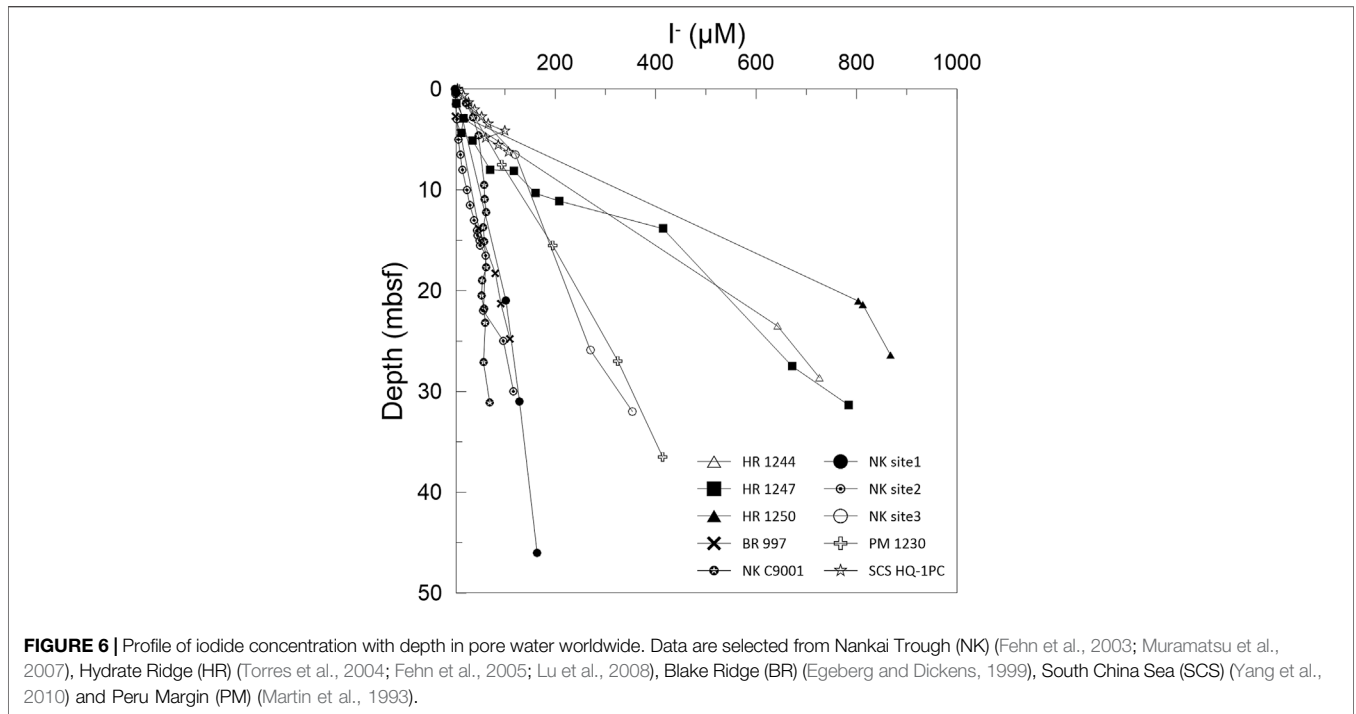
Concentrations of calcium and magnesium ions usually decrease with depth (Raiswell, 1988; Blair and Aller, 1995; Rodriguez et al., 2000; Tong et al., 2013). As the result of authigenic carbonate precipitation,  $\text{Ca}^{2+}$  exhibits a similar downward trend to that of sulfate in these gas hydrate-bearing sites (**Figure 5B**). The concentrations of calcium and magnesium ions decrease as the alkalinity rises with depth. The alkalinity often reaches its maximum in the SMTZ, as exemplified in both Blake Ridge and Hydrate Ridge (**Figure 5B**). It shows that AOM has a great effect on calcium and magnesium ions. Consequently, strong authigenic carbonate precipitation could occur in the gas hydrate-bearing areas.

