

Article

# Deeply Buried Authigenic Carbonates in the Qiongdongnan Basin, South China Sea: Implications for Ancient Cold Seep Activities

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Received: 9 November 2020; Accepted: 10 December 2020; Published: 17 December 2020



Abstract: Cold seep carbonates are important archives of pore water chemistry and ancient methane seepage activity. They also provide an important contribution to the global carbon sink. Seep carbonates at three sediment layers (3.0, 52.1, and 53.6 mbsf) were collected at site W08B in the Qiongdongnan Basin of the South China Sea. This study investigated the mineralogy, microstructure, stable carbon and oxygen isotopes, trace elements, and U-Th dates of these carbonates to identify the relationship between methane flux and authigenic carbonate precipitation. The results showed that the  $\delta^{13}$ C and  $\delta^{18}$ O values of all carbonates are similar, indicating that the carbon source for shallow carbonates and deep carbonates has remained constant over time and included biogenic and thermogenic methane. Although carbonates were found in three sediment layers, the two main stages of methane seepage events were discernible, which was likely caused by the dissociation of gas hydrates. The first methane seep took place at 131.1–136.3 ka BP. During a dramatic drop in the sea level, the seep carbonate at 52.1 mbsf formed at 136.3 ka BP through the anaerobic oxidation of methane (AOM). The carbonate at 53.6 mbsf resulted from the vertical downward movement of the sulfate-methane transition zone with decreasing methane flux at 131.1 ka BP. This is the reason for the age of carbonates at 52.1 mbsf being older than the age of carbonates at 53.6 mbsf. The second methane seep took place at 12.2 ka BP. Shallow carbonate formed at that time via AOM and is now located at 3 mbsf. Moreover, thin-section photomicrographs of deep carbonate mainly consisted of matrix micrite and biological debris and acicular aragonite occurred as vein cement filling the pore spaces between the matrix micrite. The acicular aragonite was mainly influenced by the timing of the carbonate precipitation of minerals. This research identified a long history of methane seep activity reflected by the vertical distribution of carbonates.

**Keywords:** cold seep; South China Sea; authigenic carbonate; gas hydrate; U-Th dating; rare earth element

# 1. Introduction

A deep-sea cold seep is a unique environment where deeply sourced fluids (containing methane and other hydrocarbon gases) migrate upward and seep from the seafloor [1]. Cold seep development is mainly driven by overpressure, which is caused by tectonic compression and rapid sediment deposition [2,3]. Therefore, unlike hydrothermal systems, which are mainly distributed in mid-ocean ridges [4,5], cold seeps are widely dispersed throughout the active and passive continental margins



and sedimentary basins with thick sediments [3,6–8]. Methane reacts with seawater sulfate via the sulfate-driven anaerobic oxidation of methane (SR-AOM), which produces hydrogen sulfide and bicarbonate [9], and provides nutrients for chemosynthetic communities [10–12]. Therefore, a special chemosynthetic ecosystem [13], widely distributed carbonate on the seafloor [14], and gas bubble emission from the seafloor [15,16] are important indicators for the identification of marine cold seeps. It is of great significance to study the distribution and activity of these cold seeps because they are not only used as indicators for deep-water petroleum exploration at the early stage [17], but are also closely related to global climate change [18], ocean acidification [19], and the global carbon cycle [20,21].

Seep carbonates represent important records of cold seep activities [22]. Comprehensive studies, investigating mineralogy, stable carbon isotope ( $\delta^{13}$ C) ratios, oxygen isotope ( $\delta^{18}$ O) ratios, rare earth elements (REEs), and dating (U-Th and <sup>14</sup>C), have been conducted. Seep carbonates have been sampled from various sea areas worldwide, thus providing the possibility to reconstruct the cold seep environment and its activity [23–28]. The  $\delta^{13}$ C provides particularly valuable clues for developing a better understanding of the carbon source [23], while the  $\delta^{18}$ O plays a significant role in identifying the surrounding temperature and fluid source during carbonate formation [29]. REEs are an important proxy for reconstructing the prevailing redox conditions [24]. Furthermore, dating based on U-Th and <sup>14</sup>C is often used to identify the relationship between cold seep activity and global climate change [30].

Over the past two decades, several active cold seeps have been discovered on the northern slope of the South China Sea [31], including the Jiulong seeps [32], Haima cold seeps [10], and station F [33]. In recent years, a large number of seep carbonates have been collected from these cold seeps by multiple research expeditions [30–32,34]. More information on cold seep activities has been increasingly reported. These samples were usually obtained by a gravity corer or a remotely operating vehicle (ROV) in shallow sediment. However, most carbonates in shallow sediments have ages younger than 20 ka, which cannot help to study a longer period of cold seep activity.

Controlled by various factors, such as the gas supply, deep strata pressure, changes in the sea level, global climate change, and gas hydrate and carbonate formation, cold seeps are usually intermittently and periodically active [10,14,35]. Therefore, seep carbonates buried at different depths are valuable for reconstructions of the historical activities of ancient cold seeps [26]. However, since they are buried deep in the marine sediment, these samples can only be obtained by drilling, which is very costly. Therefore, very few drilling expeditions are specifically designed for cold seep research. In 2018, the Guangzhou Marine Geological Survey (GMGS) carried out the fifth natural gas hydrate drilling expedition in the Qiongdongnan Basin of the South China Sea (Figure 1) [36]. Seep carbonates were obtained from multiple layers of site W08B (Figure 1) [30]. Based on both field data and literature research, preliminary hypotheses of the cold seep activity were formulated [30]; however, these hypotheses have not been validated by geochemical data. This study systematically investigated the seep carbonates in multiple horizons of site W08B, using mineralogy,  $\delta^{13}$ C,  $\delta^{18}$ O, U-Th dating, and REE analysis. The age, carbon and oxygen sources, and redox environment of carbonate formation were discussed. Based on the U-Th ages, the sedimentation rate in this area was further calculated. Finally, the relationship between methane flux and different carbonate textures, as well as the relationship between the historical activity of methane seeps and the distribution of carbonate, were identified.



**Figure 1.** Location of the drill site GMGS5-W08B. The topographic map and inset map were obtained from the website https://maps.ngdc.noaa.gov/viewers/fishmaps/.

## 2. Geological Settings and Site Description

The study area is located in the Qiongdongnan Basin of the South China Sea (Figure 1). The Red River Fault, which is the largest N–S strike-slip belt, marks the western boundary of the Qiongdongnan Basin [37]. The sedimentary sequence of the Qiongdongnan Basin includes Eocene lacustrine deposits, Oligocene lacustrine and shallow water deposits, and Miocene deep-water deposits [38]. Thermogenic gas is mainly derived from mature to over-mature Oligocene source rocks [39], while biogenic gas mainly originates from immature to low-maturity Miocene to Pliocene source rocks [40]. Channels, fans, and gravity deposits are widely developed in the study area [41]. In recent years, a large number of bottom simulating reflectors (BSR) and gas chimneys have been widely discovered [42], indicating the existence of both natural gas hydrates and fluid flow in the Qiongdongnan Basin.

In 2018, site W08B was drilled for natural gas hydrate exploration by the GMGS in the Qiongdongnan Basin [30]. The water depth is around 1740 m and the drilling depth was about 164 m. ROV seafloor observation identified the sporadic distribution of seep bivalve remnants and tube worms on the seafloor, indicating that the ancient cold seeps at this site were historically active; however, gas emission was not observed [30]. Seep carbonates were recovered from multiple subseafloor strata, implying intermittent cold seep activity. The drilling results identified a complex natural gas hydrate system, which had developed in the gas chimney [30]. Logging while drilling and coring results showed that gas hydrates are distributed at 6–174 mbsf. The hydrate-bound gas consists of a large volume of high-order hydrocarbons, such as ethane and propane [30].  $\delta^{13}$ C and gas composition analysis indicated that the identified hydrate-bound gases are a mixture of biogenic and thermogenic gas. The paleo-uplift resulted in the differential compaction and formation of fractures and faults, which ultimately controlled the development of gas hydrate [43]. An intermediate gas reservoir lies beneath 190 mbsf, which has been suggested to bridge the deep gas reservoir and shallow gas hydrate system [36]. Ascribed to the gas chimney and fluid flow system, the geothermal gradient at this site reaches up to 102 °C/km, which is almost twice the background value [30].

