



Production of Labile Protein-Like Dissolved Organic Carbon Associated With Anaerobic Methane Oxidization in the Haima Cold Seeps, South China Sea

Tingcang Hu¹, Min Luo^{1,2*}, Yunping Xu¹, Shanggui Gong¹ and Duofu Chen^{1*}

¹ Shanghai Engineering Research Center of Hadal Science and Technology, College of Marine Sciences, Shanghai Ocean University, Shanghai, China, ² Laboratory for Marine Geology, Qingdao National Laboratory for Marine Science and Technology, Qingdao, China

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*Correspondence:

Min Luo
mluo@shou.edu.cn
Duofu Chen
dfchen@shou.edu.cn

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Cold seeps where methane-rich fluids escape from the seafloor generally support enormous biomass of chemosynthetic organisms and associated fauna. In addition to transporting a great amount of methane toward the seafloor, cold seeps also contribute to the aged, dissolved organic carbon (DOC) pool in the deep ocean. Here, two sediment cores from the “Haima cold seeps,” northern South China Sea and a nearby reference core were analyzed for pore-water sulfate and DOC concentrations, $\delta^{13}\text{C}$ of DOC, and optical properties of dissolved organic matter (DOM). High DOC concentrations (0.9–3.7 mM) accompanied by extremely low $\delta^{13}\text{C}$ values (–43.9 to –76.2‰) suggest the conversion of methane into sedimentary DOC pool in the seep sediments. Parallel factor analysis (PARAFAC) of the fluorescence excitation-emission matrices shows higher fluorescent intensities of labile protein-like components (C2 and C4) and lower fluorescent intensities of refractory humic-like components (C1 and C3) in the seep cores compared to the reference core. The intensity of C2 is positively correlated with DOC concentrations and $\delta^{13}\text{C}$ -DOC in the seep sediments, suggesting that the labile protein-like DOM was produced by the anaerobic oxidation of methane (AOM). Moreover, low humification index (HIX) and high biological index (BIX) values also indicate intensified production of relatively labile DOM with lower degradation degree in the seep cores compared to the reference core. Hence, we highlight that methane-derived DOC may serve as important carbon and energy sources for heterotrophic microbial communities due to its relatively labile nature.

Keywords: cold seeps, dissolved organic carbon, fluorescence spectrum, protein-like, AOM

INTRODUCTION

Dissolved organic carbon (DOC) in marine sediments represents an important by-product during the mineralization of particulate organic matter (POC; Aller, 1978; Berner, 1980; Komada et al., 2013; Burdige et al., 2016). Although the majority of POC is ultimately degraded to dissolved inorganic carbon (DIC), a varying fraction of POC is converted to DOC and accumulates in marine

sediments (Burdige, 2002; Komada et al., 2013). This net production of DOC results in significantly higher pore water DOC concentrations than bottom seawater (Martin and McCorkle, 1993; Alperin et al., 1994; Burdige et al., 1999). DOC release from continental margin sediments can supply $\sim 180 \text{ Tg C year}^{-1}$ to the deep ocean, roughly equivalent to the riverine DOC input (Burdige et al., 1999), thereby affecting the characteristics of DOC in the deep ocean. Pore-water DOC in the very surface sediments is more labile and younger than the deep-ocean DOC due to rapid turnover of the labile POC component (Bauer et al., 1995; Komada et al., 2012). With the ongoing POC degradation in the sediments, increasingly amount of highly degraded, low-molecular-weight refractory DOC is produced and accumulated in the pore water. Based on numerical modeling results, Burdige et al. (2016) concluded that refractory DOC accounted for $> 95\%$ of the total pore-water DOC except that in the sediments close to the seafloor.

Marine sediments hold $\sim 500\text{--}10,000 \text{ Gt}$ carbon in the form of methane, predominantly occurred as gas hydrate (Kvenvolden, 1988; Buffet and Archer, 2004; Milkov, 2004). In the case of gas hydrate dissociation due to temperature and/or pressure changes, a large quantity of methane is released and transported toward the seafloor, forming cold seeps (Reeburgh, 2007). In addition to POC mineralization, DOC production in seep-impacted sediments is closely associated with the anaerobic oxidation of methane (AOM; Pohlman et al., 2011). As a result, significantly higher DOC concentrations have been observed in seep sediments compared to non-seep deep sea sediments (Hung et al., 2016; Amaral et al., 2021). Valentine et al. (2005) found that the proportion of methane-derived DOC increases with enhanced AOM rates and microbial activity in the cold seep sediments. Because of the influence of AOM, DOC is generally ^{13}C - and ^{14}C -depleted in seep sediments. Mass-balance calculation using $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ data showed that up to 86% of pore water DOC in the Arctic cold seep sediments was derived from fossil methane. Furthermore, Pohlman et al. (2011) suggested that methane-derived DOC accounted for up to 28% of DOC pool in the overlying bottom water, thereby likely representing an important but previously unconsidered source of pre-aged, ^{13}C -depleted carbon into the deep ocean.

The potential impact of sediment-derived DOC on the deep ocean carbon cycle mainly depends on the reactivity of DOC. Optical property provides important insights into the source, composition, and reactivity of dissolved organic matter (DOM; Burdige et al., 2004; Coble, 2007; Dittmar and Stubbins, 2014; Chen et al., 2016; Wagner et al., 2020). Microbial metabolism sustained by deeply-sourced methane-rich fluids *via* mud volcanism has been documented to significantly contribute to the production of fluorescence dissolved organic matter (FDOM), $\sim 70\%$ of which was characterized by labile, protein-like fluorescence components (Amaral et al., 2021). Apart from the microbe-derived FDOM, thermogenically altered FDOM transported from the deep subsurface has also been detected in mud volcano pore fluids (Brogi et al., 2019). Moreover, bottom water collected from methane seeps contained more protein-like and lipid-like DOM components than non-seep areas, suggesting

that cold seep sediments can be an important source of DOM to the bottom water, thereby impacting bottom-water DOM composition and reactivity (Sert et al., 2020).

