



Evidence of intense methane seepages from molybdenum enrichments in gas hydrate-bearing sediments of the northern South China Sea



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ARTICLE INFO

Article history:

Received 4 June 2016

Received in revised form 20 September 2016

Accepted 21 September 2016

Available online 22 September 2016

Keywords:

Cold seep

Anaerobic oxidation of methane

Seepage intensity

Molybdenum enrichment

Hydrate

South China Sea

ABSTRACT

The application of molybdenum (Mo) enrichment to sediments can potentially provide unique constraints on the methane seepage dynamics at continental margins. We report herein elemental and isotopic measurements for authigenic carbonates and sediment samples in drill cores (~95 m long; Site GMGS2-08 at ~800 m water depth) from gas hydrate-bearing sediments in the northern South China Sea. Five intervals that were impacted by methane seepages in the sediment profile were identified by the presence of strongly ¹³C-depleted carbonates ($\delta^{13}\text{C}$ values as low as -56.8%). The carbonates often cement chemosynthetic bivalve shell fragments and have anomalous $\delta^{18}\text{O}$ positive values. These observations suggest that methane seepage was intense during those time intervals and that carbonate precipitation occurred in the uppermost sediments, probably due to gas hydrate dissociation. Interestingly, the five intervals were all characterized by strong Mo enrichments. We thus hypothesize that the presence of strong Mo enrichments is a good indicator of past episodes of methane seepage. Such an environment results in sulfidic conditions that occur in a narrow zone in proximity to seawater close to the seafloor, leading to resultant Mo enrichments in associated sediments. In contrast, environments with low methane flux would lead to the distribution of Mo throughout a wide sulfidic zone and, consequently, an absence of Mo enrichment in the sediments. The insights into the environment for Mo enrichments at seeps have significant implications for tracing past methane seepages, their intensities, and even possible occurrences of gas hydrate dissociation.

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1. Introduction

The seepage of methane-rich fluids (namely cold seeps) at the seafloor is a widespread phenomenon along continental margins worldwide (e.g., Campbell, 2006; Judd and Hovland, 2007; Suess, 2014). Cold seeps usually breed chemosynthesis-based communities, develop authigenic carbonates, and are associated with the possible occurrence of gas hydrates (Judd and Hovland, 2007; Suess, 2014). The key biogeochemical process at seeps is the anaerobic oxidation of methane (AOM) coupled with sulfate reduction (Boetius et al., 2000; Boetius and Wenzhöfer, 2013). This process produces dissolved bicarbonate and hydrogen sulfide (H_2S) that increase pore water alkalinity, thus favoring the precipitation of authigenic carbonates (Berner, 1980). The dynamics of fluid flows at seeps are characterized by changes in flow intensity and episodic seepages as well, which might be controlled by factors such as the exhaustion of hydrocarbon sources, sea level variations and bottom water temperature fluctuations that drive the dissociation of gas hydrates (e.g., Kvenvolden, 1993; Aharon et al., 1997; Judd et al., 2002; Kennett et al., 2003; Teichert et al., 2003; Feng et al., 2010; Bayon et

al., 2015). The reconstruction of past variations in methane fluxes is largely dependent on proxies that help define the intensities of methane seepages. Numerous studies have attempted to use geochemical proxies such as the content and isotopic anomalies of authigenic carbonates, barites and pyrites to constrain methane seepage intensities and their variations (e.g., Torres et al., 1996; Aharon et al., 1997; Dickens, 2001; Teichert et al., 2003; Bayon et al., 2007; Nöthen and Kasten, 2011; Feng et al., 2010; Lim et al., 2011; Peketi et al., 2012; Borowski et al., 2013).