The carbonate samples used in this study were recovered from sediment layers at 3, 52.1, and 53.6 mbsf of borehole W08B, for which the carbonate sample numbers 3, 52.1, and 53.6 were used, respectively. Twelve sub-samples (Table 1) were collected from the three samples for X-ray diffraction and REE analysis, five of which were prepared for  $\delta^{13}$ C and  $\delta^{18}$ O. Petrographic observations were performed on samples 52.1 and 53.6 (Figure 2). U-Th dating was also performed on the three samples. All analyses were conducted at the laboratory of the GMGS, except for the U-Th dating, which was conducted in the Institute of Geology and Geophysics, Chinese Academy of Sciences.

Sample No.	Approximate Relative Percentages (%)									
	Aragonite	Calcite	High-Mg Calcite	Quartz	Illite	Gypsum	Albite			
3–1	65.3	18.3	5.4	11.0	-	-	-			
3–3	83.5	13.0	-	5.2	-	-	-			
3–2	61.1	12.5	7.6	14.0	2.7	0.4	2.4			
52-1	98.0	0.5	-	-	-	-	-			
52-2	80.5	4.2	-	11.2	2.5	-	0.6			
53-1	84.0	3.9	-	8.9	-	-	1.2			
53-2	83.8	2.4	2.2	9.6	-	-	1.2			
53–3	83.1	3.3	1.9	8.7	-	-	0.6			
53-4	83.1	8.7	1.9	3.3	-	-	0.6			
53–5	88.0	3.8	2.0	5.1	-	-	-			
53-6	94.8	1.9	-	3.2	-	-	-			
53–7	40.5	5.8	35.9	9.8	3.5	-	1.4			

 Table 1. Mineral composition of carbonate subsamples from core W08B.



**Figure 2.** Carbonate samples recovered from core W08B. Color differences resulted from different dryness. Above: Photographs of carbonate after recovery [30]. Below: Photographs of carbonate in the onshore laboratory prepared for subsampling.

Petrographic analyses of the carbonate samples were conducted by using polarized light microscopy (Zeiss Axioskop 40). Scans were run from 5° to 65° 2 $\theta$  (where  $\theta$  is the scan angle), with a step size of 0.02° and count time of 5 s per step. X-ray diffraction was used to analyze and identify the carbonate mineral composition (Table 1). The samples were first dried for 7 h and then

gently ground by a mortar. The ground sample was packed into X-ray sample holders for analysis. Scans were run at room temperature using a Rigaku D/Max 2500 X-ray diffractometer with 18 kW power. The species and content of the minerals were analyzed by using the software Jade2010 [44].

Stable carbon and oxygen isotope ratios were measured using a Thermo MAT-253 isotope ratio mass spectrometer.  $CO_2$  gas was extracted by a reaction with supersaturated phosphoric acid on a Thermo Kiel IV Carbonate Device and was introduced into the MAT-253 dual inlet system. The isotope ratios were reported relative to Vienna Peedee Belemnite (VPDB). The precisions of  $\delta^{13}C$  and  $\delta^{18}O$  were  $\pm 0.1\%$  and  $\pm 0.25\%$ , respectively.

REE analysis was performed following the procedure established by Rongemaille et al. [45]. Fifty milligrams of sample was weighed into a pre-cleaned Teflon centrifuge tube. Then, an ultra-pure solution of 5% acetic acid was added and the mixture was left to react for 24 h in a water bath to separate carbonate mineral and residue phases. Subsequently, the mixture was centrifuged to obtain the supernatant, and the process of washing and centrifugation was repeated three times. Finally, the solution was evaporated on a hotplate until complete dryness and was dissolved in 3% HNO<sub>3</sub>. REE was measured via ICP-MS (Therme Fisher Scientific, Waltham, MA, USA). The analytical precision was better than 5%. In this paper, Ce/Ce \* =  $3Ce_N/(2La_N + Nd_N)$ , Pr/Pr \* =  $2Pr_N/(Ce_N + Nd_N)$ , Eu/Eu \* =  $2Eu_N/(Sm_N + Gd_N)$ . N refers to the normalized concentration against the standard Post-Archaean Australian Shale [43].

Furthermore, 10–50 mg of each subsample from three carbonates was used to conduct the U-Th dating analyses. The chemical procedures used to separate uranium and thorium for <sup>230</sup>Th dating have been described in [46]. <sup>230</sup>Th dating was performed by using a multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS, Thermo-Scientific Neptune). Details of instrumental approaches have been described in Wang et al. [47].

### 4. Results

#### 4.1. Petrology and Mineralogy

The microphotograph shows that shallow carbonates mainly consist of matrix micrite. The thin-section photomicrographs of deep carbonate mainly consist of matrix micrite and biological debris (Figure 3). In general, acicular aragonite occurs as vein cement filling the pore spaces between the matrix micrite (Figure 3a–c). It was common to observe the accretionary overgrowth of rim cement around the foraminifera test (Figure 3d). All carbonates contain seep bivalve shells (Figure 2). XRD analysis showed that, except for sample 53–7 (Table 1), all carbonate samples are dominated by aragonite (61.1–98.0%), with a certain amount of calcite (0.5–18.3%) and a high amount of magnesium calcite (1.9–7.6%). In sample 53-7, the content of high-magnesium calcite (35.9%) is approximately as high as that of aragonite (40.5%). Sample 52–1 was collected from the loose translucent part of the carbonate and contains the highest content of aragonite (98%). In addition, most samples also contain a small amount of other minerals, such as quartz (3.2–14.0%), illite (2.5–3.5%), and albite (0.6–2.4%). Gypsum (0.4%) occurred in sample 3–2.



**Figure 3.** Thin-section photomicrographs of carbonate samples. (**a**,**b**) Sample at 52.1 mbsf. (**c**,**d**) Sample at 53.6 mbsf. m: micrite; ar: aragonite; for: foraminifer; and pore: pore space.

# 4.2. Rare Earth Elements

The total content of REEs varies significantly from 2.64 to 64.5 ppm (Table 2). The Ce/Ce \* values show a normal to slightly negative anomaly (Ce/Ce \* < 1.05), which ranges between 0.79 and 1.04. Compared with heavy REEs (Ho to Lu) and light REEs (La to Nd), medium REEs (Sm to Dy) in the carbonates are relatively enriched.

Element	Approximate Content (ppm)											
	3–1	3–2	3–3	52–1	52–2	53–1	53–2	53–3	53–4	53–5	53–6	53–7
La	11.4	13.6	5.6	0.6	9.0	4.9	9.2	10.1	9.1	2.8	6.1	9.2
Ce	23.4	28.3	10.9	0.9	17.1	9.3	17.7	18.7	17.5	5.1	9.4	17.6
Pr	2.4	2.9	1.1	0.1	1.9	1.0	1.9	2.1	1.9	0.6	1.2	1.9
Nd	9.5	11.9	4.9	0.4	7.3	4.0	7.4	8.2	7.3	2.2	5.0	7.3
Sm	1.9	2.1	0.9	0.1	1.3	0.8	1.4	1.6	1.4	0.4	0.8	1.5
Eu	0.4	0.4	0.2	0.1	0.3	0.2	0.3	0.3	0.3	0.1	0.2	0.3
Gd	1.7	1.9	0.8	0.1	1.2	0.7	1.2	1.4	1.2	0.4	0.7	1.2
Tb	0.2	0.3	0.1	0.0	0.2	0.1	0.2	0.2	0.2	0.1	0.1	0.2
Dy	1.1	1.4	0.7	0.1	0.9	0.5	0.9	0.9	0.9	0.3	0.5	0.8
Ho	0.2	0.2	0.1	0.0	0.2	0.1	0.2	0.2	0.2	0.1	0.1	0.2
Er	0.6	0.7	0.4	0.1	0.5	0.3	0.5	0.5	0.5	0.2	0.3	0.5
Tm	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.1	0.0	0.0	0.1
Yb	0.5	0.6	0.3	0.1	0.4	0.3	0.5	0.5	0.4	0.1	0.2	0.4
Lu	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.1	0.0	0.0	0.1
$\Sigma$ .EE	53.36	64.50	26.17	2.64	40.37	22.21	41.54	44.75	40.92	12.27	24.70	41.07
Ce/Ce *	1.03	1.04	0.99	0.82	0.96	0.97	0.98	0.94	0.98	0.93	0.79	0.97
Eu/Eu *	0.95	1.04	0.99	3.64	1.06	1.03	1.08	0.94	1.05	1.48	1.50	1.07
Pr/Pr *	0.96	0.94	0.92	1.02	0.99	0.94	0.97	0.99	0.98	0.98	1.05	0.98