Even though cold seep sediments have been recognized as an important source of overlying water DOM, knowledge on the reactivity of methane-derived DOM is quite limited, which hinders the assessment of the potential impact of methane-derived, fossil DOC on the deep ocean DOC pool. Here, we analyzed pore-water concentrations of sulfate (SO_4^{2-}) and DOC, stable carbon isotopic compositions ($\delta^{13}\text{C}$) of sedimentary DOC, and fluorescence properties of sedimentary DOM in the “Haima cold seeps,” northern South China Sea (SCS). This work seeks to test the hypothesis that the majority of methane-derived DOC is relatively labile that could play an important role in sustaining heterotrophic metabolism in both the sediments and overlying bottom water.

MATERIALS AND METHODS

Study Area

The “Haima cold seeps” was discovered in the Qiongdongnan basin (QDNB), located in the extensional sector of the northern SCS passive margin, by the Guangzhou Marine Geological Survey in 2015. It consists of two active seep areas (ROV1 and ROV2; 7 km apart) with the water depth of $\sim 1,400 \text{ m}$ (Figure 1). Geophysical imaging showed that the seeps were sustained by upward-migrating methane gas evidenced by the occurrence of gas chimney (Wang et al., 2008). Due to intense methane gas bubbling, methane hydrates were formed in shallow sediments, and living benthic fauna (e.g., tubeworms, clams, and mussels) were observed at the two seep sites by remotely operated vehicle (ROV) surveys (Liang et al., 2017).

Sample Collection

A gravity core (ROV1) and a push core (ROV5) were retrieved from the “Haima cold seeps” during the R/V Haiyang-6 cruise in September 2020. A reference core (QDN-C-S03) was collected from non-seep area using a gravity corer during R/V Haiyang-10 cruise in August 2019. The recovered cores were immediately brought to the onboard laboratory and sliced into 2–20 cm intervals for pore water collection using Rhizon samplers. Aliquots for DOM analysis were stored in pre-combusted (550°C for 4 h), 40 ml brown glass bottle and frozen at -20°C until further analysis. The aliquot for SO_4^{2-} analysis was acidified with HNO_3 and stored in a refrigerator ($\sim 4^\circ\text{C}$). After pore water extraction was completed, sediment samples were kept frozen at -20°C .

Analytical Methods

The concentrations of SO_4^{2-} were determined using a Dionex ICS-900 ion chromatograph after a 500-fold dilution with Milli-Q water. Ion Pac AS23-type column for anion and a mixed solution of Na_2CO_3 and NaHCO_3 was used as eluent for SO_4^{2-} concentration measurements. The analytical precision for SO_4^{2-} is better than 2%. DOC concentrations were determined by a high-temperature catalytic combustion method after a proper

dilution with Milli-Q water using Shimadzu TOC-L analyzer with an analytical precision of $\pm 3\%$. The deep seawater provided by Hansell laboratory (University of Miami) was used as the DOC standard validation. For $\delta^{13}\text{C}$ -DOC analyses, pore water samples were acidified to $\text{pH} \sim 2$ with 6 M HCl for 72 h to remove inorganic carbon and then analyzed by high-temperature combustion on a Vario Cube TOC analyser connected to an Isoprime 100 continuous flow isotope ratio mass spectrometer. The analytical precision for $\delta^{13}\text{C}$ -DOC is better than 0.2‰.

Absorption spectra were scanned from 200 to 800 nm on an ultraviolet-visible (UV-Vis) spectrophotometer (Shimadzu Inc., Japan). Fluorescence excitation-emission matrices (EEMs) were measured using a Hitachi F-7000 luminescence spectrometer (Hitachi Inc., Japan). Excitation ranged 240–450 nm with 5 nm interval, while emission encompassed between 250 and 550 nm with 1 nm interval. The EEMs correction process included blank subtraction, inner filter correction and scatter removal. Fluorescence data were converted to Raman intensity units (RU) by normalizing the fluorescence collected in arbitrary units to the Raman peak area at 350 nm. Subsequently, we used parallel factor analysis (PARAFAC) to determine the number of fluorescent components based on the split-half validation. The EEMs correction and PARAFAC modeling were performed using the MATLAB R2019a with the drEEM toolbox (Murphy et al., 2013). In addition, the optical indices, including the fluorescence index (FI), humification index (HIX) and biological index (BIX) were also analyzed. FI is a ratio of emission wavelengths at 470 and 520 nm, gained at excitation 370 nm, which is usually used to distinguish between autochthonous (microbial source) and allochthonous DOM (terrestrial source) (Mcknight et al., 2001; Cory et al., 2010). HIX is an area under the emission spectra 435–480 nm divided by the area 300–345 nm, at excitation wavelength 254 nm, which can be used to reflect the humic substance content and the degree of humification (Ohno, 2002). BIX is the ratio of emission intensity at 380 nm divided by 430 nm at excitation 310 nm, which is positively correlated with the contribution of the autotrophic produced, low-degradation degree FDOM (Huguet et al., 2009).

RESULTS

Downcore Profiles of SO_4^{2-} , Dissolved Organic Carbon, and $\delta^{13}\text{C}$ -DOC

The downcore variations in concentrations of SO_4^{2-} and DOC and $\delta^{13}\text{C}$ -DOC values are shown in **Figure 2**. At the reference core (QDN-C-S03), the SO_4^{2-} concentrations decrease slightly with depth from 26.0 to 22.4 mM. In contrast, the SO_4^{2-} concentrations decline rapidly with depth at both seep cores, forming shallow sulfate-methane transition zone (SMTZ) (~ 120 cm for ROV1 and ~ 30 cm for ROV5). Sedimentary DOC concentrations in all three cores (0.31 – 3.7 mM) are significantly higher than the average deep-ocean DOC concentration (~ 40 μM) (Hansell and Carlson, 1998). The concentrations and $\delta^{13}\text{C}$ values of DOC generally remain constant throughout the reference core, whereas both seep cores exhibit significantly higher DOC concentrations and lower $\delta^{13}\text{C}$

values (**Figure 2**). In addition, the downcore profiles of DOC concentrations mirror that of $\delta^{13}\text{C}$ values at both seep cores, with higher DOC concentrations corresponding to lower $\delta^{13}\text{C}$ values and *vice versa*.

