**Geochemical record of methane seepage in authigenic carbonates and
surrounding host sediments: A case study from the South China Sea**

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Abstract: Sediments at marine methane seep sites provide potential archives of past fluid flow that serve to explore seepage activities over time. Three gravity cores (D-8, D-F, and D-7) were collected from seep sites on the northern slope of the South China Sea where gas hydrates were drilled in the subsurface. Various carbon and sulfur contents, $\delta^{13}\text{C}$ values of total inorganic carbon ($\delta^{13}\text{C}_{\text{TIC}}$), $\delta^{34}\text{S}$ values of chromium reducible sulfur ($\delta^{34}\text{S}_{\text{CRS}}$), trace element contents, grain size, and AMS ^{14}C dating of planktonic Foraminifera in the sediments were determined to explore the availability of related proxies at seeps and to trace past methane seepage activities. Evidence for the presence of methane seepage and consequently anaerobic oxidation of methane comes from the occurrence of ^{13}C -depleted authigenic carbonate nodules ($\delta^{13}\text{C}$ values as low as -49‰) discovered at an interval of 150 cm - 200 cm in core D-7. This finding is supported by high S/C ratios and molybdenum enrichment in the same interval. However, low contents of CRS and negative $\delta^{34}\text{S}_{\text{CRS}}$ values are present. It is suggested to reflect a transient methane seepage event, which continued for about 1 ka based on the ^{14}C ages. Cores D-8 and D-F have $\delta^{13}\text{C}_{\text{TIC}}$ values close to zero, low S/C ratios and CRS contents, negative $\delta^{34}\text{S}_{\text{CRS}}$ values, and no trace element enrichment, suggesting a negligible impact of methane-seepage on the sediments. The negative $\delta^{34}\text{S}_{\text{CRS}}$ values of the studied seep-impacted and background sediments suggest that the application of $\delta^{34}\text{S}_{\text{CRS}}$ alone as a proxy to identify AOM-related process may be insufficient. Sediment carbon-sulfur-trace element systematics and ^{14}C ages used here have the potential to be a promising tool to recognize transient methane seepages and constrain their timescales.

Key words: methane seepage; sediment; authigenic carbonate; carbon; chromium
reducible sulfur; trace element; South China Sea

1. Introduction

Release of methane-rich fluids is a widely observed phenomenon in marine sedimentary strata along continental margins (e.g. Campbell, 2006; Suess, 2014, and many others). In modern oceans, most of the seeping methane is consumed by sulfate-dependent anaerobic oxidation of methane (AOM) in the uppermost sediments (Reeburgh and Alperin, 1988; Boetius et al., 2000; Reeburgh, 2007; Boetius and Wenzhöfer, 2013). In contrast, at places where AOM is less efficient substantial amounts of methane can be expelled into the water column and potentially to the atmosphere (Etiope and Milkov, 2004). As methane is mostly consumed by AOM at seeps, this process produces dissolved bicarbonate, increasing porewater alkalinity, thus favoring precipitation of authigenic carbonate close to the seafloor (Bernier, 1980; Boetius et al., 2000). The resultant authigenic carbonates are potential archives of past fluid flow, especially in combination with dating results, providing insights into the evolution of past methane seepage activities (Aharon et al., 1997; Teichert et al., 2003; Feng et al., 2010; Feng and Chen, 2015; Bayon et al., 2013, 2015). However, studies on such carbonate rocks on the seafloor may fail to reveal the complete evolution of past seepage activities due to the somewhat discontinuous occurrence or sampling limitation. Seep-impacted sediment cores can serve as another important archive to

reconstruct the evolution of past seepage activities (Bayon et al., 2015; Li et al., 2016). In addition, authigenic carbonates may also be present as small nodules within seep sediments (e.g. Rodriguez et al., 2000; Pierre et al., 2000; Bayon et al., 2007). It has been well established that precipitation of ^{13}C -depleted carbonates in cold seep environments is closely related to AOM (Peckmann and Thiel, 2004). However, AOM signals might be obscured in bulk sediments in methane seep environment due to several factors, including inactivity (or weak activity) of methane seepages, low dissolved methane contents in fluids, high bioturbation rates, high sedimentation rates and/or high fluid flow rate (Luff et al., 2004). Therefore, an integrated study of authigenic carbonates on one hand and the corresponding host sediments on the other hand can provide a window into the distribution and magnitude of ancient seep settings (Bayon et al., 2007).

The variations of methane fluxes at seeps usually drive the migration of the sulfate-methane transition zone (SMTZ) in marine sediments (Borowski et al., 1996; Borowski, 2004). Recognition of the SMTZ and constraints on its migration in seep-impacted sediments, therefore, can be used to identify methane seepage events and consequently trace the evolution of past seepage activities. Numerous studies attempted to employ various indicators in marine sediments to reveal past seepage events and recognize the SMTZ, including barium (Ba) anomalies (e.g. Torres et al., 1996; Dickens, 2001; Snyder et al., 2007; Vanneste et al., 2013), authigenic carbonate and its carbon isotope composition (Nöthen and Kasten, 2011; Lim et al., 2011; Peketi et al., 2012, 2015; Chen et al., 2015), and content of pyrite and its sulfur isotope

composition (Pu et al., 2007; Lim et al., 2011; Peketi et al., 2012, 2015; Borowski et al., 2013; Lin et al., 2016a,b,c). In particular, increasing studies have used ^{34}S -enriched sulfide minerals in sediments for the identification of AOM-related processes and the SMTZs (Pu et al., 2007; Peketi et al., 2012; Borowski et al., 2013; Lin et al., 2016c). However, due to iron limitation in the sedimentary column, low $\delta^{34}\text{S}$ values of pyrites near the SMTZs compromise its ability to recognize seepage activities (Formolo and Lyons, 2013). A few previous studies have used carbon-sulfur-trace element systematics of seep-impacted sediments to trace the SMTZs and seepage activities (Peketi et al., 2012; Sato et al., 2012; Li et al., 2016). A comprehensive study on seep-impacted sediments and hosted authigenic carbonates will thus provide insights into (1) the applicability of sulfur isotopes of pyrite and (2) the variations of methane fluxes.