Authigenic carbonates formed at seeps can be used to identify periods of methane seepage and/or gas hydrate dissociation and variations in methane fluxes by carbon and oxygen isotopic and elemental analyses (e.g., Aharon et al., 1997; Bohrmann et al., 1998; Naehr et al., 2000; Greinert et al., 2001; Teichert et al., 2003; Peckmann and Thiel, 2004; Feng et al., 2010; Han et al., 2014; Feng and Chen, 2015). However, the most important proxy, strong ¹³C-depletion in carbonates, might be altered and even shifted to ¹³C-enrichment by the incorporation of upraised ¹³C-rich fluids from the methanogenic zone (e.g., Peckmann and Thiel, 2004; Roberts et al., 2010). In addition, barium (Ba) fronts typically form slightly above sulfate methane transition zones (SMTZs; e.g., Torres et al., 1996; Dickens, 2001; Riedinger et al., 2006; Snyder et al., 2007; Vanneste et al., 2013). It has been shown that Ba fronts can

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record present and past fluid seepage events and the evolution of SMTZs in sedimentary columns (e.g., Dickens, 2001; Riedinger et al., 2006; Vanneste et al., 2013). In systems where the upward Ba^{2+} flux exceeds the downward barite flux, a prominent Ba front develops just above the depth of SO_4^{2-} depletion. A new Ba front will develop below a “paleo” front if the SO_4^{2-} gradient deepens (Dickens, 2001). That formation condition is uncommon and occasionally leads to the absence of Ba fronts at SMTZs (Peketi et al., 2012), thus limiting the application of Ba fronts to the reconstruction of past seepage events. The potential of sulfur isotopes in pyrites as a proxy for identifying AOM-related processes and seepage events has been proposed (Jørgensen et al., 2004; Peketi et al., 2012; Borowski et al., 2013; Formolo and Lyons, 2013). The application of sulfur isotopes in pyrites, however, will be limited by a complex interplay of factors that include iron availability and non-steady-state sedimentation (Borowski et al., 2013; Formolo and Lyons, 2013). Accordingly, more geochemical proxies are needed to better constrain methane seepages and their variabilities.

Recent studies have reported molybdenum (Mo) enrichments in seep-impacted sediments (Peketi et al., 2012; Sato and Hayashi, 2012), especially Mo enrichments at SMTZs (Peketi et al., 2012), which has been suggested to be capable of identifying H_2S seepages associated with methane (Peketi et al., 2012). Molybdenum behaves conservatively under oxic conditions. Under a sulfidic environment with the generation of free H_2S , dissolved Mo is scavenged from solution via organic materials or via Mo capture by iron sulfide phases (Helz et al., 1996, 2011; Zheng et al., 2000; Tribouillard et al., 2006). Although Mo enrichment is a promising proxy for tracing methane seepages, some SMTZs have shown an absence of Mo enrichments (Peketi et al., 2012), which complicates the relationship between Mo enrichments and methane (or H_2S) seepages, and further work is therefore needed to reveal the condition for the enrichment of Mo at seeps and its potential as a proxy for tracing methane seepages.

Here we investigate the solid geochemistry of sediments and associated authigenic carbonates obtained from gas hydrate-bearing sediment cores as long as ~95 m at gas hydrate drilling sites from the

northern South China Sea (SCS). The carbon and oxygen isotopes and contents of authigenic carbonates and major and trace elements of the sediments were determined. We show below that Mo enrichments in sediments can provide unique information on the intensity of methane seepages and its possible relationship to the local dissociation of gas hydrates.