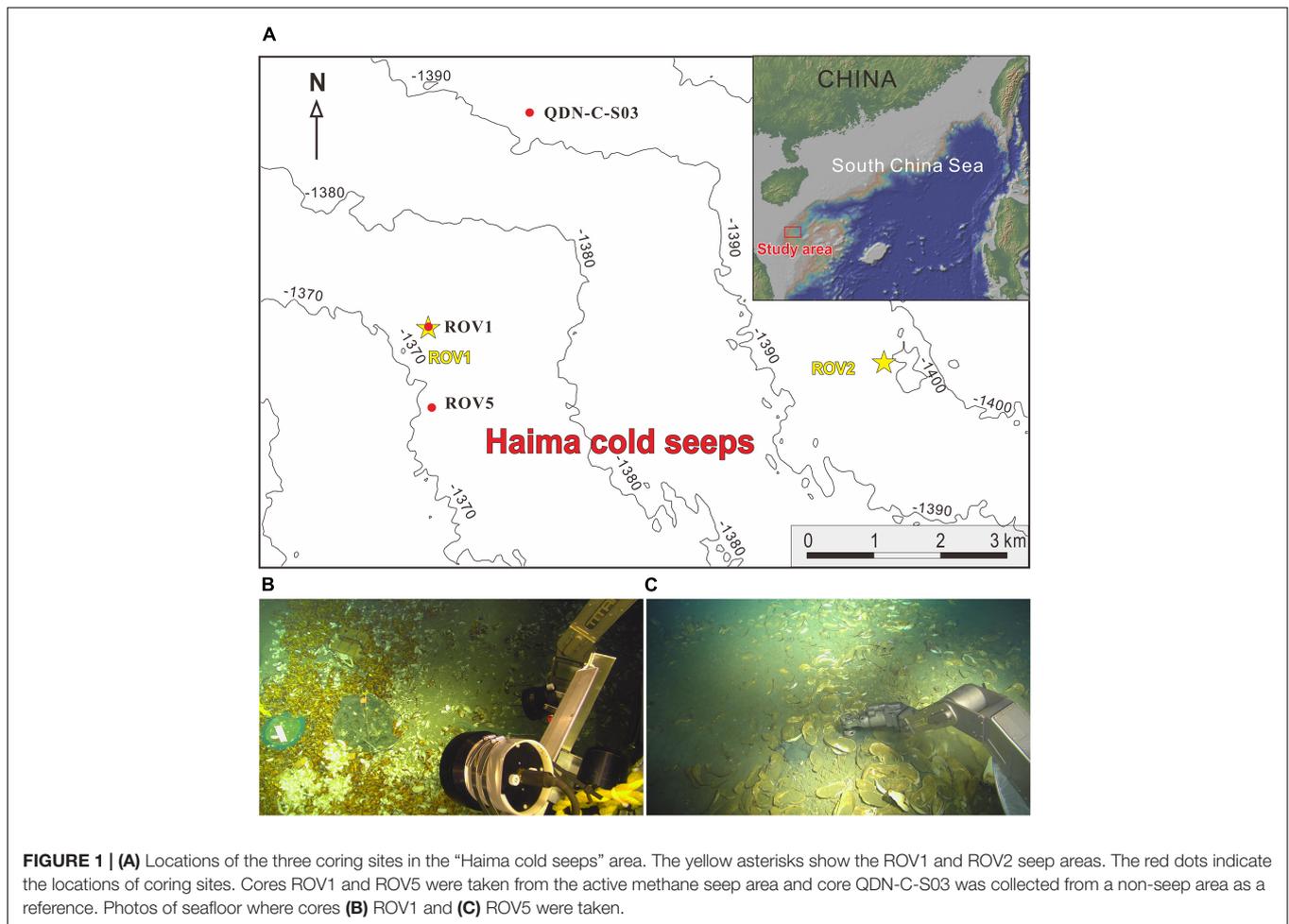
Optical Properties of Sedimentary Dissolved Organic Matter

Four fluorescent components (C1–C4) were identified based on the EEM-PARAFAC model. These components were matched to previous models in the OpenFluor database that had a 0.95 minimum similarity score for the identical match between spectra. C1 (Ex/Em maxima: 250(320)/410 nm) and C3 (Ex/Em maxima: 255(370)/472) were matched to several PARAFAC models in the OpenFluor database and assigned as relatively refractory marine/microbial humic-like and terrestrial humic-like components (Coble, 1996; Murphy et al., 2014; Chen et al., 2016; Loginova et al., 2016; **Figure 3**). A number of labile protein-like components were matched to C2 (Ex/Em maxima: 275/350) in the OpenFluor database, indicating that C2 is a ubiquitous component of natural organic matter (Murphy et al., 2014). C4 (Ex/Em maxima: 265/285), also identified as a labile protein-like component, was matched to four studies focusing on seawater (Coble, 1996; Burdige et al., 2004; Murphy et al., 2014; Loginova et al., 2016). More specifically, C2 and C4 were thought to represent tryptophan-like and tyrosine-like compounds, respectively, in a variety of natural environments (Murphy et al., 2008; Chen et al., 2018). In addition, these labile protein-like components were also likely associated with aliphatic hydrocarbons (Dvorski et al., 2016; Podgorski et al., 2018; Mirnaghi et al., 2019). However, given the biogenic origin of methane in the “Haima” cold seeps (Wei et al., 2020), we presume a negligible contribution of petroleum-derived aliphatic compounds to the labile protein-like components. The fluorescence intensity of protein-like components (C2 + C4) account for $63\% \pm 17\%$ of the total FDOM intensity (C1 + C2 + C3 + C4) at the seep cores, which is significantly higher than those at the reference core ($17\% \pm 8\%$). FI values (1.67–2.03) do not show significant differences between the seep cores and the reference core (**Figure 4**). In contrast, HIX values at the reference core (0.84–0.92) are higher than those at the seep cores (0.47–0.71), while BIX values show an opposite pattern with slightly higher values at the seep cores than at the reference core.