Here we investigated the geochemistry of three sediment gravity cores (D-8, D-7, and D-F) collected near Site 3 of “Jiulong Methane Reef” in Dongsha Area of the South China Sea (SCS). Carbon-sulfur-trace element systematics as well as grain size and AMS ^{14}C dating of planktonic Foraminifera in the sediments were determined to explore the applicability of AOM-related proxies at seeps and reveal past methane seepage variations.

2. Geological background

The SCS is a marginal sea characterized by the occurrence of both passive and active continental margins and high sedimentation rates (Taylor and Hayes, 1983).

The northern SCS represents the part of the passive continental margins, and is characterized by well-developed troughs, seamounts and scarps, and a series of sedimentary basins (e.g. Pearl River Mouth Basin, Taixinan Basin; Peng et al., 2004). The Dongsha Area is located in the southwest of the Taixinan Basin. The submarine scarps and canyons are well developed and intense gravity flow erosion is common in the area (Suess, 2005; Gong et al., 2012). The widely observed faults and mud diapirs in the area can serve as effective pathways for hydrocarbon migration (Suess, 2005; Wu et al., 2005; Yan et al., 2006). The existence of gas hydrates in this region has been identified by effective indicators, such as bottom simulating reflectors (BSR) and blanking zones (e.g. McDonnell et al., 2000; Suess, 2005; Wu et al., 2005; Li et al., 2013; Liu et al., 2015). Gas hydrates have been recovered in the shallow (~18 mbsf) sediments through drilling during the 2013 cruise conducted by the Guangzhou Marine Geological Survey (Fig. 1; Sha et al., 2015; Zhang et al., 2015). Authigenic carbonates from cold seeps were recovered in the Dongsha Area during several cruises from 2002 to 2013 (e.g. Chen et al., 2005, 2006; Suess et al., 2005; Han et al., 2008; Feng and Chen, 2015). An active cold seep with a methane gas plume, abundant living mussels and massive authigenic carbonates was reported in the northeast of Dongsha Area in recent years (Liu et al., 2008; Feng and Chen, 2015; Feng et al., 2015). In particular, there is a large carbonate buildup named “Jiulong Methane Reef” at Site 3 that is characterized by abundant seep-related bivalve shells and shell fragments (Suess et al., 2005; Han et al., 2008). Both faults and mud diapirs are considered as fluid conduits at Site 3, allowing methane to migrate upward and

causing free gas zones beneath BSRs, hydrate zones and seafloor methane seepages (Li et al., 2015).

3. Sampling and analytical methods

Sediment samples (core D-7, D-8, and D-F) were obtained using gravity cores from the Dongsha Area along the northern SCS continental slope during a Haiyang-4 cruise conducted by the Guangzhou Marine Geological Survey in October 2013. The sediment cores (D-7 and D-8) were recovered ~500 meters away from Site 3, and D-8 core was collected at the hydrate drilling site (Fig. 1). The three sampling sites have water depths ranging from 766 m to 1485 m (Fig. 1). The pore water geochemistry of the three cores revealed AOM-related signals in D-7 and D-F (Hu et al., 2015). Core D-8 and D-F show uniform lithologies, containing primarily green-gray clay silt. The dominant lithology of core D-7 begins with a homogenous green-gray clay silt in the topmost meter, followed downcore by a gradual increase of sandy size Foraminifera. The contents of Foraminifera reach a maximum at ~170 cm depth, and gradually decrease downcore until ~250 cm depth, and the rest of core D-7 is dominated by gray clay silt. Authigenic carbonate nodules 1-3 cm in diameter were found in core D-7 at 34 cm and 150-200 cm sediment depths (Fig. 3). The retrieved sediment cores was sub-sampled at 2 cm, 5 cm or 10 cm intervals, packed into plastic bags, and stored at -20°C in a refrigerator. All sediment samples were freeze-dried for further analyses.

Carbon and sulfur contents of freeze-dried and ground sediment samples were determined using a Vario EI-III Elemental Analyzer at the State Key Laboratory of

Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS). The analytical precision was about 2%. About 25 mg ground sediments were used to measure total carbon (TC) and total sulfur (TS). Total organic carbon (TOC) contents were determined using pre-acidified ground sediments. The acidified sediments were obtained by treatment with 4N HCl for 12 h, thoroughly rinsed with deionized water, and freeze-dried. Total inorganic carbon (TIC) contents were calculated as the difference between TC and TOC contents.