#### 4.1.2 Decomposition of Organic Matter

The gas source that is necessary for hydrate formation, thermogenic or biogenic, ultimately originates from the decomposition of organic matter (Kvenvolden and McMenamin, 1980; Kvenvolden, 1998; Clennell et al., 1999; Wallmann et al., 2006). Biophilic elements such as iodine are

**TABLE 1** | The detailed data of core sites, which are used to draw contour maps.

Core site	BSR present?	Water Depth	Sulfate gradient (mM/m)	r <sup>2</sup> value	Ca + Mg gradient (mM/m)	r <sup>2</sup> value	Iodide gradient (μM/m)	r <sup>2</sup> value
HS23PC	Yes	1301	-2.79	0.92	-0.49	0.78	6.98	0.98
HS57PC	Yes	2930	-0.31	0.91	-0.20	0.35	0.18	0.81
60PC	Yes	2314	-0.92	0.8	0.30	0.73	0.13	0.38
HS217PC	Yes	1204	-1.85	0.75	-0.18	0.71	10.08	0.89
HS219PC	Yes	1266	-1.62	0.82	-2.68	0.54	5.17	0.99
HS243PC	Yes	2072	-0.69	0.65	-0.85	0.36	1.75	0.13
HS247PC	Yes	2505	-0.66	0.49	-0.69	0.24	1.07	0.96
HS251PC	Yes	2282	-0.2	0.37	-0.18	0.52	0.54	0.12
HS253PC	Yes	2453	-0.53	0.69	-1.81	0.06	0.78	0.94
HS260PC	Yes	2794	-0.22	0.55	-1.25	0.29	0.31	0.25
HS296PC	Yes	1094	-1.77	0.72	-3.15	0.04	8.29	0.99
HS359PC	Yes	940	-2.56	0.77	-1.88	0.67	10.35	0.93
HS08-5PC	Yes	2140	-0.58	0.99	0.71	0.06	0.84	0.95
HS08-6PC	Yes	2385	-0.53	0.9	0.94	0.46	0.5	0.88
HS08-7PC	Yes	2660	-0.65	0.98	-1.48	0.01	0.93	0.99
HS08-14PC	Yes	3320	-0.39	0.83	0.54	0.01	0.43	0.88
HS389PC	No	1380	-1.48	0.83	-1.64	0.01	3.17	0.62
HS396PC	No	1210	-2.76	0.94	-1.62	0.78	10.75	0.93
HS412PC	No	740	-2.65	0.91	-2.85	0.67	8.23	0.94
HS428PC	No	766	-3.72	0.98	-2.12	0.27	11.3	0.99
HS446PC	No	710	-2.47	0.75	-1.11	0.4	3.04	0.19
HS08-8PC	No	1960	-0.36	0.87	-1.76	0.34	0.38	0.79
HS08-11PC	No	2178	-0.63	0.98	-1.02	0.16	0.8	0.99

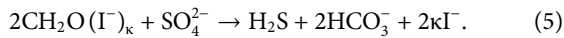


also released in the process of organic matter decomposition, contributing dissolved iodide ( $I^-$ ) to pore waters:



Where  $\kappa$  represents the molar fraction of iodide in organic matter.

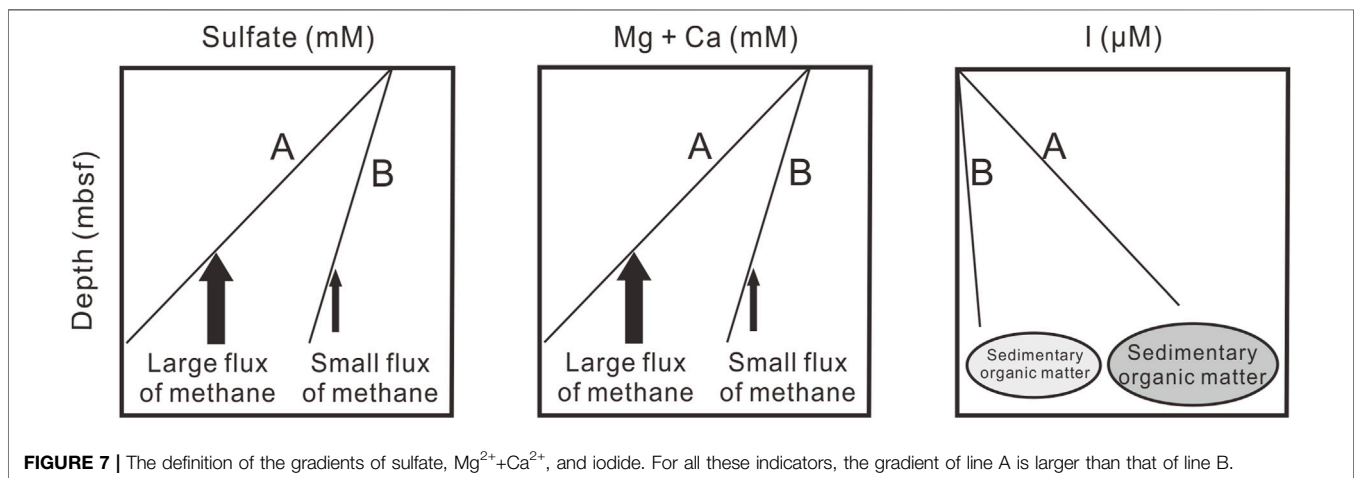
Within sulfate reduction zone, the organic matters are reduced by sulfate, and also release the iodide:



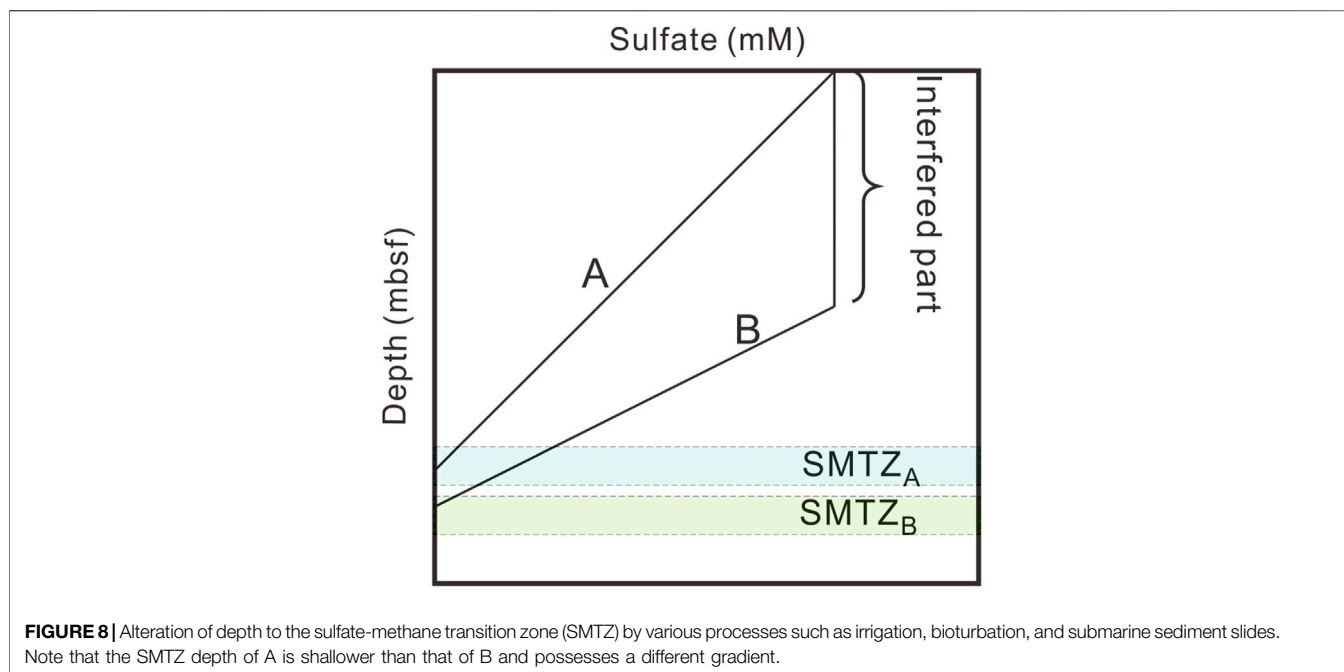
Where  $\kappa$  also represents the molar fraction of iodide in organic matter. High iodide gradient implies a high organic matter decomposition rate, no matter in gas source region below SMTZ or sulfate reduction zone, which will cause a high reaction rate of both methanogenesis and OSR. Therefore, high methane flux can still be indicated by high iodide

gradient although the OSR rate can be high. In addition, the iodide migrates from gas source can elevate the iodide gradient to several magnitude high (e.g., HS428PC relative to 60PC), which is much more significant than the iodide released from OSR.