Table 2. Rare earth element (REE) contents of the authigenic carbonates.

 $\label{eq:ce} Ce/Ce *-3Ce_N/(2La_N + Nd_N). \ Pr/Pr *-2Pr_N/(Ce_N + Nd_N). \ Eu/Eu *-2Eu_N/(Sm_N + Gd_N). \ N \ refers to the normalized concentration against the standard Post-Archaean Australian Shale [43].$ 

# 4.3. $\delta^{13}C$ and $\delta^{18}O$ Values

The  $\delta^{13}$ C and  $\delta^{18}$ O of the five carbonate sub-samples are presented in Figure 4 The result shows that the  $\delta^{13}$ C and  $\delta^{18}$ O of samples 53–1 and 52–1 are –38.1‰ and –38.0‰, and 4.6‰ and 5.0‰, respectively. Compared with deeply buried samples (53–1 and 52–1), shallowly buried samples (3–1, 3–2, and 3–3) have higher  $\delta^{13}$ C values (between –33.8‰ and –25.6‰) and lower  $\delta^{18}$ O values (between 3.6‰ and 3.8‰).



**Figure 4.** Stable carbon isotope ( $\delta^{13}$ C) values and oxygen isotope ( $\delta^{18}$ O) values of authigenic carbonates at deferent sediment layers. Shallowly buried samples (3–1, 3–2, and 3–3) have higher  $\delta^{13}$ C values (between –33.8‰ and –25.6‰) and lower  $\delta^{18}$ O values (between 3.6‰ and 3.8‰). The  $\delta^{13}$ C values of 53–1 and 52–1 are –38.1‰ and –38.0‰. Modified from reference [31].

# 4.4. U-Th Age of Carbonates

The U-Th ages of the three carbonate samples are presented in Table 3. The result shows that the age of sample 3 (~3 mbsf) is  $12.2 \pm 2.3$  ka. The ages of the samples at 52.1 and 53.6 mbsf are very similar, namely  $136.3 \pm 3.6$  and  $131.1 \pm 2.5$  ka, respectively.

Sample No	<sup>230</sup> Th/ <sup>232</sup> Th		<sup>234</sup> U		<sup>230</sup> Th/ <sup>238</sup> U		<sup>230</sup> Th age (yr)		<sup>230</sup> Th age (yr)	
	(AT ×	10 <sup>-6</sup> )					(not cali	brated)	(calib	rated)
3	20.0	±0.4	144.0	±3.7	0.1512	±0.0013	15,408	±155	12,210	±2269
52	92.9	±2.0	112.9	±3.9	0.8190	$\pm 0.0069$	139,969	±2585	136,281	$\pm 3605$
53	113.9	±2.3	101.1	$\pm 2.4$	0.7913	$\pm 0.0037$	134,088	±1351	131,143	$\pm 2461$

Table 3. Activity ratios used for age calculation and isochron U-Th ages.

## 5. Discussion

## 5.1. Fluid Source and Environment of Seep Carbonate Formation

At cold seeps, the anaerobic oxidation of methane (AOM) typically proceeds in anoxic sub-surface sediments, which leads to increased alkalinity levels in pore waters and, as a consequence, often results in carbonate precipitation [27,31,44,48–62]. Occurrences of authigenic carbonate deposits at the

sea floor or in sedimentary records are therefore often related to the paleo-seepage of methane-rich fluids at continental margins. At GMGS5, carbonates were collected at 3, 52, and 53 mbsf layers of the Qiongdongnan Basin of the South China Sea. Gas hydrates have been found at 6 and 136 mbsf and the current sulfate and methane transition zone (SMTZ) is located at about 0.47 mbsf [43]. Therefore, GMGS5 is an ideal experimental site for studying the long history and the relationship between carbonate formation and methane leakage.

REEs have been widely applied as a redox proxy in the marine environment [37–46]. Diagenetic processes generally alter the REE composition of carbonates and cause a negative correlation between Ce/Ce \* and  $Dy_N/Sm_N$  and a positive correlation between Ce/Ce \* and  $\Sigma REE$  [47]. In the studied samples, no such correlation was found (Figure 5d,f). Hence, it can be assumed that all studied samples retained their original REE budget. Feng et al. (2009) considered that small MREE enrichment or flat REE patterns of methane-seep carbonates are indicative of intermittent redox conditions [46,48–51]. The REE/PAAS patterns in shallow carbonates and deeper carbonates are flat REE patterns with small MREE enrichments in both carbonates. The intermittent redox conditions indicate that the deeper carbonates and shallow carbonates formed in the sulfate methane transition zone. This is because the redox environment of deep sediments remains stable and will not be affected by debris input. On the contrary, the redox environment of the shallow sediments, which is close to the water-sediment surface, is stable under the influence of debris input. Large number of seep bivalve shells that can only survive on the seafloor were cemented in the carbonates [52,53]. This also indicates that the methane flux was high at the time of carbonate formation. Moreover, none of the carbonate samples show Ce anomalies (Figure 5a). There were no Ce anomalies or slightly negative Ce anomalies ranging from 0.79 to 1.05 (Table 2), mainly indicating that seep carbonates were formed in a reducing condition [23,48–50,54,55]. Remarkably, the deeper carbonates at 52.1 and 53.6 mbsf show positive Eu anomalies, indicating the mixing of reducing porewater (positive anomaly) with variable proportions of seawater (no Eu anomaly). An additional factor to be considered is the possible contribution of deep-sourced fluids that generally carry an Eu-enriched signal generated by Eu fractionation at elevated temperatures [42]. Based on the widely distributed gas chimneys and deep faults in the area [43], it is reasonable to assume that deeper fluids may also have influenced the REE budget and partly contributed to the development of positive Eu anomalies in the porewater [43]. These data are indicative of precipitation under variable redox conditions as the frequency observed in modern and ancient cold seep carbonates.

In marine sediments, methane is mainly produced via biogenic and thermogenic processes [12,13,27–35,48]. Generally, the  $\delta^{13}$ C values of biogenic methane typically fall within the range of -110% to -50%, whereas the values of thermogenic methane typically range from -50%to -30% [31,34,56,63]. Moreover,  $\delta^{13}$ C values of sedimentary organic matter are about -25.0% on average. The  $\delta^{13}$ C values of carbonates always inherit the  $\delta^{13}$ C characteristic of the carbon source for carbonates. The pore water dissolved inorganic carbon (DIC) includes different carbon sources (methane-derived carbon, seawater DIC, and DIC from organic matter degradation). Therefore,  $\delta^{13}$ C of the seep carbonates can be used to indicate the carbon source of the seeping fluids [42,43]. The  $\delta^{13}$ C values of deeper carbonates and shallow carbonates varied from -38.1‰ to -25.6‰, covering the range for biogenetic gas and thermogenic gas, and also covering the sedimentary organic matter. Accordingly, it is reasonable to propose that carbon sources for shallow carbonates and deep carbonates are diverse, including biogenic and thermogenic methane and sedimentary organic matter. Among them, biogenic methane is mainly derived from the Miocene source rock and its overlying strata, while thermogenic methane mainly originates from Oligocene source rocks [48]. However, it is difficult to identify methane sources, based on the  $\delta^{13}$ C values of carbonates, because the great variability in  $\delta^{13}$ C values demonstrates the geochemical complexity of these sites.