DISCUSSION

Sources of Dissolved Organic Carbon in the Seep Sediments

Dissolved organic carbon in continental margin sediments is generally produced during the process of POC mineralization (Komada et al., 2013; Burdige et al., 2016). In the seep sediments, in addition to POC mineralization, DOC production is also associated with AOM process (Valentine et al., 2005; Pohlman et al., 2011). DOC concentrations at both seep cores (ROV1 and



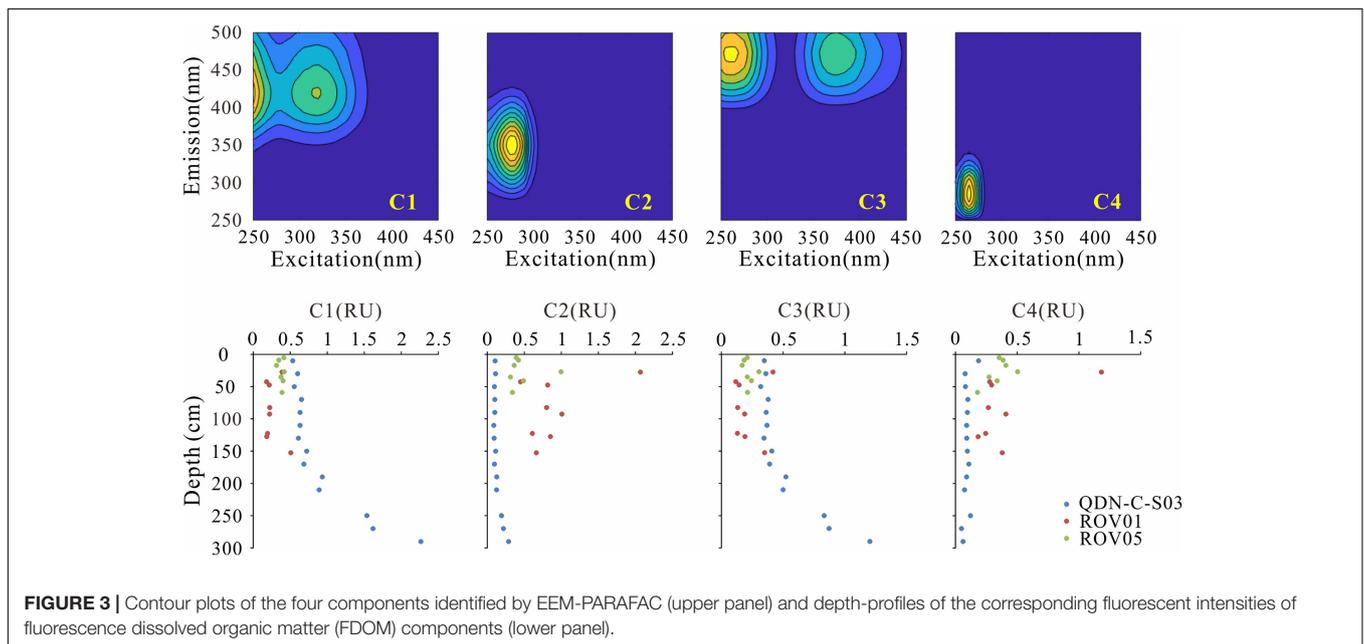
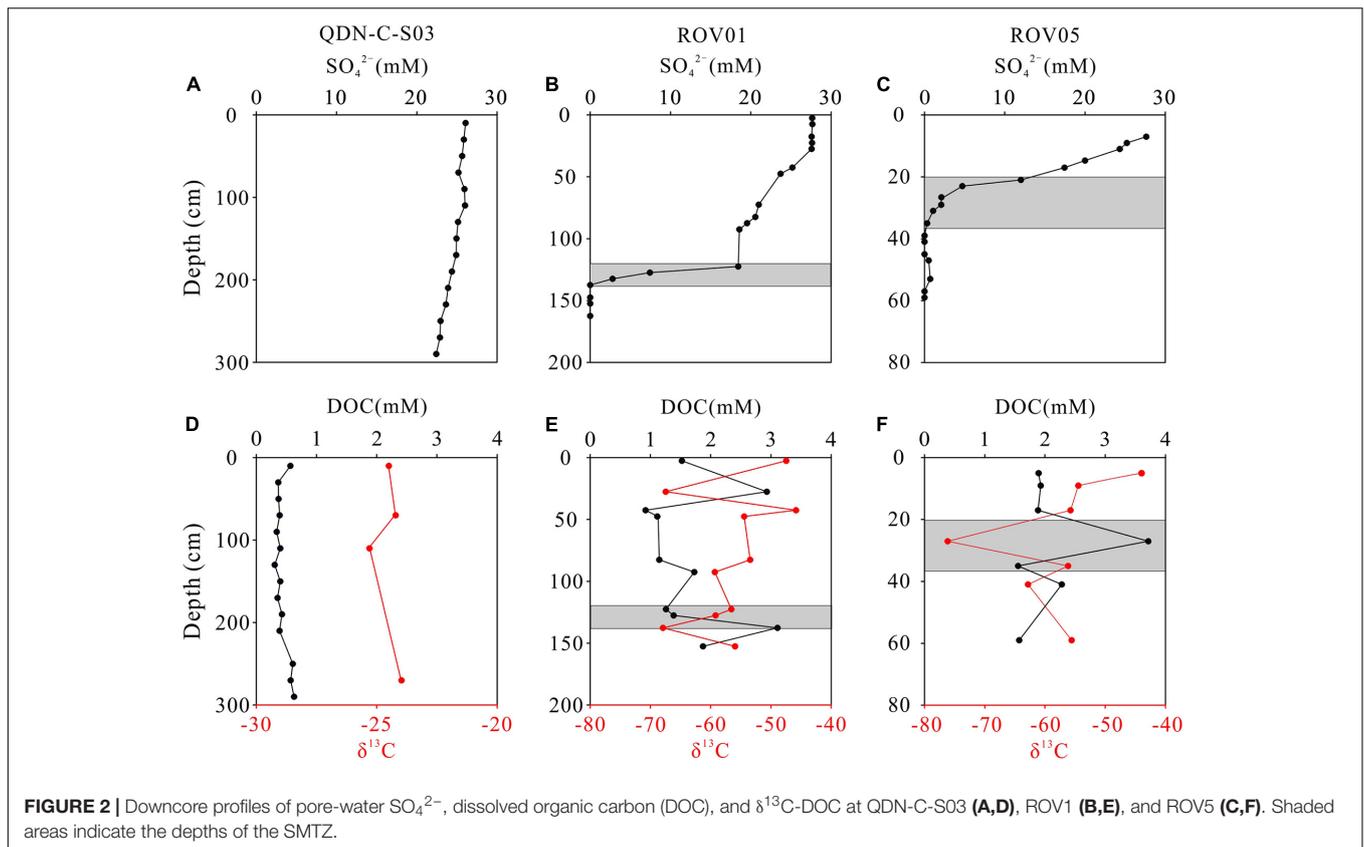
ROV5) are higher than those at the reference core (QDN-C-S03), and ROV5 with shallower SMTZ exhibits higher average pore-water DOC compared to ROV1 with deeper SMTZ. These observations suggest that seep sediments contribute to DOC production with elevated methane flux and resulting AOM rate corresponding to enhanced DOC production. Moreover, ^{13}C -depleted DOC measured at the seep cores (-43.9 to -76.2‰) also points to a predominately methane-derived DOC as methane collected from “Haima cold seeps” is mostly biogenic in origin with $\delta^{13}\text{C}$ values ranging between -72.3 and -71.5‰ (Wei et al., 2020). In contrast, at the reference core absent of methane seepage, the $\delta^{13}\text{C}$ values of DOC are significantly higher, exhibiting similar values of sedimentary TOC in the Qiongdongnan basin that receives both marine and terrestrial organic matter input (Cao et al., 2017). The slight decrease in SO_4^{2-} at the reference core points to the dominance of particulate organic carbon sulfate reduction (POCSR) rather than AOM in consuming SO_4^{2-} , which is consistent with the inference of sedimentary TOC-derived DOC. Pore-water DOC production dominated by POCSR has also been observed in the anoxic sediments of the Arctic Ocean (Chen et al., 2016).