As a result, iodide exhibits abnormally high concentration in gas hydrate-bearing areas (Kastner et al., 1993; Martin et al., 1993; Egeberg and Dickens, 1999; Fehn et al., 2003; Fehn et al., 2006; Yang et al., 2010). As shown in **Figure 6** in gas hydrate-bearing areas, the iodide concentration of pore water ( $[I^-]_{\text{porewater}}$ ) increases to several hundred times that of the seawater value ( $[I^-]_{\text{seawater}}$ ). There is also a regional variation in iodide gradient because the types and activity of organic matter that have a regional difference could affect the process of decomposition. The organic matter of large activity is liable to decomposition. It is noteworthy that the abnormally high concentration of iodide is







not only supplied by the decomposition of local organic matter but may also be influenced by other sources (Fehn et al., 2006; Lu et al., 2008). Fehn et al. (2006) proposed that a large fraction of the iodine is derived from another source that was located to the east (40 km) of Hydrate Ridge through the iodine isotopic dating of pore water. Because of the similar diffusion coefficients between iodide and methane, external fluids from organic matter decomposition simultaneously transport iodine and methane to this site, which promotes the gas hydrate formation by offering a major fraction of methane in the Oregon Hydrate Ridge. To conclude, the high concentration of iodide would reflect massive organic matter decomposition, no matter from internal or external sources, which is helpful to the formation of gas hydrate.

## 4.2 Definition of Anomaly Indicators

In gas hydrate-bearing areas, the upward methane flux usually exists due to the more likely methane seepage, which may lead to steep sulfate gradients and carbonate precipitation. What's more, the enrichment of iodide may also indicate the existence of the regional methane source because the iodine and methane may be derived from the same source. Accordingly, we use three pore-water geochemical indicators – sulfate gradients, calcium plus magnesium gradients (a proxy for authigenic carbonate formation), and iodide gradient to recognize potential gas hydrate occurrence in underlying sediments. In each case, the higher the gradient, the greater the possibility of gas hydrate formation (Figure 7).

As mentioned above, magnesium and calcium are sensitive to the flux of methane, and iodine reflects the potentiality of the gas source. The indicator proposed here has several advantages over the SMTZ depth proxy. One major shortcoming of using the SMTZ depth as the indicator for hydrate recognition is that the SMTZ depth is liable to be altered by environmental factors such