Figure 5. (a) Shale-normalized REE pattern of the seep carbonates. (b) Plot of Ce/Ce \* with the  $La_N/Sm_N$ ; (c) plot of Ce/Ce \* with the Dy<sub>N</sub>/Sm<sub>N</sub>; (d) plot of Ce/Ce \* with the Pr/Pr \*; and (e) plot of Ce/Ce \* with the REE.

The  $\delta^{18}$ O values of shallow carbonates range from 3.6‰ to 3.8‰ and the  $\delta^{18}$ O values of deep carbonates range from 4.6‰ to 5.0‰. Both samples show obviously higher  $\delta^{18}$ O values than seawater. The fact that anomalously positive  $\delta^{18}$ O values of carbonate are obviously different from those of modern seawater points to the precipitation of carbonate from <sup>18</sup>O-enriched fluids. At a constant bottom water temperature during carbonate formation, the anomalous  $\delta^{18}$ O of carbonate can be explained by the presence of exotic <sup>18</sup>O-enriched fluids. In general, the source of <sup>18</sup>O-enriched fluids is the dehydration of clay minerals at great depths and or dissolution of gas hydrate [57,63–65]. For the first case, the reaction of clay mineral dehydration takes place at least 2 km below the seafloor and the gas source rock depth in our study area is not compatible with that process. Therefore, the possible influence of the dehydration of clay minerals on  $\delta^{18}$ O values could be excluded in the first place. For the second case, the enrichment in  $\delta^{18}$ O of interstitial fluids in the study area is best explained by gas hydrate dissolution. The  $\delta^{18}$ O values of carbonates 52–1 and 53–1 (5.0 ‰ and 4.6 ‰, respectively) are rather heavy compared to most recent samples (3.6–3.8‰) and might reflect paleo-gas hydrate dissociation. It can be speculated that in the process of the upward migration of methane-rich fluids, released by the deeper hydrate (136 mbsf), a large amount of released methane will reform at the shallow hydrate layer (6 mbsf) under an appropriate temperature and pressure environment.

#### 5.2. Influence of Methane Flux on the Formation of Authigenic Carbonate

This section addresses three questions: (1) As mentioned above, the deeper carbonates and shallow carbonates are formed by AOM, and the organic characteristic of different layers is consistent. What mechanism causes methane seeps? (2) The U-Th date of carbonate at 3 mbsf is the  $12.2 \pm 2.2$  ka period, while for carbonate at 52.1 mbsf, it is the  $136.3 \pm 3.6$  ka period, and for carbonate at 53.6 mbsf, it is the  $131.1 \pm 2.5$  ka period. What are the causes of the older age of carbonate at 52 mbsf than the age of carbonate at 53 mbsf? (3) There are two major types of aragonite: The shallow carbonates cement by microcrystalline aragonite in the matrix, while the surface of the cavities in the deep carbonates cement by acicular aragonite (Figure 3). What are the causes of the different morphologies of aragonite?

With regard to the first question, in general, methane flux has been assumed to be influenced by changes in sea level and tectonic activities at continental margins [55–60,63–65]. Among these changes, the change of sea level has been regarded as the prominent factor, leading to the decomposition of gas hydrate in geological history [61]. The U-Th dates of all samples fall within periods in which the sea level was 110 m lower than the present sea level (Figure 6) [61,62,66–68]. The coincidence with a low stand is very strong evidence for relationships between seep activity and the sea level. This suggests that sea level change was the main factor that triggered the leakage of methane-rich fluid [68]. Combined with the gas hydrate distribution at 6 and 136 mbsf, this study proposes that the methane-rich fluids were mainly produced by gas hydrate dissociation. This result is consistent with other research conclusions, indicating that the seep carbonates formed in a period of carbonate formation with lower sea levels [52–56].

With regard to the second question (why carbonates at 52 mbsf are older than those at 53 mbsf), in this study area, the sulfate and methane transition zone was not stable during the geological history. At about 136 ka BP, the global sea level dropped rapidly, and the methane-rich fluids diffused from the bottom and reacted with sulfate when it was close to the sediment-water interface. With the AOM, the carbonate gradually precipitated in the sulfate and methane transition zone. Then, between 131 and 136 ka BP, with an increasing temperature, the sea level gradually rose. With this change in sea level, the methane flux gradually decreased. Previous studies have suggested that the sulfate and methane transition zone (SMTZ) was influenced by the methane flux and sedimentation rate [46,47]. The sediments in the Qiongdongnan Basin are mainly from rivers and gravity deposits with a sedimentation rate of up to 1 m/ka [30,47]. However, the Qiongdongnan Basin is very broad, with large spatial differences in sedimentation rates. Based on the ages of the three samples obtained by U-Th dating, the deposition rate of this site was calculated to be approximately 0.41 m/ka. However, due to the scarcity of dating data, the calculated deposition rate is unreliable. It can be found from the seismic profile of site W08 that there is no development of turbidity sediments. Therefore, the influence of turbidity can be eliminated (Figure 7); therefore, the age reversal was not caused by debris input or the turbidity of the sediment. Hence, the main reason for the age reversal was a change in methane flux. In general, the more intense the methane flux, the shallower the SMTZ, and the weaker the methane flux, the deeper the SMTZ. Therefore, as the methane flux decreased with the changing sea level, the SMTZ moved downward. The younger carbonate at 53.6 mbsf formed at a deeper SMTZ.



**Figure 6.** (a) The sea level change [59] and the distribution of carbonate. The sun symbols represent the time of carbonate formation. (b) The sedimentation rate estimated based on the U-Th carbonate ages.



**Figure 7.** Pseudo-3D seismic profiles showing the characteristics of the bottom simulating reflector (yellow line: BSR) and mass transport depositions (MTDs) at site GMGS5-W08-2018 [43].

