Deep-Sea Research II 122 (2015) 84–94

Contents lists available at ScienceDirect

Deep-Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

Impact of anaerobic oxidation of methane on the geochemical cycle of redox-sensitive elements at cold-seep sites of the northern South China Sea

Yu Hu [a,d], Dong Feng [b], Qianyong Liang [c], Zhen Xia [c], Chen Linying[b], Duofu Chen [a,*]

[a] *CAS Key Laboratory of Marginal Sea Geology, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*
[b] *CAS Key Laboratory of Marginal Sea Geology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China*
[c] *Guangzhou Marine Geological Survey, Guangzhou 510740, China*
[d] *University of Chinese Academy of Sciences, Beijing 100049, China*

ARTICLE INFO

Available online 27 June 2015

Keywords:
Anaerobic oxidation of methane (AOM)
Trace element
Pore water
Cold seep
Northern South China Sea

ABSTRACT

Cold hydrocarbon seepage is a frequently observed phenomenon along continental margins worldwide. However, little is known about the impact of seeping fluids on the geochemical cycle of redox-sensitive elements. Pore waters from four gravity cores (D-8, D-5, D-7, and D-F) collected from cold-seep sites of the northern South China Sea were analyzed for SO_4^{2-}, Mg^{2+}, Ca^{2+}, Sr^{2+}, dissolved inorganic carbon (DIC), $\delta^{13}C_{DIC}$, dissolved Fe, Mn, and trace elements (e.g. Mo, U). The sulfate concentration–depth profiles, $\delta^{13}C_{DIC}$ values and $(\Delta DIC+\Delta Ca^{2+}+\Delta Mg^{2+})/\Delta SO_4^{2-}$ ratios suggest that organoclastic sulfate reduction (OSR) is the dominant process in D-8 core. Besides OSR, anaerobic oxidation of methane (AOM) is partially responsible for depletion of sulfate at D-5 and D-7 cores. The sulfate consumption at D-F core is predominantly caused by AOM. The depth of sulfate–methane interface (SMI) and methane diffusive flux of D-F core are calculated to be $\sim$7 m and 0.035 mol m^{-2} yr^{-1}, respectively. The relatively shallow SMI and high methane flux at D-F core suggest the activity of gas seepage in this region. The concentrations of dissolved uranium (U) were inferred to decrease significantly within the iron reduction zone. It seems that AOM has limited influence on the U geochemical cycling. In contrast, a good correlation between the consumption of sulfate and the removal of molybdenum (Mo) suggests that AOM has a significantly influence on the geochemical cycle of Mo at cold seeps. Accordingly, cold seep environments may serve as an important potential sink in the marine geochemical cycle of Mo.

1. Introduction

Seepage of methane-rich fluids out of the sedimentary column, the so call cold seep, is a widespread phenomenon along continental margins worldwide (Campbell, 2006; Judd and Hovland, 2007 and references therein). At cold seeps, once the upward migration of methane from sedimentary column meets downward diffusion of sulfate from overlying seawater, methane is mostly consumed within sediments by sulfate-dependent anaerobic oxidation of methane (AOM; Boetius et al., 2000). The produced dissolved inorganic carbon (DIC) during AOM is characterized by highly depleted ^{13}C that derived from methane (e.g. Haese et al., 2003; Yoshinaga et al., 2014). The ^{13}C-depleted pore water DIC generated by AOM may be blurred by relatively somewhat less ^{13}C-depleted DIC derived from organoclastic sulfate reduction (OSR; Masuzawa et al., 1992) or sulfate reduction driven by higher hydrocarbons/oil (Joye et al., 2004). The concentrations of pore water chemical composition (SO_4^{2-}, Ca^{2+}, Mg^{2+} and DIC), on the other hand, are critical parameters to distinguish the relative contributions between AOM and OSR in the absence of higher hydrocarbons/oil contribution (e.g. Masuzawa et al., 1992; Chen et al., 2010; Luo et al., 2013).