In addition, the significant inverse correlation between DOC concentrations and $\delta^{13}\text{C}$ -DOC values at both seep cores was

observed (**Figure 5**), which was explained as the coupling between AOM and DOC production (Pohlman et al., 2011). The extremely low $\delta^{13}\text{C}$ -DOC values and high DOC concentrations at the SMTZ of both seep cores are associated with AOM. Meanwhile similar phenomenon also observed above the current SMTZ at ROV1 (**Figure 2E**). This shallower depth interval featuring DOC and $\delta^{13}\text{C}$ -DOC anomalies may represent the pale-SMTZ where intense AOM and resulting DOC production was occurring when upward methane flux was higher compared to the current conditions. Fluctuation of SMTZ due to the variations in methane seepage intensities has been suggested to take place in the “Haima cold seeps” (Hu et al., 2019) and other seep areas worldwide (e.g., Borowski et al., 1999; Peketi et al., 2012; Sultan et al., 2016).

Enhanced Production of Labile Dissolved Organic Carbon in the Seep Sediments

The positive linear correlations were observed for DOC concentrations and total FDOM intensities (**Figure 6**), indicating the coupled production mechanisms of DOC and FDOM at the study cores. The y-intercepts are 0.26 mM for QDN-C-S03, 0.39 mM for ROV1 and -0.70 mM for ROV5, respectively, which represent the non-fluorescence fraction of DOM. Because



of the average DOC concentrations at QDN-C-S03 and ROV1 are 0.44 and 1.70 mM, we estimated that 41 and 77% of DOC pool are composed of fluorescence material at QDN-C-S03 and ROV1, respectively. The negative intercept value at ROV5 may imply a contribution of dissolved organic sulfur to FDOM pool.

Sulfurization of organic matter is a common process during early diagenesis stage through reaction of polysulfide and bisulfide on C-C double bonds and oxo-groups (Schouten et al., 1994; Werne et al., 2008; Raven et al., 2015). HS^- produced by microbial sulfate reduction represents the major source for the

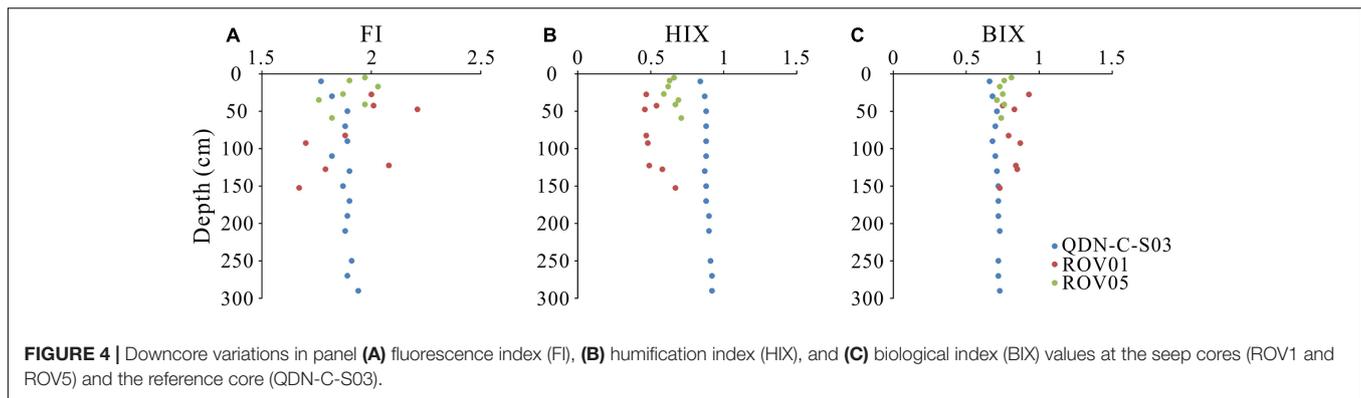


FIGURE 4 | Downcore variations in panel (A) fluorescence index (FI), (B) humification index (HIX), and (C) biological index (BIX) values at the seep cores (ROV1 and ROV5) and the reference core (QDN-C-S03).