Chromium reducible sulfur (CRS) in sulfide minerals (S^0 , FeS, FeS₂) were extracted following the method of Canfield et al. (1986). Sediment samples were reacted with 1M CrCl₂ in an oxygen free reaction vessel with continuous nitrogen flow. Hydrogen sulfide (H₂S) produced from sulfide reduction by CrCl₂ was trapped as Ag₂S in AgNO₃ solution. The Ag₂S precipitate was dried and weighed to determine the CRS contents. Sulfur isotope analysis of the Ag₂S precipitate was performed using a Costech Elemental Analyzer (EC4010) coupled with a Thermo Finnigan Delta V Advantage in a continuous flow mode at the Stable Isotope Research Facility (SIRF) at Indiana University. Sulfur isotope ratios are reported in permil (‰) using the δ notation relative to the Vienna Canyon Diablo Troilite (VCDT). Sulfur isotope results are reproducible within $\pm 0.3\text{‰}$. For carbon isotope analysis of TIC and authigenic carbonate nodules of sediments, the analyses were conducted using a Gasbench II-Delta V Advantage mass spectrometer at the Third Institute of Oceanography, State Oceanic Administration. The CO₂ gas was produced by reacting with 100% phosphoric acid at 90 °C. Carbon isotope ratios are reported in the $\delta^{13}\text{C}$ notation

relative to the Vienna Pee Dee Belemnite (VPDB). Reproducibility of $\delta^{13}\text{C}$ values was on the order of 0.1‰ (2 σ).

Ground sediments for major and trace element analysis were placed in Teflon beakers, dissolved by 1 ml of HF and 1 ml of HNO₃. The method used for the chemical treatment procedure was the same as that described in Hu et al. (2014). Major and trace elements were determined using a Varian Vista Pro ICP-AES and a Perkin-Elmer Sciex ELAN 6000 ICP-MS, respectively. The measurements were conducted at the Institute of Geochemistry, CAS. Certified reference materials (GSR-1, OU-6, 1633-a, GXR-2, GXR-5) were used for quality control. Precision and accuracy were both better than 5% for major elements, barium (Ba), and uranium (U), and 10% for molybdenum (Mo).

For grain size measurements, sediment samples were dispersed by approximately 1 ml (0.05 N) sodium metaphosphate in a test tube while submerged in an ultrasonic cleaner for 1 min, and then analyzed with Mastersizer 2000 laser grain size analyzer at the South China Sea Institute of Oceanology, CAS. The detection limit was between 0.5 μm and 2000 μm . The analysis error of replicate testing is less than 2%. Five ^{14}C AMS dates were obtained on monospecific samples of planktonic Foraminifera (*G. sacculifer*) at Beta Analytic Inc., Miami, Florida, USA. Pretreatment, preparation, and measurement were finished at Beta Analytic Inc. Stable carbon isotope ratios ($^{13}\text{C}/^{12}\text{C}$) were obtained to verify the purity of the samples and to apply the standard correction to measured radiocarbon age to obtain the conventional radiocarbon age. Calibrated dates are presented in years before present (BP; before

AD 1950) with standard deviation of 2σ .

4. Results

4.1 Carbon and sulfur contents and S/C ratios

The contents of TOC, TIC, TS, and CRS and S/C ratios are shown in Fig. 2 (Complete data set can be found in supplementary materials). The three cores all exhibit low TOC contents ($\leq 0.62\%$) with an average content of 0.51% in D-8, 0.52% in D-F, and 0.40% in D-7. The TIC contents in cores D-8 and D-F are generally low, while D-7 shows relatively higher TIC contents, especially between 100 cm and 250 cm depths. Cores D-8, D-F, and D-7 have TS contents ranging from 0.08% to 0.25%, 0.08% to 0.13%, and 0.08% to 0.24%, respectively. The three cores have low CRS contents averaging 0.07% in D-8, 0.02% in D-F, and 0.04% in D-7. Down core variation of TS in the three cores is similar. Bulk sediment TS/TOC (S/C) ratios in D-8 (from 0.15 to 0.42) and D-F (from 0.17 to 0.26) are lower or close to that in normal oxic-suboxic marine sediments (mean S/C ratio: 0.36; Berner, 1982). In contrast, the interval of 150 cm-200 cm in D-7 has S/C ratios as high as 0.6. The same section also shows the highest contents of TIC, the lowest contents of TOC, and the presence of authigenic carbonate nodules (Fig. 2C).

4.2 Carbon and sulfur isotopes

The carbon isotope values of total inorganic carbon ($\delta^{13}\text{C}_{\text{TIC}}$) in cores D-8 and D-F range from -1.0‰ to 1.0‰ (Fig. 3). The $\delta^{13}\text{C}_{\text{TIC}}$ values in D-7 fall in the range of

-1.0‰ to 1.0‰, except for the 34 cm depth interval with slightly a negative value (-3.9‰). Carbonate nodules observed at 34 cm depth and in the interval of 150 cm-200 cm in core D-7 have $\delta^{13}\text{C}$ values as low as -49.8‰ (Fig. 3). Sulfur isotopes of CRS ($\delta^{34}\text{S}_{\text{CRS}}$) in cores D-8, D-F, and D-7 are low ranging from -42.0‰ to -18.1‰, -22.6‰ to -14.6‰, and -38.1‰ to -21.9‰, respectively. Overall, $\delta^{34}\text{S}_{\text{CRS}}$ values in sediments decrease with depth in the three cores despite some scatter (Fig. 3).