With regard to the third question (the causes of the difference between shallow carbonates and deep carbonates), the petrology and mineral composition of seep carbonates are useful for understanding the environmental changes underlying carbonate formation [25,51,52]. XRD showed that both aragonites are pure minerals, containing no other components. Furthermore, allogenic terrigenous minerals, quartz, and feldspar comprise a minor portion of authigenic carbonate rock (Figure 8a). Moreover, XRD analyses showed that the aragonite content is high, except for the carbonate at 53.6 mbsf, which has high contents of high-Mg calcite. It is indicated that shallow carbonates and deeper carbonates were formed under high  $SO_4^{2-}$  environments. As a typical authigenic carbonate mineral, aragonite is more likely to be affected by the fluid environment [56–61,63–65]. Of the allogenic terrigenous minerals, quartz is the most thermodynamically stable as most natural fluids achieve supersaturation concerning quartz [53]. In this study, the plot of aragonite content vs. quartz content shows an obvious negative correlation (Figure 8b). This relationship was also observed in the seep carbonates of the Gulf of Mexico [53–56,63,64]. The quartz and aragonite content can be used as indicators of the evolution of a seepage system, to a certain extent. In fact, the formation and dissolution of carbonate minerals in authigenic carbonates follow a time sequence. At the early stage, high-Mg calcite and aragonite are the primary cement, while the quartz content is low. However, at the dissolution stage, aragonite starts to dissolve. At the last stage, the quartz increases because the HMC and aragonite are replaced by silica and quartz [57,65,67,68]. At the studied site, the deeper carbonate and shallow carbonate show a high content of aragonite and low content of quartz. This indicates that all carbonates are not significantly affected by diagenetic alteration. In general, aragonite seems to be favored in high  $SO_4^{2-}$  environments with high total alkalinity concentrations [69,70]. The crystallization of magnesium calcite preferentially occurs under conditions with lower  $SO_4^{2-}$  and total alkalinity concentrations [71]. Furthermore, it is suggested that the occurrence of aragonite reflects high methane flux and efficient methane oxidation [71,72]. In deep and shallow carbonates, minerals are mainly composed of aragonite. It is indicated that all the carbonates formed under high  $SO_4^{2-}$ . However, the microphotographs show that shallow carbonates mainly consist of matrix micrite. The thin-section photomicrographs of deep carbonate mainly consist of matrix micrite and biological debris (Figure 3). In general, acicular aragonite occurs as vein cement filling the pore spaces between the matrix micrite (Figure 3a–c). It was common to observe the accretionary overgrowth of rim cement around the foraminifera test. Harry et al. considered that seep carbonates precipitated in a high sulfate concentration environment are characterized by sparitic and acicular aragonite cements [73,74]. Higher sulfate concentrations tend to promote aragonite precipitation [69–73]. Such conditions represent deeper carbonates formed in an environment where HCO<sub>3</sub><sup>-</sup>-rich fluids mix with sulfate-rich bottom water. This conclusion is supported by the large fragments of chemosynthetic bivalves observed. Xi et al. found that the in situ Raman spectra of the authigenic carbonates exhibited the highest crystallinity in the fauna-rich area. Scanning electron microscopy and X-ray diffraction analyses of the samples supported the conclusion that the aragonite in the fauna-rich area is more euhedral than that in the fauna-poor area [69]. Therefore, this suggests that the differences can also be caused by different methane fluxes [69]. The difference between the morphologies of shallow and deep aragonite in this article are also more likely caused by the growth time of the minerals. A longer growth time leads to euhedral minerals [54–56,63,67,68].



**Figure 8.** (a) Mineral distributions of all carbonate samples. (b) Plot of the aragonite content and the quartz content.

### 5.3. Mechanism of Seep Carbonate Formation and Methane Seep Evolution

In the studied area, the REE patterns and the lack of Ce anomalies indicate that all carbonates formed in a reduced environment. The low  $\delta^{13}$ C values indicate that carbonate formation has a close relationship with methane seep. In the studied area, three stages of methane seepage could be identified.

The first stage: About 136 ka BP years ago, the sea level decreased dramatically. This caused a decrease in hydrostatic pressure. Under such a condition, gas hydrate became unstable and released methane into shallower sediments. When it reached the sediment–water interface, the released methane reacted with sulfate and carbonate precipitated as a by-product of AOM. At first, the carbonates at 51.2 mbsf were mainly cement by microcrystalline aragonite under a high concentration of SO<sub>4</sub><sup>2–</sup> (Figure 9a).

The second stage: From 131 to 136 ka BP, the methane flux gradually decreased with the gradually increasing sea level. Hence, the SMTZ moved down and was fixed at new balanced layers. At the same time, the carbonate at 53.6 mbsf formed at the bottom of carbonate at 51.2 mbsf. As time went by, the formed carbonate mineral at 51.2 mbsf was gradually cemented by sparitic and acicular aragonitein cavities (Figure 9b).

The third stage: At about 12 ka BP, the newly formed hydrate was influenced by the drop of the sea level and released methane into shallow sediments. With the help of AOM, carbonate at 3 mbsf formed. Since the growth of aragonite is short, the carbonate matrix mainly cemented by microcrystalline aragonite (Figure 9c).



**Figure 9.** (a) Formation mechanism of carbonate at 52 mbsf: the sea level decreased dramatically. This caused a decrease in hydrostatic pressure. Under such a condition, gas hydrate became unstable and released methane into shallower sediments. When it reached the sediment–water interface, the released methane reacted with sulfate and carbonate precipitated as a by-product of AOM. (b) formation mechanism of carbonate at 53 mbsf: The methane flux gradually decreased with the gradually increasing sea level. Hence, the SMTZ oved down and was fixed at new balanced layers. At the same time, the carbonate at 53.6 mbsf formed at the bottom of carbonate at 51.2 mbsf and (c) formation mechanism of carbonate at 3 mbsf: At about 12 ka BP, the newly formed hydrate was influenced by the drop of the sea level and released methane into shallow sediments. With the help of AOM, carbonate at 3 mbsf formed.

### 6. Conclusions

Systematic analyses, including those on the mineralogy, petrography, stable carbon and oxygen isotopes, REE, and U-Th dating, were conducted on three seep carbonate samples (3, 52.1, and 53.6 mbsf) recovered from site W08B in the Qiongdongnan Basin, China. Based on comprehensive analyses, the following major conclusions were drawn: Two distinct stages of methane seepage events are discernible, which were likely caused by the dissociation of gas hydrates. The first methane seep took place at 131–136 ka BP. The methane seepage caused carbonates at 52.1 and 53.6 mbsf, formed during 131–136 ka BP. Meanwhile, the methane flux changes caused the vertical downward movement of the sulfate-methane transition zone. Furthermore, the carbonate at 53.6 mbsf formed at the bottom of carbonates at 52.1 mbsf. This is the reason why the age of carbonate at 52.1 mbsf is older than the age of carbonates at 53.6 mbsf. The second methane seep took place at 12.2 ka BP. Shallow carbonates formed at that time via AOM and are now located at 3 mbsf. The shallow carbonate and deep carbonate minerals are mainly composed of aragonite, indicating that all carbonates formed at a high  $SO_4^{2-}$ concentration. The higher  $SO_4^{2-}$  concentration close to the seafloor also indicates a higher methane flux. However, the thin-section photomicrographs of deep carbonate mainly consist of matrix micrite and biological debris and acicular aragonite occurs as vein cement filling the pore spaces between the matrix micrite. It was common to observe the accretionary overgrowth of rim cement around the foraminifera test. Th thin-section photomicrographs of shallow carbonate mainly consist of matrix micrite and biological debris. The differences between shallow carbonates and deeper carbonates were mainly caused by the duration of the carbonate precipitation of minerals. Moreover, the  $\delta^{18}O$ values and  $\delta^{13}$ C values of the deeper carbonates and shallow carbonates indicate that the carbon source for carbonates remained constant through time and included biogenic and thermogenic methane. This research reveals the history of methane seep and the relationship between the methane seep activity and the vertical distribution of carbonates.

Author Contributions: Conceptualization, R.X. and T.W.; methodology, R.X.; software, Y.D.; validation, J.C., J.F. and J.L.; formal analysis, W.Z.; investigation, R.X.; resources, W.Z.; data curation, W.Z.; writing—original draft preparation, J.W.; writing—review and editing, R.X. and T.W.; visualization, P.L.; supervision, J.Z.; project administration, J.W.; funding acquisition, J.W. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Key Research and Development Program of China (No. 2018YFC0310000), Key Special Project for Introduced Talents Team of Southern Marine Science and Engineering Guangdong Laboratory (Guangzhou) (GML2019ZD0201), Key Laboratory of Marine Mineral Resources, Ministry of Land and Resources (No. KLMMR-2015-A-07, KLMMR-2017-A-12), and China Geological Survey Project (No. DD20160227).

Acknowledgments: We thank all the participants in the GMGS5 expedition for their great support. We also thank the reviewers for their comments during the review process.

Conflicts of Interest: The authors declare no conflict of interest.