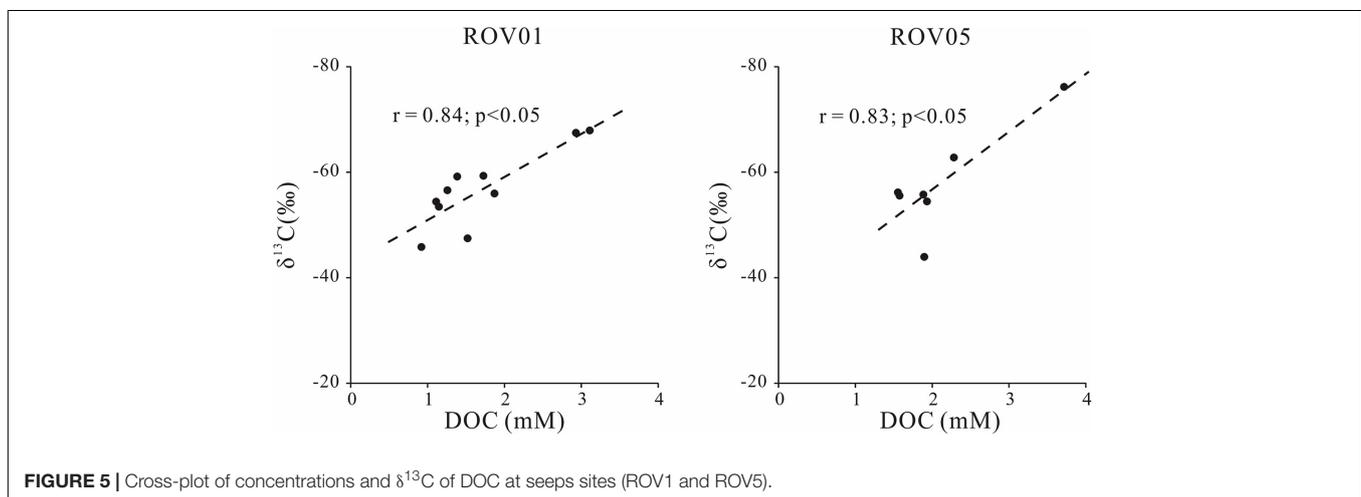


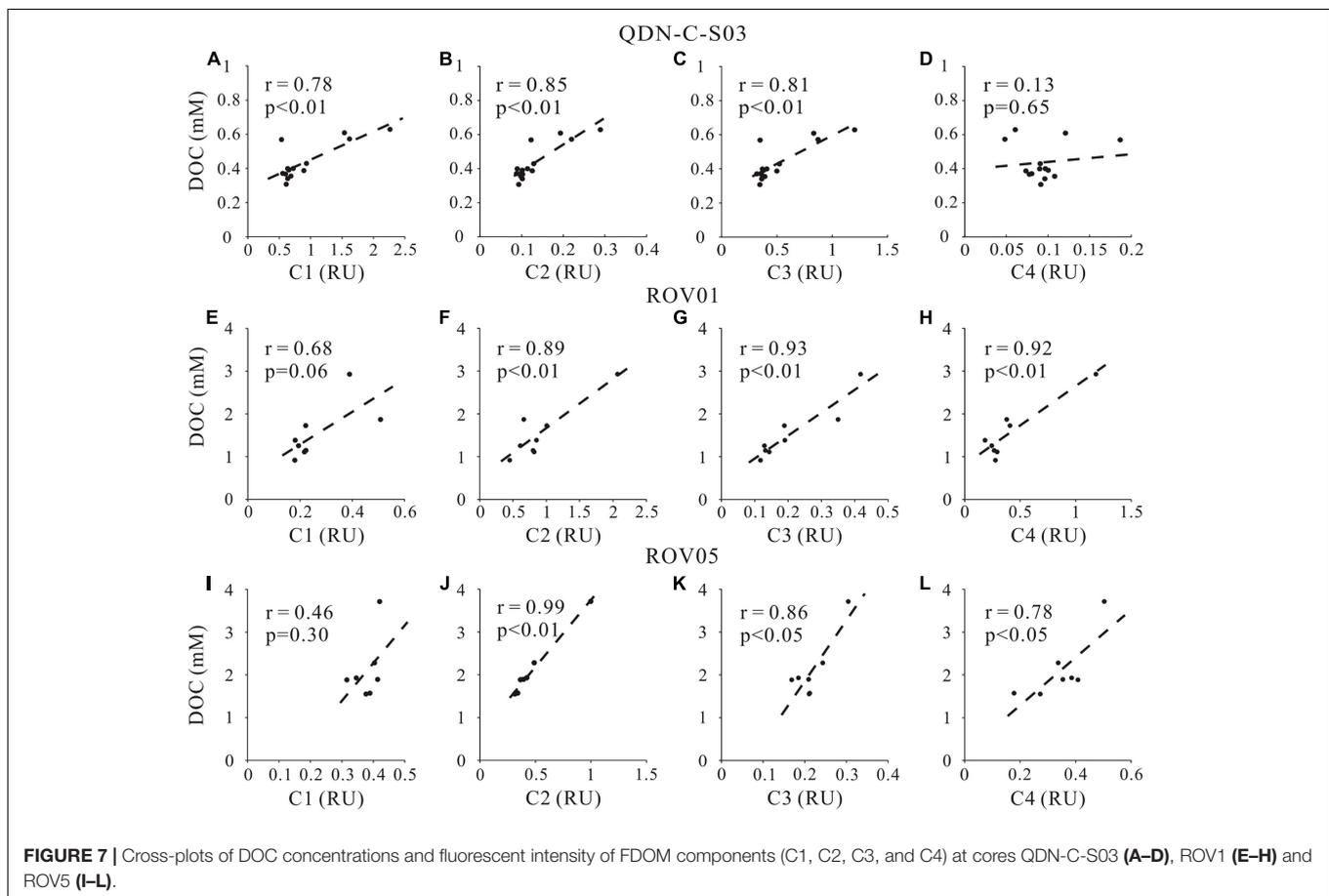
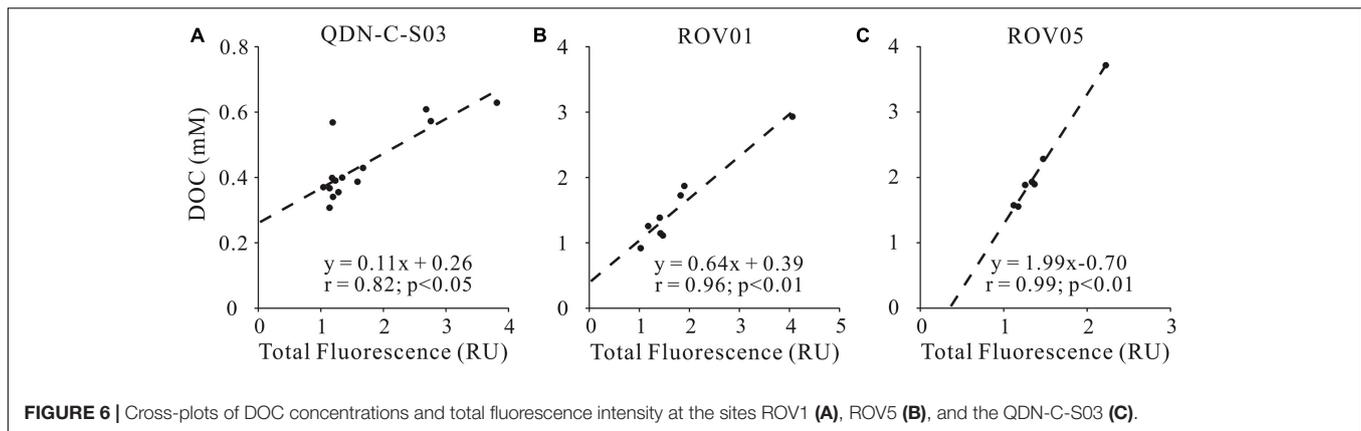
FIGURE 5 | Cross-plot of concentrations and $\delta^{13}\text{C}$ of DOC at seeps sites (ROV1 and ROV5).