4.3 Major and trace elements

Selected major and trace element contents are present in Table 1. The Al contents range from 5.21% to 8.88% in core D-8 (mean 7.24%), 6.94% to 7.32% in D-F (mean 7.17%), and 5.07% to 8.83% in D-7 (mean 5.95%). Average contents of Fe in cores D-8, D-F, and D-7 are 3.75%, 3.92% and 3.53%, respectively. The contents of manganese (Mn), Ba, U, and Mo with depth in the three cores almost keep constant (Table 1). The Mn contents range from 0.03% to 0.05%, except for 2 cm depth in D-7 (0.16%) likely resulting from the formation of Mn oxide-hydroxides under oxic conditions. All U contents are below 3.6 ppm. Only at 195 cm depth in D-7 a high Mo content of 6.0 ppm was observed, and the other Mo contents are below 1.5 ppm. To circumvent the interference of the lithogenic fraction on the authigenic fraction, especially for trace metals, element/Al ratios are used to assess the authigenic fraction of the respective element (Tribovillard et al., 2006). As seen in Fig. 4, only at 195 cm depth of D-7 a strong authigenic enrichment of Mo and slightly authigenic enrichment of Fe and U are observed. No authigenic enrichment of trace elements is present at the

other depths in the studied sediment cores.

4.4 Grain size parameters and AMS ^{14}C ages

Grain size parameters were obtained for sediment core D-7 (Fig. 5A; Supplementary Materials). The sand contents slightly decrease with depth in the interval of 0-80 cm, begin to gradually increase and reach a maximum at ~170 cm depth, then gradually decrease downcore until ~270 cm, and finally keep low values to 330 cm depth. The silt and clay contents with depth are almost completely opposite to that of the sand contents. The average grain size and sorting coefficient with depth show almost the same variation trends as that of sand contents (Fig. 5A).

The AMS ^{14}C dating results of planktonic Foraminifera in D-7 are listed in Table 2. The dating results show increased ages with depth (Fig. 5A). Based on depth intervals and determined ages, the sedimentation rates are calculated (Fig. 5A). The ages at certain depths can roughly be estimated based on the sedimentation rates in the range of dating results. Therefore, the calculated ages at depths of 100 cm, 150 cm, and 200 cm are ~4.1 ka, ~5.4 ka, and ~6.5 ka, respectively.

5. Discussion

5.1. Variable methane fluxes constrained by pore waters and authigenic carbonates

At cold seeps, the produced dissolved inorganic carbon (DIC) via AOM generally is highly depleted in ^{13}C , reflecting the predominant origin from methane (e.g. Haese et al., 2003; Yoshinaga et al., 2014). Consequently, authigenic carbonates formed at

seeps are characterized by a major depletion in ^{13}C that is derived from the ^{13}C -depleted DIC (e.g. Lim et al., 2011; Peketi et al., 2012, 2015; Borowski et al., 2013). This makes it possible to recognize AOM signal and trace methane seepage activities using highly ^{13}C -depleted authigenic carbonates in sediments. Based on pore water sulfate and DIC concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ values in the three cores, the core D-8 reflects background sedimentation, and sulfate consumption at D-F is predominantly caused by AOM, while AOM is partially responsible for sulfate depletion at D-7 (Hu et al., 2015; Fig. 2). The AOM signals between pore waters and sediments are inconsistent in these three cores. In fact, only core D-7 revealed highly ^{13}C -depleted authigenic carbonates in sediments that indicate intense AOM. The $\delta^{13}\text{C}$ values of authigenic carbonates in D-7 are as low as -49‰ (Fig. 3), and are close to the $\delta^{13}\text{C}$ values of seep carbonates from nearby sites (Chen et al., 2005; Tong et al., 2013; Han et al., 2014). The highly negative $\delta^{13}\text{C}$ values suggest that biogenic methane is the predominant carbon source.

Although turbidity deposits and submarine landslide are well developed in the study region (Yan et al., 2006; Gong et al., 2012), grain size results of core D-7 reveal that the sedimentation was not impacted by turbidites, which typically have strikingly changing grain sizes at the bottom and the feature of C=M (Fig. 5B; Passega, 1964). The relatively constant ratios of Ti/Al and Zr/Rb indicate stable input of terrigenous fraction (Table 1). In addition, the AMS ^{14}C ages in D-7 reveal the normal successive layering of hemipelagic background sediments (Fig. 5A). It is therefore suggested that the authigenic carbonates in D-7 were in situ deposits, indicating the past methane

seepage activities at D-7 site. The burial depth is less than ~200 cm in the presence of authigenic carbonates in sediments at D-7. It illustrates that the past SMTZ had migrated to a sediment depth of less than ~200 cm during the formation of the authigenic carbonates. However, the pore water geochemistry of D-7 points to the deeper position of current SMTZ (>350 cm) (Hu et al., 2015). This decoupled record between sediments and pore waters is commonly observed at cold seeps (e.g. Mazumdar et al., 2009; Nöthen and Kasten, 2011; Lim et al., 2011; Wehrmann et al., 2011), and is considered to reflect the variation of methane fluxes and the SMTZ in the sedimentary column (Nöthen and Kasten, 2011). The presence of authigenic carbonate and age constraints (from 6.5 ka to 5.4 ka BP) on the host sediment suggest that methane seepage lasted about 1 ka. The occurrence of ^{13}C -depleted carbonates at 34 cm depth in core D-7 is an indicator of more recent methane seepage, but the age of this seepage is unknown. It probably reflects rapid response of pore water signatures and formation of authigenic carbonates during AOM at seeps (cf. Luff et al., 2004; Ussler and Paull, 2008). Observations and numerical modeling suggest that AOM can generate pore water signatures on timescales of centuries and authigenic carbonates on the order of thousands of years, even centuries (Luff et al., 2004; Ussler and Paull, 2008). Therefore, enough time has passed to allow for the rapid response of pore water signatures and formation of authigenic carbonates at core D-7 since ~6.5 ka BP.