## References

- 1. Judd, A.A.G.; Hovland, M. Seabed Fluid Flow: The Impact of Geology, Biology and the Marine Environment; Cambridge University Press: Cambridge, UK, 2007.
- Suess, E.; Bohrmann, G.; Von Huene, R.; Linke, P.; Wallmann, K.; Lammers, S.; Sahling, H.; Winckler, G.; Lutz, R.A.; Orange, D. Fluid venting in the eastern Aleutian Subduction Zone. *J. Geophys. Res. Solid Earth* 1998, 103, 2597–2614. [CrossRef]
- 3. Giletycz, S.; Lin, A.T.-S.; Chang, C.-P.; Shyu, J.B.H. Relicts of mud diapirism of the emerged wedge-top as an indicator of gas hydrates destabilization in the Manila accretionary prism in southern Taiwan (Hengchun Peninsula). *Geomorphology* **2019**, *336*, 1–17. [CrossRef]
- 4. Agarwal, D.K.; Roy, P.; Prakash, L.S.; Kurian, P.J. Hydrothermal signatures in sediments from eastern Southwest Indian Ridge 63° E to 68° E. *Mar. Chem.* **2020**, *218*, 103732. [CrossRef]

- Schmid, F.; Peters, M.; Walter, M.; Devey, C.W.; Petersen, S.; Yeo, I.; Köhler, J.; Jamieson, J.W.; Walker, S.; Sültenfuß, J. Physico-chemical properties of newly discovered hydrothermal plumes above the Southern Mid-Atlantic Ridge (13°–33° S). *Deep Sea Res. Part I Oceanogr. Res. Pap.* 2019, 148, 34–52. [CrossRef]
- 6. Klaucke, I.; Sahling, H.; Weinrebe, R.W.; Blinova, V.; Bürk, D.; Lursmanashvili, N.; Bohrmann, G. Acoustic investigation of cold seeps offshore Georgia, eastern Black Sea. *Mar. Geol.* **2006**, *231*, 51–67. [CrossRef]
- Torres, M.E.; McManus, J.; Hammond, D.; De Angelis, M.; Heeschen, K.; Colbert, S.; Tryon, M.; Brown, K.; Suess, E. Fluid and chemical fluxes in and out of sediments hosting methane hydrate deposits on Hydrate Ridge, OR, I: Hydrological provinces. *Earth Planet. Sci. Lett.* 2002, 201, 525–540. [CrossRef]
- 8. Wei, J.; Pape, T.; Sultan, N.; Colliat, J.-L.; Himmler, T.; Ruffine, L.; De Prunelé, A.; Dennielou, B.; Garziglia, S.; Marsset, T.; et al. Gas hydrate distributions in sediments of pockmarks from the Nigerian margin—Results and interpretation from shallow drilling. *Mar. Pet. Geol.* **2015**, *59*, 359–370. [CrossRef]
- Omoregie, E.O.; Niemann, H.; Mastalerz, V.; De Lange, G.; Stadnitskaia, A.; Mascle, J.; Foucher, J.-P.; Boetius, A. Microbial methane oxidation and sulfate reduction at cold seeps of the deep Eastern Mediterranean Sea. *Mar. Geol.* 2009, 261, 114–127. [CrossRef]
- 10. Wei, J.; Li, J.; Wu, T.; Zhang, W.; Li, J.; Wang, J.; Tao, J.; Chen, Z.; Wu, Z.; Chen, W. Geologically controlled intermittent gas eruption and its impact on bottom water temperature and chemosynthetic communities—A case study in the "HaiMa" cold seeps, South China Sea. *Geol. J.* **2020**, *55*, 6066–6078. [CrossRef]
- Fischer, D.; Sahling, H.; Nothen, K.; Bohrmann, G.; Zabel, M.; Kasten, S. Interaction between hydrocarbon seepage, chemosynthetic communities, and bottom water redox at cold seeps of the Makran accretionary prism: Insights from habitat-specific pore water sampling and modeling. *Biogeosciences* 2012, *9*, 2013–2031. [CrossRef]
- 12. Brooks, J.M.; Kennicutt, M.C.; Bidigare, R.R.; Fay, R.A. Hydrates, oil seepage, and chemosynthetic ecosystems on the Gulf of Mexico slope. *Eos Trans. Am. Geophys. Union* **1985**, *66*, 106. [CrossRef]
- 13. Marcon, Y.; Ondréas, H.; Sahling, H.; Bohrmann, G.; Olu, K. Fluid flow regimes and growth of a giant pockmark. *Geology* **2014**, *42*, 63–66. [CrossRef]
- Loher, M.; Marcon, Y.; Pape, T.; Römer, M.; Wintersteller, P.; Ferreira, C.D.S.; Praeg, D.; Torres, M.; Sahling, H.; Bohrmann, G. Seafloor sealing, doming, and collapse associated with gas seeps and authigenic carbonate structures at Venere mud volcano, Central Mediterranean. *Deep Sea Res. Part I Oceanogr. Res. Pap.* 2018, 137, 76–96. [CrossRef]
- 15. Römer, M.; Sahling, H.; Pape, T.; Ferreira, C.D.S.; Wenzhöfer, F.; Boetius, A.; Bohrmann, G. Methane fluxes and carbonate deposits at a cold seep area of the Central Nile Deep Sea Fan, Eastern Mediterranean Sea. *Mar. Geol.* **2014**, *347*, 27–42. [CrossRef]
- Weber, T.C.; Mayer, L.; Jerram, K.; Beaudoin, J.; Rzhanov, Y.; Lovalvo, D. Acoustic estimates of methane gas flux from the seabed in a 6000 km2region in the Northern Gulf of Mexico. *Geochem. Geophys. Geosyst.* 2014, 15, 1911–1925. [CrossRef]
- 17. Cortes, J.; Aguilera, R.; Wilches, O.; Osorno, J.; Cortes, S. Organic geochemical insights from oil seeps, tars, rocks, and mud volcanoes on the petroleum systems of the Sinü-San Jacinto basin, Northwestern, Colombia. *J. S. Am. Earth Sci.* **2018**, *86*, 318–341. [CrossRef]
- 18. Teichert, B.M.A.; Luppold, F.W. Glendonites from an Early Jurassic methane seep—Climate or methane indicators? *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2013**, *390*, 81–93. [CrossRef]
- Punshon, S.; Azetsu-Scott, K.; Sherwood, O.; Edinger, E.N. Bottom water methane sources along the high latitude eastern Canadian continental shelf and their effects on the marine carbonate system. *Mar. Chem.* 2019, 212, 83–95. [CrossRef]
- 20. Xu, W.; Ruhl, M.; Hesselbo, S.P.; Riding, J.B.; Jenkyns, H.C. Orbital pacing of the Early Jurassic carbon cycle, black-shale formation and seabed methane seepage. *Sedimentology* **2017**, *64*, 127–149. [CrossRef]
- 21. Macdonald, I.R.; Sager, W.W.; Peccini, M.B. Gas hydrate and chemosynthetic biota in mounded bathymetry at mid-slope hydrocarbon seeps: Northern Gulf of Mexico. *Mar. Geol.* **2003**, *198*, 133–158. [CrossRef]
- 22. Bohrmann, G.; Greinert, J.; Suess, E.; Torres, M. Authigenic carbonates from the Cascadia subduction zone and their relation to gas hydrate stability. *Geology* **1998**, *26*, 647–650. [CrossRef]
- 23. Feng, D.; Chen, D.; Peckmann, J.; Bohrmann, G. Authigenic carbonates from methane seeps of the northern Congo fan: Microbial formation mechanism. *Mar. Pet. Geol.* **2010**, *27*, 748–756. [CrossRef]