Methane that ascends upwards along seabed sediment-fractures is intermediately stored in hydrate deposits (Tryon et al., 2002; Chen and Cathles, 2003, 2005; Cao et al., 2013a, 2013b), which host about 500–2000 Gt of carbon worldwide (Wallmann et al., 2012). The total reservoir of methane along continental slopes is even larger, as much of the methane can be found dissolved or in gas bubbles below and above the hydrate stability zone (Buffett and Archer, 2004). Despite this large reservoir, the oceans contribute only about 2% of the annual global flux of methane to the atmosphere (Cicerone and Oremland, 1988).

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[*] Corresponding author. Tel.: +86 20 85290286; fax: +86 20 85290130.
E-mail address: cdf@gig.ac.cn (D. Chen).

http://dx.doi.org/10.1016/j.dsr2.2015.06.012
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This is largely due to AOM, which consumes upward diffusing methane before it can release into the hydrosphere (Reeburgh and Alperin, 1988; Reeburgh, 2007). In addition, AOM also contributes very significantly to global sulfur reservoirs (Hensen et al., 2003). Sulfur fixed in the sediments by AOM is estimated about twice the global value of the recent global sulfur burial in marine sediments as previously estimated (Hensen et al., 2003). Consequently, AOM at cold seeps along continental margins plays a significant role in marine carbon and sulfur cycling.

Recent studies revealed that emission of dissolved barium (Ba) at cold seeps had significant impact on the local marine Ba budget (Torres et al., 1996, 2002; Dickens, 2001; Castellini et al., 2006; McQuay et al., 2008). However, little attention has been paid on the other trace elements. The influence of seeping fluids and AOM on marine trace-element chemistry is also not clear. Recently, very limited rare earth element (REE) studies on pore water aim at the impact of cold seeping fluids on REE biogeochemistry (Bayon et al., 2011; Himmler et al., 2013). Similarly, to our best knowledge, there has been no comparable work for trace redox-sensitive elements (e.g. Mo and U) focusing on geochemistry cycling in pore water at cold seeps. Redox-sensitive elements such as uranium (U) and molybdenum (Mo) that are strongly enriched under anoxic conditions have been extensively studied (e.g. Helz et al., 1996, 2011; Zheng et al., 2000, 2002; McManus et al., 2006; Tribovillard et al., 2006; Algeo and Tribovillard, 2009; Sato et al., 2012; Hu et al., 2014). The widespread seepage of reducing fluids usually containing abundant hydrogen sulfide that is expected to significantly affect the geochemical cycle of some of redox-sensitive elements. Interestingly, recent work on cold seep sediments revealed anomalous Mo enrichment, and cold seep was considered as a potential sink for Mo (Sato et al., 2012). However, more direct analysis on pore fluids, as a more immediate biogeochemical archive during early diagenesis comparing with sediments, is needed to further confirm the assumption at cold seeps.

Here we investigated pore water geochemistry of four sediment gravity cores (D-8, D-5, D-7, and D-F) collected from cold-seep sites in Dongsha Area of the South China Sea, where drilling results shown massive hydrate occurrence in shallow subsurface (Zhang et al., 2014). The major constituents (SO_4^{2-}, Ca^{2+}, Mg^{2+}, and DIC), dissolved trace elements (Fe, Mn, Sr, Mo, and U), and $\delta^{13}C_{DIC}$ values of pore water were determined to elucidate the biogeochemical processes associated with sulfate consumption and preliminarily discuss the impact of AOM on the geochemical cycle of redox-sensitive elements.