5.2. The development and preservation of AOM-related signals in sediments

In cold seep sediments near the SMTZ, intense AOM promotes the formation of authigenic carbonates and sulfides, affecting the content and isotope anomalies of TIC and CRS, and sometimes cause the enrichment of certain trace elements (e.g. Mo and Ba) in sediments (e.g. Torres et al., 1996; Dickens, 2001; Hensen et al., 2003; Snyder et al., 2007; Lim et al., 2011; Peketi et al., 2012, 2015; Sato et al., 2012; Borowski et al., 2013). These anomalies in sediments in turn can be used to recognize AOM and trace the position of the SMTZ. However, some indicators of AOM may not appear due to complex controlling factors, such as multiple episodes of seepage activities and alteration of different early diagenesis. For instance, numerous studies on Ba anomalies (namely “Ba fronts”) in cold seep sediments revealed that the development and preservation of Ba fronts may be controlled by the variation of methane fluxes, sedimentation rates, and early diagenesis (e.g. Torres et al., 1996; Dickens, 2001; Riedinger et al., 2006; Snyder et al., 2007; Henkel et al., 2012; Vanneste et al., 2013). Similarly, these factors may control the other anomalies in cold seep sediments, and the variable methane fluxes mentioned above might control the development and preservation of these AOM-related signals in the studied sediments.

5.2.1. TIC contents and $\delta^{13}C$ values

Authigenic carbonates at seeps are characterized by great depletion in ^{13}C that serves as an important indicator of past methane seepages (e.g. Peckmann and Thiel, 2004). However, minor or no occurrence of authigenic carbonates might prevent the identification of past seepages. Nevertheless, the TIC contents and $\delta^{13}C_{TIC}$ values may

allow recognizing past methane seepages where there is a minor amount of authigenic carbonates dispersed in sediments (e.g. Lim et al., 2011; Peketi et al., 2012). In core D-7, high contents of TIC, but $\delta^{13}\text{C}_{\text{TIC}}$ values from 0.7‰ to 1.1‰ in the range of $\delta^{13}\text{C}$ values of DIC in seawater occurred in the interval of 150-200 cm. This illustrates that high contents of TIC in sediments are mainly contributed from skeletal carbonates. The $\delta^{13}\text{C}_{\text{TIC}}$ value reaching -3.9‰ at 34 cm depth of D-7 suggest that some authigenic carbonates in sediments were generated by AOM. The $\delta^{13}\text{C}_{\text{TIC}}$ values (-1.0‰-1.0‰) of core D-8 and D-F agree with a TIC source corresponding to skeletal carbonates.

5.2.2. S/C ratios, CRS contents and $\delta^{34}\text{S}_{\text{CRS}}$ values

In marine sediments, the production of H_2S is mainly controlled by organoclastic sulfate reduction (OSR) and AOM coupled sulfate reduction, thus the intensity of the two microbial mediated processes largely control the contents of sulfides in sediments (Berner, 1980; Canfield, 1991; Hensen et al., 2003). The contents of TS and TOC in normal marine sediment controlled by OSR generally show a positive correlation with a relatively constant S/C ratio of 0.36 (Berner, 1982). In TOC-lean and methane-rich sediments, AOM dominates over OSR, and contributes a significant fraction of sulfides, resulting in the prominently increase of S/C ratios in sediments (Kaneko et al., 2010; Lim et al., 2011; Sato et al., 2012). Cores D-8, D-F, and D-7 are TOC-lean sediments as revealed by low TOC contents ($\leq 0.62\%$; Fig. 2). Core D-8 has S/C ratios lower or close to 0.36 and positive correlations of CRS-TOC and CRS-TS contents, suggesting that the sulfides in sediments are derived from OSR (Fig. 3; Fig.

6). The low S/C ratios of D-F below 0.36 imply the OSR origin of sulfides in sediments. The peak S/C ratios (maximum=0.60) of D-7 occurs within the interval of 150 cm-200 cm corresponding to the presence of ^{13}C -depleted authigenic carbonates (Fig. 3). The high S/C ratios of D-7 suggest that AOM contributes a fraction of sulfides to the sulfur pool in sediments. This AOM origin of sulfides explains the lack of correlation between CRS and TOC contents in D-7 sediments (Fig. 6).

The differences between $\delta^{34}\text{S}_{\text{CRS}}$ and $\delta^{34}\text{S}$ of seawater sulfate ($\delta^{34}\text{S}_{\text{SW}} = \sim +21\text{‰}$) mostly exceed 46‰ in cores D-8 and D-7. The fractionation greater than 46‰ in this study may be attributed to the disproportionation of intermediate sulfur generated during the oxidation of sulfur in the uppermost sulfate reduction zone (Kaplan and Rittenberg, 1964; Canfield and Teske, 1996; Habicht and Canfield, 2001). Alternatively, such large fractionation could directly be induced by a single-step sulfate reduction without the disproportionation, particularly at extremely low sulfate reduction rates (SRR), as revealed by theoretical modeling (Wortmann et al., 2001; Brunner and Bernasconi, 2005) and recent culture experiments (Canfield et al., 2010; Sim et al., 2011). In addition, $\delta^{34}\text{S}_{\text{CRS}}$ values in the studied three sediment cores trend to decrease with depth (Fig. 3). The downcore decrease of $\delta^{34}\text{S}_{\text{CRS}}$ values was frequently observed in other marine sediments (Peketi et al., 2012 ; Borowski et al., 2013; Zhu et al., 2013). This phenomenon was suggested to be a combined result of (1) the preservation of isotopically light CRS formed early in an open system of the uppermost layer and (2) the accumulation of more ^{34}S -depleted CRS at later stages under low SRR owing to gradually increasing resistance of organic matter to sulfate

reducer at greater depth (Zhu et al., 2013).