- 24. Feng, D.; Lin, Z.; Bian, Y.; Chen, D.; Peckmann, J.; Bohrmann, G.; Roberts, H.H. Rare earth elements of seep carbonates: Indication for redox variations and microbiological processes at modern seep sites. *J. Asian Earth Sci.* **2013**, *65*, 27–33. [CrossRef]
- 25. Himmler, T.; Bach, W.; Bohrmann, G.; Peckmann, J. Rare earth elements in authigenic methane-seep carbonates as tracers for fluid composition during early diagenesis. *Chem. Geol.* **2010**, 277, 126–136. [CrossRef]
- Himmler, T.; Sahy, D.; Martma, T.; Bohrmann, G.; Plaza-Faverola, A.; Bünz, S.; Condon, D.J.; Knies, J.; Lepland, A. A 160,000-year-old history of tectonically controlled methane seepage in the Arctic. *Sci. Adv.* 2019, *5*, eaaw1450. [CrossRef] [PubMed]
- Tamborrino, L.; Himmler, T.; Elvert, M.; Conti, S.; Gualtieri, A.F.; Fontana, D.; Bohrmann, G. Formation of tubular carbonate conduits at Athina mud volcano, eastern Mediterranean Sea. *Mar. Pet. Geol.* 2019, 107, 20–31. [CrossRef]
- 28. Bayon, G.; Henderson, G.M.; Bohn, M. U-Th stratigraphy of a cold seep carbonate crust. *Chem. Geol.* **2009**, 260, 47–56. [CrossRef]
- Bayon, G.; Dupré, S.; Ponzevera, E.; Etoubleau, J.; Chéron, S.; Pierre, C.; Mascle, J.; Boetius, A.; De Lange, G.J. Formation of carbonate chimneys in the Mediterranean Sea linked to deep-water oxygen depletion. *Nat. Geosci.* 2013, *6*, 755–760. [CrossRef]
- Chen, F.; Wang, X.; Li, N.; Cao, J.; Bayon, G.; Peckmann, J.; Hu, Y.; Gong, S.; Cheng, H.; Edwards, R.L.; et al. Gas Hydrate Dissociation During Sea-Level Highstand Inferred From U-Th Dating of Seep Carbonate from the South China Sea. *Geophys. Res. Lett.* 2019, *46*, 13928–13938. [CrossRef]
- 31. Feng, D.; Qiu, J.-W.; Hu, Y.; Peckmann, J.; Guan, H.; Tong, H.; Chen, C.; Chen, J.; Gong, S.; Peckmann, J.; et al. Cold seep systems in the South China Sea: An overview. *J. Asian Earth Sci.* **2018**, *168*, 3–16. [CrossRef]
- Han, X.; Suess, E.; Huang, Y.; Wu, N.; Bohrmann, G.; Su, X.; Eisenhauer, A.; Rehder, G.; Fang, Y. Jiulong methane reef: Microbial mediation of seep carbonates in the South China Sea. *Mar. Geol.* 2008, 249, 243–256. [CrossRef]
- 33. Guan, H.; Feng, D.; Wu, N.; Chen, D. Methane seepage intensities traced by biomarker patterns in authigenic carbonates from the South China Sea. *Org. Geochem.* **2016**, *91*, 109–119. [CrossRef]
- 34. Ye, J.; Wei, J.; Liang, J.; Lu, J.; Lu, H.; Zhang, W. Complex gas hydrate system in a gas chimney, South China Sea. *Mar. Pet. Geol.* **2019**, *104*, 29–39. [CrossRef]
- 35. Bangs, N.L.B.; Hornbach, M.J.; Berndt, C. The mechanics of intermittent methane venting at South Hydrate Ridge inferred from 4D seismic surveying. *Earth Planet. Sci. Lett.* **2011**, *310*, 105–112. [CrossRef]
- Wei, J.; Liang, J.; Lu, J.; Zhang, W.; He, Y. Characteristics and dynamics of gas hydrate systems in the northwestern South China Sea—Results of the fifth gas hydrate drilling expedition. *Mar. Pet. Geol.* 2019, 110, 287–298. [CrossRef]
- Taylor, B.; Hayes, D.E. The Tectonic Evolution of the South China Sea Basin. In *The Tectonic and Geologic Evolution of Southeast Asian Seas and Islands*; Geophysical Monograph Series; American Geophysical Union: Washington, DC, USA, 1980; Volume 23.
- 38. Zhao, Z.; Sun, Z.; Wang, Z.; Sun, Z.; Liu, J.; Zhang, C. The high resolution sedimentary filling in Qiongdongnan Basin, Northern South China Sea. *Mar. Geol.* **2015**, *361*, 11–24. [CrossRef]
- 39. Huang, B.; Tian, H.; Li, X.; Wang, Z.; Xiao, X. Geochemistry, origin and accumulation of natural gases in the deepwater area of the Qiongdongnan Basin, South China Sea. *Mar. Pet. Geol.* **2016**, *72*, 254–267. [CrossRef]
- 40. Huang, H.; Huang, B.; Huang, Y.; Li, X.; Tian, H. Condensate origin and hydrocarbon accumulation mechanism of the deepwater giant gas field in western South China Sea: A case study of Lingshui 17-2 gas field in Qiongdongnan Basin. *Pet. Explor. Dev.* **2017**, *44*, 409–417. [CrossRef]
- Yuan, S.; Wu, S.; Thomas, L.; Yao, G.; Lv, F.; Feng, C.; Wang, H.; Li, L. Fine-grained Pleistocene deepwater turbidite channel system on the slope of Qiongdongnan Basin, northern South China Sea. *Mar. Pet. Geol.* 2009, 26, 1441–1451. [CrossRef]
- Zhang, W.; Liang, J.; Su, P.; Wei, J.; Gong, Y.; Lin, L.; Liang, J.; Huang, W. Distribution and characteristics of mud diapirs, gas chimneys, and bottom simulating reflectors associated with hydrocarbon migration and gas hydrate accumulation in the Qiongdongnan Basin, northern slope of the South China Sea. *Geol. J.* 2019, 54, 3556–3573. [CrossRef]
- 43. Liang, J.; Zhang, W.; Lu, J.; Wei, J.; Kuang, Z.; He, Y. Geological occurrence and accumulation mechanism of natural gas hydrates in the eastern Qiongdongnan Basin of the South China Sea: Insights from site GMGS5-W9-2018. *Mar. Geol.* **2019**, *418*, 106042. [CrossRef]