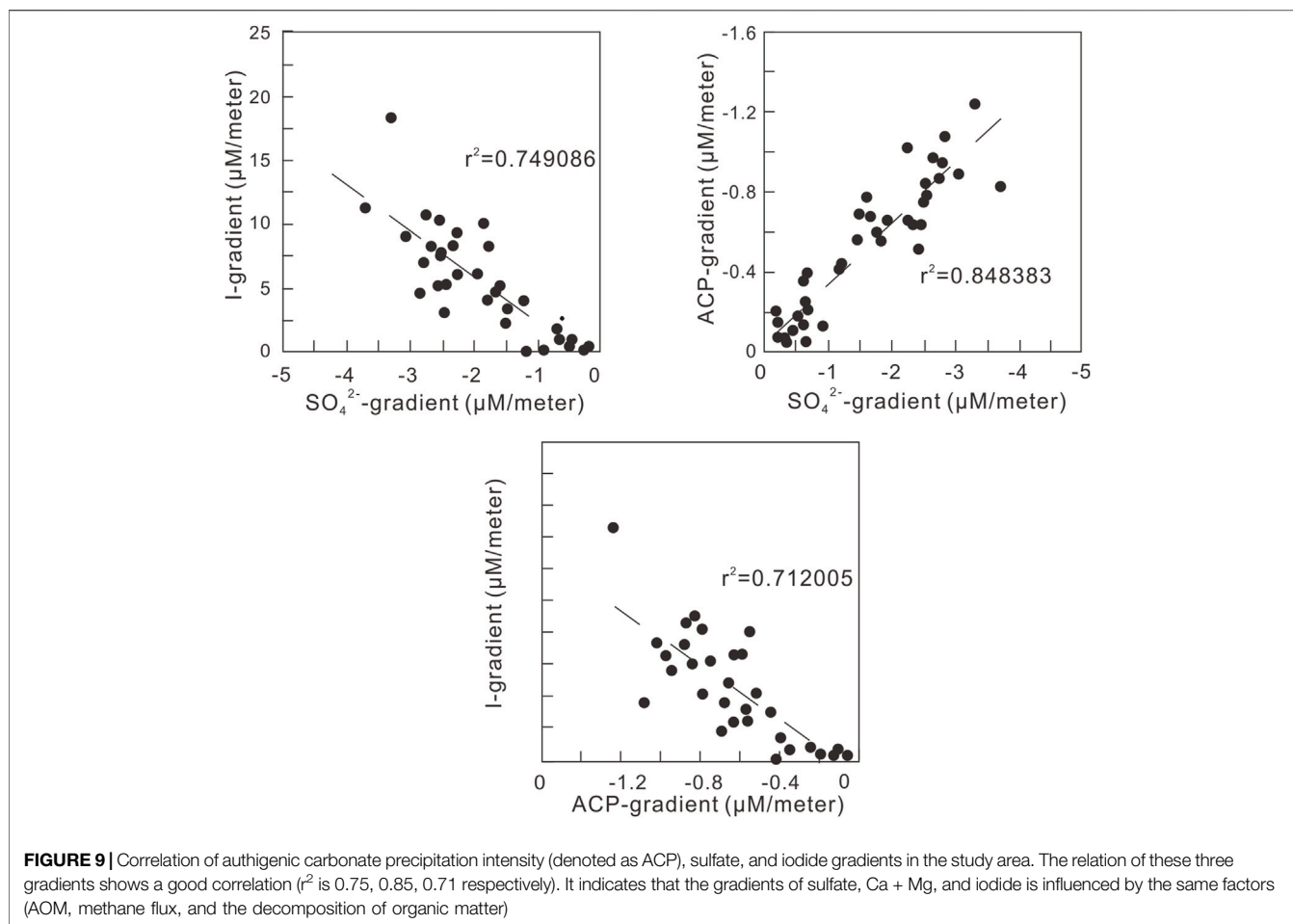
as irrigation, bioturbation, and submarine slide displacement (Fossing et al., 2000; Zabel and Schulz, 2001; Croguennec et al., 2016). As shown in Figure 8, the SMTZ of Site A is shallower than that of Site B, which nevertheless contains an interfered part. In this case, using the SMTZ depth as the indicator for hydrate recognition may result in erroneous results. However, by using the gradient of sulfate as the indicator, the correct conclusion can be obtained.

## 4.3 The Contour Maps of three Indicators and Corresponding $r^2$ Value in the Shenhu Area

We have accumulated sizeable piston-coring data in the study area during the past decade, which provides us with an ideal chance to test the robustness of this new criterion. The gradients of the three indicators (i.e., sulfate,  $Mg^{2+}+Ca^{2+}$ , and iodine) of all the core sites in the research area are presented in the form of contour maps. For each indicator, the  $r^2$  values are also given in the corresponding contour map to characterize the shape and linearity of the concentration profile and further assess its relationship to AOM and underlying gas hydrate. The distribution of BSRs on contour maps is acquired from Guangzhou Marine Geological Survey reports.