The abundance of CRS and $\delta^{34}\text{S}_{\text{CRS}}$ values in marine sediments are primarily dependent on the availability of iron and H_2S in the pore water (Canfield et al., 1992) and the SRR which in turn is dependent on OSR or/and AOM pathways (Peketi et al., 2015). In an open system with sufficient supply of sulfate, the OSR pathway in normal marine sediments is dominant with low SRR, resulting in the formation of sulfides characterized by high ^{34}S depletion (e.g. Zhu et al., 2013). In cold seep sediments, intense AOM induces high SRR, leading to the continuous depletion of sulfate in pore water and ^{34}S enrichment of the residual sulfate, thus the production of ^{34}S -rich H_2S by sulfate reduction near the SMTZ (Jørgensen, 1979; Aharon and Fu, 2000, 2003; Jørgensen et al., 2004). These processes favor the formation of AOM induced sulfides characterized by ^{34}S enrichment (Jørgensen et al., 2004; Pu et al., 2007; Wehrmann et al., 2011; Peketi et al., 2012, 2015; Borowski et al., 2013). Accordingly, enrichment of $^{34}\text{S}_{\text{CRS}}$ in core D-7 would be expected in the presence of ^{13}C -depleted authigenic carbonates produced by AOM, however, all $\delta^{34}\text{S}_{\text{CRS}}$ values are quite negative in core D-7 (Fig. 3). This phenomenon was also observed by recent studies on other cold seep sediments near the SMTZ (e.g. Peketi et al., 2012; Borowski et al., 2013; Formolo and Lyons, 2013). The low $\delta^{34}\text{S}$ values of pyrite in seep-impacted sediments was attributed to low sedimentation rates that caused iron limitation, which lead to most of the pyrite forming early from ^{32}S -enriched H_2S (Formolo and Lyons, 2013). On the other hand, the occurrence of the largest enrichments in $^{34}\text{S}_{\text{CRS}}$ was suggested to be under dynamic conditions where methane

flux and AOM operated at the same horizon in the sedimentary column for appreciable lengths of geologic time (Borowski et al., 2013). Relatively high sedimentation rates in core D-7 imply that iron limitations might be not the cause of the low $\delta^{34}\text{S}_{\text{CRS}}$ values. Besides, it is likely that the depleted $^{34}\text{S}_{\text{CRS}}$ in D-7 sediments of 150 cm-200 cm interval and 34 cm depth reflects a formation environment in which AOM operated at the same horizon for only a short time. Under such a condition, most of CRS in core D-7 of 150 cm-200 cm interval and 34 cm depth are formed by OSR pathway through the disproportionation process and/or low SRR, resulting in low content of CRS and highly depleted $^{34}\text{S}_{\text{CRS}}$.

5.2.3. Trace elements

The enrichments of trace elements (e.g. Mo and Ba) have been frequently reported in cold seep sediments (e.g. Torres et al., 1996; Dickens, 2001; Sato et al., 2012; Peketi et al., 2012; Vanneste et al., 2013). Cores D-8 and D-F show no anomalies of Fe, Mn, Mo, U, and Ba. Only core D-7 exhibits strongly enrichment of Mo and slight enrichment of Fe and U at 195 cm depth, but without Ba enrichment (Fig. 4). The lack of Ba enrichment in cold seep sediments was generally linked to high sedimentation rates, a low productivity linked, limited Ba flux to the sediment, or upward movement of the SMTZ causing possible dissolution of barite (e.g. Snyder et al., 2007; Peketi et al., 2012; Vanneste et al., 2013). In core D-7, the relatively high sedimentation rates and low productivity inferred from low TOC contents may be the causes of the lack of a Ba enrichment. Generally, dissolved Mo is highly sensitive to

H₂S in pore water (e.g. Zheng et al., 2000; Helz et al., 2011). The H₂S produced by intense AOM near the SMTZ tends to result in strongly enrichments of Mo in sediments (Peketi et al., 2012; Sato et al., 2012). However, only an enrichment of Mo occurring in D-7 at 195 cm depth may reflect a temporary H₂S flux produced by AOM resulting from transient methane seepage.

The Mo enrichment and negative $\delta^{34}\text{S}_{\text{CRS}}$ values in core D-7 in the 150 cm-200 cm interval reflect the occurrence of a transient methane seepage event that lasted for about 1 ka, resulting in extremely ¹³C-depleted authigenic carbonates and high S/C ratios. Such transient methane seepages are common due to the commonly observed temporal changes of flow intensity at seeps (cf. Solomon et al., 2008; Tyron et al., 1999; Tyron and Brown, 2004). Accordingly, the carbon-sulfur-trace element systematics used here are a promising tool to evaluate transient methane seepages in sediments, which might result in inapparent Mo enrichments and low values of $\delta^{34}\text{S}_{\text{CRS}}$. Although high values of $\delta^{34}\text{S}_{\text{CRS}}$ in seep-impacted sediments are useful for constraining seepage activity as revealed by many previous studies (e.g. Pu et al., 2007; Lim et al., 2011; Peketi et al., 2012, 2015; Borowski et al., 2013; Lin et al., 2016c), low values of $\delta^{34}\text{S}_{\text{CRS}}$ observed by Formolo and Lyons (2013) and in this study illustrate that $\delta^{34}\text{S}_{\text{CRS}}$ patterns may be very different from one seep area to the other. The ³⁴S compositions of pyrite to recognize seep activities in the geological record should be applied with caution. Besides iron limitation might result in the low values of $\delta^{34}\text{S}_{\text{CRS}}$ in seep-impacted sediments in some cases (Formolo and Lyons, 2013), the transient methane seepages similar to that recognized in core D-7 may be

another factor causing low $\delta^{34}\text{S}_{\text{CRS}}$ values at seeps.

