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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 150–200 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.

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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 (Berner, 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

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(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, 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, 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 m 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 El-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 4 N 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, FeS_2) were extracted following the method of Canfield et al. (1986). Sediment samples were reacted with 1 M CrCl_2 in an oxygen free reaction vessel with continuous nitrogen flow. Hydrogen sulfide (H_2S) produced from sulfide reduction by CrCl_2 was trapped as Ag_2S in AgNO_3 solution. The Ag_2S precipitate was dried and weighed to determine the CRS contents. Sulfur isotope analysis of the Ag_2S 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 Triolite (VCDT). Sulfur isotope results are reproducible within ± 0.3 ‰. 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 CO_2 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).

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