S-bearing organic compounds in anoxic sediments (Schmidt et al., 2009; Seidel et al., 2014; Sleighter et al., 2014). Also, the amount of S-bearing molecular formulas formed in the sediments is dependent upon the HS^- concentrations in the pore water resulting from microbial sulfate reduction (Schmidt et al., 2017). Therefore, despite a lack of HS^- data for both seep cores, the much higher AOM rates suggested by considerably shallower SMTZ at ROV5 than ROV1 likely explain a significant production of dissolved organic sulfur.

Although the exact formation mechanism of methane-derived DOC is currently unclear, biochemical processes including methane-sourced carbon incorporation into acetate or larger biomolecules, microbial excretion, and biomass degradation have been proposed (Hoehler et al., 1994; Yang et al., 2020). Here, greater amount of fluorescent protein-like components (C2 and C4) and correspondingly less amount of humic-like components (C1 and C3) at the seep cores (ROV1, ROV5) than those at the reference core (QDN-C-S03) suggests enhanced microbial activities and resulting release of more labile, protein-like components at the seep cores (Figure 3). These results are consistent with the observation of significantly elevated microbial abundance in the seep sediments (Levin, 2005; Niu et al., 2017). Meanwhile, low HIX values, large fraction of protein-like components (46–80%) and high BIX values also indicate intensified production of relatively labile FDOM with

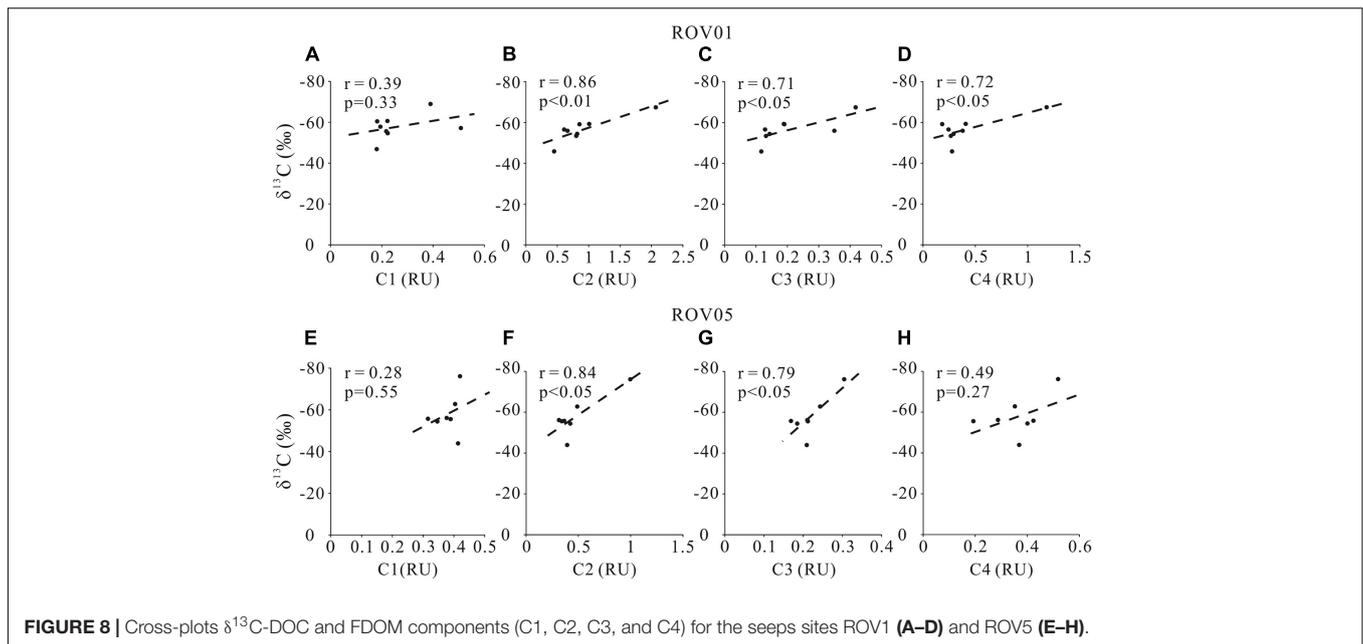
lower degradation degree associated with AOM at the seep cores compared to the reference core where sedimentary DOM is mostly produced by POCSR (Figure 4). Similar results have been reported at the mud volcanoes in the Gulf of Cádiz where the protein-like components accounted for ~70% of the total FDOM (Amaral et al., 2021).