2. Geological background

The South China Sea (SCS) represents one of the largest marginal seas of the low latitude West Pacific located at the junction of three plates, the Eurasian, the Pacific and the Indo-Australian plate. It is characterized by occurrence of both passive and active continental margins and high sedimentation rates (Taylor and Hayes, 1983). As a part of the passive continental margins, the northern SCS is characterized by well-developed troughs, seamounts and scarps, and a series of sedimentary basins (e.g. Qiongdongnan Basin, Pearl River Mouth Basin, Taixinan Basin) (Peng et al., 2004). The Dongsha Area is situated at the southwest of Taixinan Basin. The submarine topography is very complex, and scarps and canyons are well developed in the area (Suess, 2005). Faults and mud diapirs have been widely observed in the Dongsha Area that serve as pathways for hydrocarbon migration (Suess, 2005; Yan et al., 2006). Bottom simulating reflectors and blanking zones are considered as effective indicators of the existence of gas hydrate in this region (e.g. McDonnell et al., 2000; Suess, 2005; Wu et al., 2005; Li et al., 2013). In addition, seep carbonates were recovered in the Dongsha Area during several cruises from 2002 to 2004 (e.g. Chen et al., 2005, 2006; Suess, 2005; Han et al., 2008; Tong et al., 2013). In 2013, gas hydrates have been recovered in the shallow subsurface less than ~200 mbsf (meter below the seafloor) through drilling program during the scientific expedition conducted by the Guangzhou Marine Geological Survey (Zhang et al., 2014). Cold seepage related features such as acoustic plume, acoustic void, and mud volcanoes were identified in the study area (Liu et al., 2015). The core recovery sites (e.g. D-7 and D-8) are just hundreds of meters away from the Site 3 named “Jiulong Methane Reef” (Fig. 1). Jiulong Methane Reef is a large chemoherm carbonate buildup that is characterized by abundant seep-related shells and shell fragments (Suess, 2005; Han et al., 2008). This site is still weakly active as indicated by the methane concentration profiles of the water column (Suess, 2005). In particular, carbonate nodules collected from D-7 core have $\delta^{13}C$ values as low as −46.0‰ VPDB

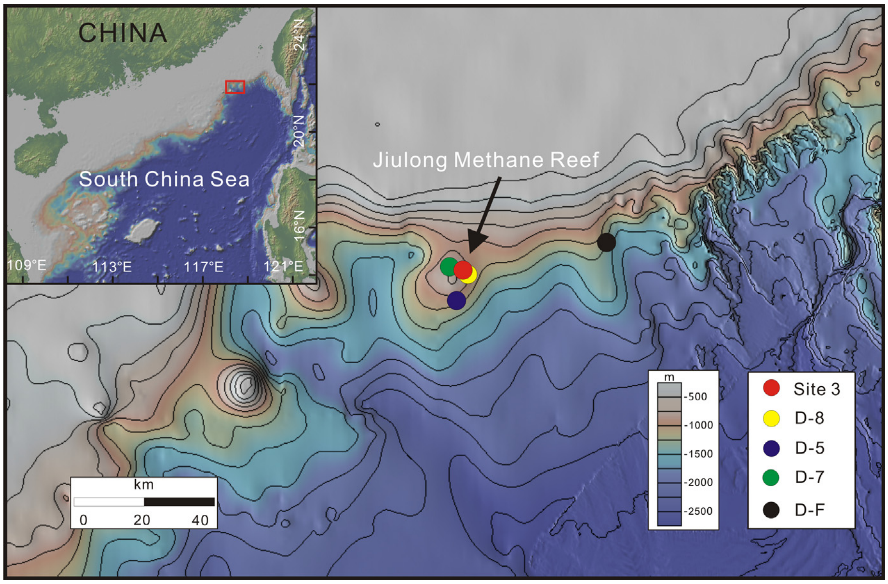

Fig. 1. Map showing the study region (red rectangle) located at Dongsha Area of the South China Sea. Core locations of D-8, D-5, D-7, and D-F, where water depths are 814 m, 1176 m, 766 m, and 1485 m, and core lengths are 405 cm, 412 cm, 350 cm, and 445 cm, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)