### 4.3.1 Sulfate Gradient

Mapping results of sulfate gradients are shown in Figure 2A. In Figure 2A, the lighter the color is, the larger the sulfate gradient is (see Figure 7 for the definition), which corresponds to a larger possibility of hydrate existence. The lightest colors can be found mainly in the northeast of the study area and are roughly divided into two parts. Both two parts (red circles) are the most promising areas for gas hydrate occurrence. The yellow stars and blue stars in



**Figure 2** are drill sites where gas hydrate samples have been collected in GMGS1 and GMGS3 expedition (yellow represents GMGS1, blue represents GMGS3), including the first gas hydrate sample of China, recovered during the GMGS1 expedition, 2007 (Wu et al., 2013). The yellow squares and blue squares in **Figure 2** represent drill sites that have no gas hydrate samples recovered. It is shown in **Figure 2A** that the stars locate mostly in one of the red circles, while squares locate mainly out of the red circles. It indicates that the gradient of the sulfate is related to the occurrence of gas hydrate to some extent. Corresponding  $r^2$  values of stars are also high (close to 1) in the contour map of  $r^2$  (**Figure 2B**). The other red circle is the promising area predicted by this criterion for gas hydrate occurrence and it needs to be tested by future exploration.

#### 4.3.2 Authigenic Carbonate Precipitation Intensity

The contour map of the intensity of authigenic carbonate precipitation exhibits a similar result to that of sulfate gradients (**Figure 3A**). It also suggests that the northeastern part of the study area, which however could be roughly divided into three small parts, is the most promising area of gas hydrate occurrence. The stars are located in the middle red circle, which is coherent with the mapping result of the criterion. Also, the other two red circles are

promising areas for gas hydrate occurrence. In **Figure 3B**, the corresponding  $r^2$  values in the red circles are high (close to 1), which ensures the reliability of the gradient estimation.

#### 4.3.3 Iodide Gradient

As for iodide, in the contour map (**Figure 4**), the lighter (white area) the color is, the larger the gradient is. In **Figure 4A**, two promising areas (red circles) for gas hydrate occurrence are identified. For the third time, the stars are located in one of the red circles, which is again coherent with the mapping result of the criterion. The other circle is a promising area for the existence of gas hydrate. The  $r^2$  values in the red circles are also close to 1, which again supports the reliability of the gradient values.

#### 4.4 The Correlation of Anomaly Indicators

Through the correlation diagrams of authigenic carbonate precipitation intensity, sulfate, and iodine gradients of the study area, there is some correlation among them (**Figure 9**). It suggests that all of them are controlled by similar factors, i.e., the decomposition of organic matter and methane production. On the one hand, the organic matter fermentation and disintegration (both biological and thermal decomposition) could release methane and iodide, so the increase in methane and iodide are coupled to some degree. On the other hand, an increased flux of

methane would strengthen the AOM process, which fuels the sulfate reduction and the precipitation of calcium and magnesium. Thus, we propose that these three indicators could be used together as powerful tools in the exploration of gas hydrates.

## 5 CONCLUSION

We investigated the concentration profiles of sulfate, calcium, magnesium and iodide in pore water from worldwide main gas hydrate-bearing sites. Each kind of ion has a similar trend in different sites, but shows different downward gradients.

The gradients of sulfate concentration, calcium plus magnesium concentration and authigenic carbonate precipitation intensity can indicate the rate of AOM, which is mainly influenced by the flux of methane. Iodide concentration is strongly affected by the decomposition of organic matter from gas source, and can indicate the methane flux from below or other sources. Thus, the higher the values of these indicators are, the more likely gas hydrate exists in the deep. Also, in some cases where irrigation, bioturbation or submarine slide displacement occurs, the depth of SMTZ is not accurate to indicate the flux of methane, and the sulfate gradient can be a more accurate one.

According to the response of pore water composition in shallow sediment to the high flux of methane in gas hydrate-bearing areas, we proposed that the gradients of sulfate, authigenic carbonate precipitation, and iodide together could be comprehensively employed as the indicators in the exploration of gas hydrate. These indicators were applied to the Shenhu area, SCS, and the results were presented in the form of contour maps. Satisfactory, the most promising area for

hydrate occurrence predicted in the three contour maps is consistent with the discovery of GMGS1 and GMGS3 expeditions, which indicates the availability of this criterion. According to the criterion, a new promising area for the existence of gas hydrate was identified, though it needs to be tested by future exploration. We believe that this new geochemical criterion will benefit the exploration of gas hydrate in the future.

## DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

## AUTHOR CONTRIBUTIONS

TY provided the main idea and financial support. XA wrote the main part of the manuscript. RZ checked the English and finished the manuscript. YL finished the experiments in the manuscript. PS gave some important suggestions about manuscript revision.

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