- 44. Weiss, C.A.; Torres-Cancel, K.; Moser, R.D.; Allison, P.G.; Gore, E.R.; Chandler, M.Q.; Malone, P. Influence of temperature on calcium carbonate polymorph formed from ammonium carbonate and calcium acetate. *J. Nanotech. Smart Mater.* **2014**, *1*, 1–6. [CrossRef]
- 45. Rongemaille, E.; Bayon, G.; Pierre, C.; Bollinger, C.; Chu, N.; Fouquet, Y.; Riboulot, V.; Voisset, M. Rare earth elements in cold seep carbonates from the Niger delta. *Chem. Geol.* **2011**, *286*, 196–206. [CrossRef]
- 46. Tong, H.; Feng, D.; Cheng, H.; Yang, S.; Wang, H.; Min, A.G.; Edwards, R.L.; Chen, Z.; Chen, D. Authigenic carbonates from seeps on the northern continental slope of the South China Sea: New insights into fluid sources and geochronology. *Mar. Pet. Geol.* **2013**, *43*, 260–271. [CrossRef]
- Wang, L.; Ma, Z.; Sun, Z.; Wang, Y.; Wang, X.; Cheng, H.; Xiao, J. U concentration and 234 U/ 238 U of seawater from the Okinawa Trough and Indian Ocean using MC-ICPMS with SEM protocols. *Mar. Chem.* 2017, 196, 71–80. [CrossRef]
- Sun, Y.; Gong, S.; Li, N.; Peckmann, J.; Jin, M.; Roberts, H.H.; Chen, D.; Feng, D. A new approach to discern the hydrocarbon sources (oil vs. methane) of authigenic carbonates forming at marine seeps. *Mar. Pet. Geol.* 2020, 114, 104230. [CrossRef]
- 49. Himmler, T.; Birgel, D.; Bayon, G.; Pape, T.; Ge, L.; Bohrmann, G.; Peckmann, J. Formation of seep carbonates along the Makran convergent margin, northern Arabian Sea and a molecular and isotopic approach to constrain the carbon isotopic composition of parent methane. *Chem. Geol.* **2015**, *415*, 102–117. [CrossRef]
- 50. Bayon, G.; Loncke, L.; Dupré, S.; Caprais, J.-C.; Ducassou, E.; Duperron, S.; Etoubleau, J.; Foucher, J.-P.; Fouquet, Y.; Gontharet, S.; et al. Multi-disciplinary investigation of fluid seepage on an unstable margin: The case of the Central Nile deep sea fan. *Mar. Geol.* **2009**, *261*, 92–104. [CrossRef]
- 51. Tong, H.; Feng, D.; Peckmann, J.; Roberts, H.H.; Chen, L.; Bian, Y.; Chen, D. Environments favoring dolomite formation at cold seeps: A case study from the Gulf of Mexico. *Chem. Geol.* **2019**, *518*, 9–18. [CrossRef]
- 52. Wang, S.; Yan, W.; Chen, Z.; Zhang, N.; Chen, H. Rare earth elements in cold seep carbonates from the southwestern Dongsha area, northern South China Sea. *Mar. Pet. Geol.* **2014**, *57*, 482–493. [CrossRef]
- Sahling, H.; Rickert, D.; Lee, R.; Linke, P.; Suess, E. Macrofaunal community structure and sulfide flux at gas hydrate deposits from the Cascadia convergent margin, NE Pacific. *Mar. Ecol. Prog. Ser.* 2002, 231, 121–138. [CrossRef]
- Mazzini, A.; Jonk, R.; Duranti, D.; Parnell, J.; Cronin, B.; Hurst, A. Fluid escape from reservoirs: Implications from cold seeps, fractures and injected sands Part I. The fluid flow system. *J. Geochem. Explor.* 2003, 78, 293–296. [CrossRef]
- 55. Hu, Y.; Feng, D.; Peckmann, J.; Roberts, H.H.; Chen, D. New insights into cerium anomalies and mechanisms of trace metal enrichment in authigenic carbonate from hydrocarbon seeps. *Chem. Geol.* **2014**, *381*, 55–66. [CrossRef]
- Aminzadeh, F.; Berge, T.B.; Connolly, D.L. 3. Carbonate Precipitation at Gulf of Mexico hydrocarbon Seeps: An Overview. In *Hydrocarbon Seepage from Source to Surface*; Society of Exploration Geophysicists and the American Association of Petroleum Geologists: Tulsa, OK, USA, 2013; pp. 43–61.
- 57. Crémière, A.; Lepland, A.; Chand, S.; Sahy, D.; Kirsimäe, K.; Bau, M.; Whitehouse, M.J.; Noble, S.R.; Martma, T.; Thorsnes, T.; et al. Fluid source and methane-related diagenetic processes recorded in cold seep carbonates from the Alvheim channel, central North Sea. *Chem. Geol.* **2016**, *432*, 16–33. [CrossRef]
- 58. Crémière, A.; Chand, S.; Sahy, D.; Thorsnes, T.; Martma, T.; Noble, S.; Pedersen, J.H.; Brunstad, H.; Lepland, A. Structural controls on seepage of thermogenic and microbial methane since the last glacial maximum in the Harstad Basin, southwest Barents Sea. *Mar. Pet. Geol.* 2018, *98*, 569–581. [CrossRef]
- 59. Cao, H.; Sun, Z.; Wu, N.; Liu, W.; Liu, C.; Jiang, Z.; Geng, W.; Zhang, X.; Wang, L.; Zhai, B.; et al. Mineralogical and geochemical records of seafloor cold seepage history in the northern Okinawa Trough, East China Sea. *Deep Sea Res. Part I Oceanogr. Res. Pap.* 2020, 155, 103165. [CrossRef]
- 60. Chen, D.F.; Huang, Y.Y.; Yuan, X.L.; Cathles, L.M. Seep carbonates and preserved methane oxidizing archaea and sulfate reducing bacteria fossils suggest recent gas venting on the seafloor in the Northeastern South China Sea. *Mar. Pet. Geol.* **2005**, *22*, 613–621. [CrossRef]
- Xie, R.; Wu, D.; Liu, J.; Sun, T.; Liu, L.; Wu, N. Evolution of gas hydrates inventory and anaerobic oxidation of methane (AOM) after 40ka in the Taixinan Basin, South China Sea. *Deep Sea Res. Part I Oceanogr. Res. Pap.* 2019, 152, 103084. [CrossRef]

- 62. Wu, T.; Wei, J.; Liu, S.; Guan, Y.; Zhang, R.; Su, M.; Wang, H.; Meng, D.; Liu, B.; Zhang, W. Characteristics and formation mechanism of seafloor domes on the north-eastern continental slope of the South China Sea. *Geol. J.* **2020**, *55*, 1–10. [CrossRef]
- 63. Greinert, J.; Bohrmann, G.; Suess, E. Gas hydrate-associated carbonates and methane-venting at hydrate ridge: Classification, distribution, and origin of authigenic lithologies. *Nat. Gas Hydrates Occur. Distrib. Detect.* **2001**, *124*, 99–113.
- 64. Haley, B.A.; Klinkhammer, G.P.; McManus, J. Rare earth elements in pore waters of marine sediments. *Geochim. Cosmochim. Acta* 2004, *68*, 1265–1279. [CrossRef]
- 65. Ge, L.; Jiang, S.-Y.; Swennen, R.; Yang, T.; Yang, J.-H.; Wu, N.-Y.; Liu, J.; Chen, D.-H. Chemical environment of cold seep carbonate formation on the northern continental slope of South China Sea: Evidence from trace and rare earth element geochemistry. *Mar. Geol.* **2010**, *277*, 21–30. [CrossRef]
- Li, J.; Peng, X.; Bai, S.; Chen, Z.; Van Nostrand, J.D. Biogeochemical processes controlling authigenic carbonate formation within the sediment column from the Okinawa Trough. *Geochim. Cosmochim. Acta* 2018, 222, 363–382. [CrossRef]
- 67. Lin, Z.; Sun, X.; Lu, Y.; Xu, L.; Gong, J.; Lu, H.; Teichert, B.M.; Peckmann, J. Stable isotope patterns of coexisting pyrite and gypsum indicating variable methane flow at a seep site of the Shenhu area, South China Sea. *J. Asian Earth Sci.* **2016**, *123*, 213–223. [CrossRef]
- 68. Wei, J.; Wu, T.; Deng, X.; Yu, Z.; Wang, L. Acoustic characteristics of cold-seep methane bubble behavior in the water column and its potential environmental impact. *Acta Oceanol. Sin.* **2020**, *39*, 133–144. [CrossRef]
- 69. Argentino, C.; Lugli, F.; Cipriani, A.; Conti, S.; Fontana, D. A deep fluid source of radiogenic Sr and highly dynamic seepage conditions recorded in Miocene seep carbonates of the northern Apennines (Italy). *Chem. Geol.* **2019**, *522*, 135–147. [CrossRef]
- Xi, S.; Zhang, X.; Luan, Z.; Du, Z.; Li, L.; Wang, B.; Lian, C.; Yan, J. Biogeochemical implications of chemosynthetic communities on the evolution of authigenic carbonates. *Deep Sea Res. Part I Oceanogr. Res. Pap.* 2020, 162, 103305. [CrossRef]
- 71. Luff, R.; Greinert, J.; Wallmann, K.; Klaucke, I.; Suess, E. Simulation of long-term feedbacks from authigenic carbonate crust formation at cold vent sites. *Chem. Geol.* **2005**, *216*, 157–174. [CrossRef]
- Luff, R.; Wallmann, K. Fluid flow, methane fluxes, carbonate precipitation and biogeochemical turnover in gas hydrate-bearing sediments at Hydrate Ridge, Cascadia Margin: Numerical modeling and mass balances. *Geochim. Cosmochim. Acta* 2003, 67, 3403–3421. [CrossRef]
- 73. Greinert, J.; Veloso, M.; De Batist, M.A.; Mienert, J. Hydroacoustic quantification of free-gas venting offshore Svalbard, Arctic: Changes in space and time. *AGUFM* **2013**, *2013*, B311-07.
- 74. Whiticar, M.J. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem. Geol.* **1999**, *161*, 291–314. [CrossRef]

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