6. Conclusions

Carbon-sulfur-trace element systematics, grain size and AMS ^{14}C dating of planktonic Foraminifera in three sediment cores (D-8, D-F, and D-7) from the South China Sea were investigated. Only sediments from core D-7 were identified to be influenced by methane seepage. Grain size analysis and AMS ^{14}C ages suggest that the extremely ^{13}C -depleted carbonate nodules from core D-7 precipitated in situ by anaerobic oxidation of methane (AOM) and were the products of past methane seepage. The ^{13}C -depleted carbonates and high S/C ratios developed in the 150-200 cm interval in core D-7. Low contents of chromium reducible sulfur (CRS), extreme $^{34}\text{S}_{\text{CRS}}$ depletion, and Mo enrichment in the same interval are interpreted to reflect a transient methane seepage event. The results suggest that the application of $\delta^{34}\text{S}_{\text{CRS}}$ alone as a proxy to identify AOM-related process is insufficient. Sediment carbon-sulfur-trace element systematics used here are shown to be a promising tool to evaluate transient methane seepage in seep environments.

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Figure captions

Fig. 1 Map showing the study region (red rectangle) located at Dongsha area of the South China Sea continental slope. Sampling locations were in the vicinity of Jiulong Methane Reef (Site 3; Han et al., 2008). Gas hydrates have been recovered in the shallow sediments (~18 mbsf; Sha et al., 2015; Zhang et al., 2015) at the drilling sites. The water depths of cores D-8, D-F, and D-7 are 814 m, 1485 m, and 766 m, and core lengths are 405 cm, 445 cm, and 350 cm, respectively.

Fig. 2 Contents of total organic carbon (TOC), total inorganic carbon (TIC), total sulfur (TS), and chromium reducible sulfur (CRS), S/C ratios, and sulfate concentrations with depth in sediment cores of D-8(A), D-F (B), and D-7 (C). The sulfate concentration profiles were taken from Hu et al. (2015).

Fig. 3 $\delta^{13}\text{C}_{\text{TIC}}$ and $\delta^{34}\text{S}_{\text{CRS}}$ values of bulk sediments in cores D-8 (A), D-F (B), and D-7 (C). Data next to the black dots in (C) represent $\delta^{13}\text{C}$ values of authigenic carbonate nodules. The gray band corresponds to a horizon with the presence of authigenic carbonate nodules.

Fig. 4 Fe/Al, Mn/Al, Mo/Al, U/Al, and Ba/Al ratios of bulk sediments in cores D-8 (A), D-F (B), and D-7 (C). The dashed and the dot-dashed lines are Mo/Al and U/Al ratios of the Post Archean Australian Shale (PAAS; Taylor and McLennan, 1985), respectively.

Fig. 5 Grain size parameters and age model of the sediment core D-7. (A) Sand, silt, and clay contents, average grain size, sorting coefficient, and AMS ^{14}C dating results of planktonic Foraminifera are all shown with depth. Sedimentation rates were calculated based on intervals of depths and radiocarbon dates. The calculated ages at depths of 100 cm, 150 cm, and 200 cm were inferred from the sedimentation rates. (B) Passega C-M diagram (Passega, 1964). C= maximum (D99; first percentile) grain size, M= median grain size. Red dots represent the interval (100 cm-250 cm) with higher

sand content, average grain size, and sorting coefficient.

Fig. 6 (A) TOC (%) vs. CRS (%) and (B) TS (%) vs. CRS (%) patterns for sediment cores D-8, D-F, and D-7.

(A) D-8

(B) D-F

(C) D-7

Table captions

Table 1. Selected element contents, isotope data, and Ti/Al and Zr/Rb ratios in sediment cores D-8, D-F, and D-7.