2. Regional setting

The northern SCS is a passive continental margin controlled by complex interactions between the Eurasian, Pacific, and Indian-Australian plates (Taylor and Hayes, 1983). The study site is situated in the Dongsha Area of the northern SCS (Fig. 1). The widely observed faults and mud diapirs in the study area can serve as effective pathways for hydrocarbon migration (Suess, 2005; Wu et al., 2005; Yan et al., 2006). In the vicinity of the study site, a number of bottom simulating reflectors, faults, and mud diapirs have been observed in seismic profiles (Li et al., 2013, 2015; Zhang et al., 2015). Massive authigenic carbonates on the seafloor were discovered during the joint Chinese-German RV SONNE Cruise 177 in June 2004 (Suess, 2005; Han et al., 2008). An active cold seep with a methane gas plume, living mussels and authigenic carbonates was reported at Site F in the Dongsha Area (Liu et al., 2008; Feng and Chen, 2015; Feng et al., 2015). In addition, recent studies have reported occurrences of gas hydrates from log data and core samples at this site obtained during China's second gas hydrate drilling expedition (GMGS-2) between May and September in 2013 (Sha et al., 2015; Zhang et al., 2015). Biogenic methane was determined to be the gas source of the gas hydrates (Zhang et al., 2015).

3. Sampling and analytical methods

The sediment samples were obtained from a drilling program during the GMGS-2 gas hydrate expedition (Fig. 1). The GMGS08 site is one of 13 drilled sites and has a water depth of 801 m. Five sediment cores (08B, 08C, 08E, 08F, and 08G) were drilled and collected, and the drilling

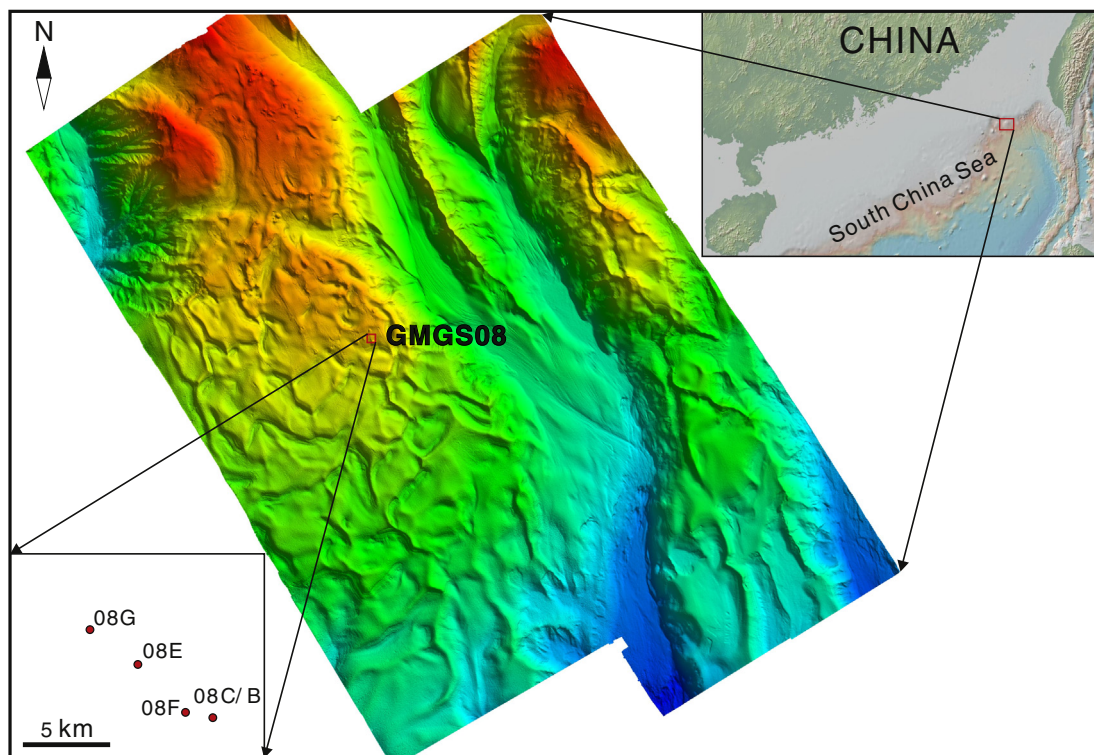


Fig. 1. Maps showing the locations of the study region, GMGS08 site, and drill cores (08B, 08C, 08E, 08F, and 08G) on the northern continental slope of the South China Sea (modified from Sha et al., 2015).

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