The positive correlations of C2 intensity with DOC concentrations and $\delta^{13}\text{C}$ -DOC at both seep cores (Figures 7, 8) also support our argument that labile protein-like DOM production is closely related to AOM. However, the correlation between the fluorescent intensity of the other protein-like component-C4 and DOC concentration as well as $\delta^{13}\text{C}$ -DOC at both seep cores is less remarkable compared to C2, likely implying complicated sources and formation mechanism of C4. Although the specific chemical composition of methane-derived DOC has yet to be investigated, it has been suggested that methane could be converted to low-molecular-weight, labile organic materials (e.g., acetate) by AOM (Yang et al., 2020). This inference was demonstrated by the identification of a complete archaeal acetogenesis pathway in the ANME-2a genome and the activity of the key enzymes in acetate generation (Yang et al., 2020). Notably, the acetate may account for a small fraction of the methane-derived labile DOC pool, which can subsequently sustain the highly divergent heterotrophic communities in the seep sediments (Valentine et al., 2005).



In addition to producing protein-like components, AOM and accompanying microbial metabolism also produce humic-like refractory materials as shown by the positive correlations between humic-like component (C3) and DOC concentrations as well as $\delta^{13}\text{C}$ -DOC values at both seep cores (Figures 7, 8). No significant correlations were found between marine/microbial humic-like (C1) and DOC concentrations or $\delta^{13}\text{C}$ -DOC values (Figures 7, 8), indicating potential uncoupling of C1 production with AOM at seeps. However, the general positive correlations between C1 and DOC concentrations at the reference core may

suggest a potential close relationship between C1 production and POC degradation (Figure 7). Indeed, higher C1 content at the reference core compared to the seep cores also suggests a greater contribution of POCSR at the reference core, likely reflecting inhibition of POCSR in the seep sediments (Niewohner et al., 1998; Figure 3). It is worth noting that the refractory property of the humic-like components in aquatic environments may not be necessarily associated with their chemical structures, but rather due to the environmental conditions such as their concentrations (Arrieta et al., 2015; Cerro-Gálvez et al., 2019a),



nutrient availability (Cerro-Gálvez et al., 2019b), microbial ecology, enzyme function, and steric hindrance (i.e., matrix protection) (Kleber, 2010). Therefore, it may be possible that the humic-like component would change and become less refractory to microbial metabolism when they enter the ocean (Arrieta et al., 2015).

Potential Impact of the Labile Dissolved Organic Carbon From Seep Sediments on the Deep Ocean Dissolved Organic Carbon Pool

In general, the lability of DOC in the ocean is thought to vary with its ages, with younger, unaltered DOC being more easily utilized by aquatic heterotrophs than older, heavily modified one (Bauer et al., 1995; Raymond and Bauer, 2001; Raymond et al., 2007). However, Hood et al. (2009) found the glaciers runoff can supply a considerable amount of labile but aged DOC to marine ecosystems. Also, recent studies suggested that the reactivity of DOC is not directly related to its age, but mainly affected by its intrinsic chemical composition and extrinsic environments (Jiao et al., 2010; Wagner et al., 2020; Dittmar et al., 2021). Likewise, in the seep-impacted sediments, methane-derived DOC is extremely depleted in ^{14}C because methane is mostly produced by microbial or thermal degradation of pre-aged organic matter (Kuivila et al., 1990). Valentine et al. (2005) speculated that DOC in seep sediments contained labile compounds that could feed the heterotrophic microbial community. In this study, our optical analyses of sedimentary DOM demonstrate an enhanced production of relatively labile protein-like materials at both seep cores compared to the reference core, thereby supplying additional food sources and energy for heterotrophic prokaryotes in the seep sediments. Indeed, the observation of highly ^{13}C -depleted lipid biomarkers in the seep carbonates

likely suggested the uptake of AOM-derived OC by methane-oxidizing and sulfate-reducing consortia (Guan et al., 2019). In addition to supporting heterotrophic microbial activity in the seep sediments, DOC sourced from the seep sediments could also feed heterotrophy in the overlying seawater (Walker et al., 2017). The estimated $\sim 20.3 \text{ Tg C yr}^{-1}$ methane-derived DOC from seep sediments to the global ocean represents an important carbon and energy source for the heterotrophic communities in the deep ocean (Pohlman et al., 2011; Hung et al., 2016; Fu et al., 2020). Although the labile methane-derived DOC in the seep sediments is rapidly recycled, it could have a significant impact on the deep ocean DOC pool as aged and refractory DOC can also be produced during microbial metabolism.

Furthermore, in the geological past when major methane release from sediments due to gas hydrate dissociation, e.g., during the Palaeocene-Eocene Thermal Maximum (PETM), methane-derived DOC efflux could be substantially greater than the present-day condition (Zachos et al., 2005). As a result, a large amount of methane-derived DOC was subsequently converted to microbial biomass and buried in the sediments. We postulate that an enhanced production of labile protein-like DOC in the seep sediments may help explain the carbon isotopic excursion of sedimentary organic matter in the geological history and have implications in understanding the global DOC cycle.

CONCLUSION

Analyses and comparison of pore-water SO_4^{2-} , DOC concentrations and $\delta^{13}\text{C}$ of DOC in the sediment cores taken from the “Haima cold seeps” regions (the northern SCS) suggest a significant contribution of methane-derived DOC at the seep cores. PARAFAC of the fluorescence excitation-emission matrices shows higher amount of protein-like fluorescent at the

seep cores than the reference core. The enhanced production of relatively labile, protein-like fluorescent component is associated with AOM, as also reflected by the extremely low $\delta^{13}\text{C}$ of DOC. We highlight that the methane-derived DOC could serve as important carbon and energy sources for the heterotrophic communities and that it may contribute to explaining the $\delta^{13}\text{C}$ excursion of sedimentary organic carbon in the geological history when major methane emission events took place.

DATA AVAILABILITY STATEMENT

The datasets presented in this study can be found in online repositories. The names of the repository/repositories and accession number(s) can be found below: <https://doi.org/10.6084/m9.figshare.16802116>.

AUTHOR CONTRIBUTIONS

TH: investigation, sample collection, methodology, data analysis, and writing—original manuscript. ML: conceptualization,

methodology, data analysis, funding acquisition, and writing—review and editing. YX: methodology and writing—review and editing. SG: sample collection and methodology. DC: conceptualization, writing—review and editing, and funding acquisition. All authors contributed to manuscript preparation.

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