Sample ID	Depth interval (cm bsf)	Plot depth (cm bsf)	CRS (wt %)	$\delta^{34}\text{S}_{\text{CRS}}$ (‰; VCDT)	$\delta^{13}\text{C}_{\text{TIC}}$ (‰; VPDB)	Al (%)	Fe (%)	Mn (%)	Mo (ppm)	U (ppm)	Ba (ppm)	Ti (%)	Rb (ppm)	Zr (ppm)	Ti/Al ×100	Zr/Rb
D8-2	19-21	20	0.019	-18.1	1.0	5.2	2.8	0.03	0.8	2.7	323	0.32	90.2	137	6.2	1.5
D8-6	59-61	60	0.015	-26.4	0.4	6.8	3.6	0.03	0.6	3.3	409	0.42	109	164	6.2	1.5
D8-11	105-110	110	0.018	-31.0	1.0	6.2	3.3	0.03	0.6	2.9	377	0.39	103	169	6.4	1.6
D8-17	165-170	170	0.030	-33.4	0.5	7.1	3.6	0.04	0.6	3.1	394	0.40	112	165	5.7	1.5
D8-25	245-250	250	0.080	-42.0	-0.2	8.0	4.3	0.04	0.6	3.4	437	0.47	135	154	5.9	1.1
D8-30	295-300	300	0.138	-41.5	-0.2	8.9	4.6	0.05	0.5	3.6	475	0.49	166	155	5.6	0.9
D8-37	365-370	370	0.178	-40.1	0.2	8.7	4.6	0.05	0.9	3.3	454	0.45	165	148	5.2	0.9
D8-40	395-400	400	0.054	-39.5	1.0	7.1	3.2	0.04	1.1	3.6	387	0.39	117	151	5.5	1.3
DF-1a	0-5	5	0.022	-14.6	-0.5	7.3	4.1	0.06	0.5	2.6	420	0.44	124	164	6.1	1.3
DF-5	45-50	50	0.026	-14.7	-0.4	7.2	4.0	0.05	0.6	2.8	431	0.44	129	165	6.1	1.3
DF-10	95-100	100	0.026	-17.2	-0.6	6.9	4.0	0.05	0.5	2.8	419	0.46	119	174	6.6	1.5
DF-20	195-200	200	0.031	-22.6	-0.5	7.1	3.7	0.05	0.8	3.0	422	0.44	115	181	6.2	1.6
DF-31	305-310	310	0.010	-20.9	-0.4	7.3	3.9	0.05	0.8	2.9	422	0.44	123	171	6.0	1.4
DF-43	425-430	430	0.028	-21.1	-0.5	7.2	4.0	0.05	0.9	3.0	424	0.44	120	170	6.2	1.4
D7-1a	0-2	2	0.036	-21.9	0.9	5.2	3.6	0.16	1.4	2.3	352	0.33	92.3	133	6.4	1.4
D7-3a	30-32	32	0.012	-23.4	0.5	6.2	3.6	0.04	0.6	2.8	400	0.40	112	163	6.5	1.5
D7-3b	32-34	34	0.013	-26.9	-3.9	5.7	3.5	0.04	1.6	3.0	384	0.38	114	156	6.7	1.4

D7-3c	34-36	36	0.012	-25.8	n.m.	6.2	3.7	0.04	0.7	2.8	395	0.40	116	157	6.5	1.4
D7-4	36-40	40	0.019	-25.2	n.m.	6.8	3.8	0.04	1.3	2.7	400	0.40	112	158	5.9	1.4
D7-6a	66-68	68	0.018	-25.8	0.2	7.0	3.9	0.04	0.5	3.1	413	0.43	131	170	6.1	1.3
D7-8	78-80	80	0.013	-23.1	0.4	6.8	3.9	0.04	0.4	3.2	417	0.43	138	165	6.3	1.2
D7-10a	100-105	105	0.046	-29.3	0.8	6.0	3.6	0.03	0.8	2.6	359	0.36	105	158	6.1	1.5
D7-14	135-140	140	0.031	-31.8	0.7	5.4	3.3	0.03	0.5	2.3	322	0.33	93.3	140	6.2	1.5
D7-15	145-150	150	0.034	-28.7	1.0	5.3	3.3	0.03	0.6	2.3	329	0.34	98	139	6.4	1.4
D7-15a	150-155	155	n.m.	n.m.	n.m.	5.3	3.3	0.03	0.7	2.3	339	0.33	95.5	147	6.2	1.5
D7-16	155-160	160	0.046	-32.5	0.7	4.9	3.2	0.03	0.6	2.1	307	0.30	87.4	150	6.1	1.7
D7-17	165-170	170	0.056	-31.2	0.9	5.0	3.4	0.03	1.0	2.0	306	0.32	86.8	136	6.4	1.6
D7-18	175-180	180	0.040	-30.9	0.9	5.1	3.3	0.03	0.8	2.2	311	0.32	89.7	140	6.4	1.6
D7-19	185-190	190	0.048	-34.0	1.0	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.		
D7-19a	190-195	195	0.031	-35.3	n.m.	5.3	3.1	0.03	6.0	2.6	346	0.27	91.9	138	5.2	1.5
D7-20	195-200	200	0.038	-33.3	1.1	5.2	3.2	0.03	0.7	2.2	320	0.32	92.1	147	6.2	1.6
D7-20a	200-205	205	0.037	-34.4	n.m.	5.1	3.1	0.03	1.0	2.2	319	0.32	91.3	134	6.3	1.5
D7-23	225-230	230	0.035	-30.9	0.9	5.3	3.1	0.03	0.8	2.2	323	0.32	94.3	142	6.0	1.5
D7-25	245-250	250	0.030	-33.7	0.4	6.3	3.5	0.04	0.4	2.5	369	0.39	112	161	6.3	1.4
D7-29	285-290	290	0.071	-38.1	-0.1	8.0	4.1	0.04	0.7	3.2	417	0.44	141	161	5.5	1.1
D7-30	295-300	300	0.119	-37.4	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.		
D7-33	325-330	330	0.066	-37.7	-0.4	8.8	4.7	0.05	0.7	3.1	451	0.46	145	148	5.2	1.0

n.m., not measured.

Table 2. AMS ^{14}C dating results of planktonic Foraminifera (*G. sacculifer*) in sediment core D-7.

Sample ID	Laboratory code	depth intervals (cmbsf)	Uncorrected ^{14}C age (yr B.P.)	Corrected age (yr B.P.)	$\delta^{13}\text{C}$ (‰ , VPDB)
D7-a	Beta-404849	72-78	1990±30	2410±30	+0.6
D7-b	Beta-404850	100-105	4070±30	4490±30	+0.6
D7-c	Beta-404851	170-175	5490±30	5920±30	+1.0
D7-d	Beta-404852	250-255	7320±30	7760±30	+1.6
D7-e	Beta-404853	270-275	7720±30	8150±30	+1.2

B.P. stands for “Before Present” where the “Present” is defined as the year 1950 A.D.