



Research paper

Using sediment geochemistry to infer temporal variation of methane flux at a cold seep in the South China Sea

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ABSTRACT

Release of methane from the seafloor throughout the world's oceans and the biogeochemical processes involved may have significant effects on the marine sedimentary environment. Identification of such methane release events in marine sediment records can hence provide a window into the magnitude of ancient seeps. Here, we report on analysis of the geochemical composition of samples in a 12.3 m long sediment core (DH-5) collected from a seep site in the South China Sea (SCS). Our aim has been to investigate whether the evidence for the presence of methane release event within sediments is discernible from solid-phase sediment geochemistry. We show that sedimentary total sulfur (TS), $\delta^{34}\text{S}$ values of chromium reducible sulfur ($\delta^{34}\text{S}_{\text{CRS}}$) along with total organic carbon (TOC) and total inorganic carbon (TIC) content can be used to infer the presence of methane release events in cold seep settings. At least three methane release events were identified in the studied core (Unit I at 400–550 cm, Unit II at 740–820 cm, and Unit III at 1000–1150 cm). According to the characteristic of redox-sensitive elements (eg., Mo, U and Mn), we suggest that methane flux has been changed from relatively high (Unit I) to low (Unit II and III) rates. This inference is supported by the coupled occurrence of ^{34}S -enriched sulfides in Unit II and III. AMS ^{14}C dates from planktonic foraminifera in Unit I suggest that high methane flux event occurred at ~15.4–24.8 kyr BP, which probably resulted in locally-focused aerobic methane oxidation. Overall, our results suggest that TS, TOC, TIC and $\delta^{34}\text{S}_{\text{CRS}}$ have potential for identifying present and fossil methane release events in marine sediments.

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1. Introduction

The seepage of hydrocarbon-rich fluids (mainly methane) in marine sediments is common in continental margins worldwide (e.g. Campbell et al., 2002; Campbell, 2006). A large quantity of methane could release into the water column and atmosphere owing to the glacial-interglacial sea level fluctuations and bottom water temperature changes driving massive gas hydrate destabilization (Watanabe et al., 2008; Westbrook et al., 2009; Ménot and Bard, 2010; Han et al., 2014; Feng et al., 2014). As a greenhouse gas, methane is 25 times more effective in trapping heat than carbon dioxide (Chang et al., 2012). Some high temperature events

in geological time, such as the Paleocene-Eocene Thermal Maximum (PETM) are likely related to substantial methane release due to gas hydrate dissociation (Dickens et al., 1995; Zachos et al., 2005). The latest study shows that the activity of Bacteria and Archaea in seep areas may contribute significant organic matter to the deep ocean (Pohlman et al., 2011; Coffin et al., 2014, 2015).

Modern seep activity can be detected through seabed observations, pore water analysis, methane anomaly detection, and many other methods (Borowski et al., 1996, 1999; Borowski, 2004; Newman et al., 2008; Bayon et al., 2009b, 2011; Mazumdar et al., 2012a, 2014; Brothers et al., 2013, 2014; Lemaitre et al., 2014; Skarke et al., 2014), but temporal variations in methane flux in the past are not well constrained because it is difficult to select the appropriate indicators in quantifying and age determining the occurrence of seep activity. Consequently, little is known about the impact of methane seepage on the surrounding sediment environment in seep settings.

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Geochemical proxies such as stable carbon isotope records of authigenic carbonates have been applied to evaluate the temporal variation of methane seep, owing to their very negative $\delta^{13}\text{C}$ (Peckmann and Thiel, 2004; Han et al., 2004, 2008, 2013; Mazumdar et al., 2009, 2011; Bayon et al., 2009a, 2013, 2015; Crémière et al., 2013; Tong et al., 2013; Tribovillard et al., 2013; Feng et al., 2014, 2015a,b). However, such carbonates are most intense at intermediate flow rates, and usually do not form in low and high flux conditions (Luff and Wallmann, 2003; Karaca et al., 2010). Moreover, low dissolved methane content of fluids, high bioturbation rates, and/or high sedimentation rates can also result in the absence of authigenic carbonates in marine sediments (Luff et al., 2004; Bayon et al., 2007). In fact, numerous recent studies reveal that seep-impacted sediment cores generally have relatively complete sequence and may serve as another important archive to reconstruct the evolution of past seepage activities (Bayon et al., 2007; Peketi et al., 2015).

Methane-involved biogeochemical processes at seep sites mainly include anaerobic oxidation of methane (AOM) and aerobic oxidation of methane (Reeburgh, 2007):



In low-flux seep environments the methane may be completely consumed by AOM. In high-flux seep environments the sulfate methane transition zone (SMTZ) is typically very shallow, and methane may escape directly into the bottom waters (Paull et al., 2005; Castellini et al., 2006). In this scenario, most of the methane that escapes is then consumed by methanotrophic aerobic microbes in the bottom waters, resulting locally in anoxic conditions (Niemann et al., 2006; Reeburgh, 2007; Consolaro et al., 2015):



The AOM process in cold seep systems are increasingly understood (e.g. Boetius and Wenzhöfer, 2013), but little is known about the process of aerobic oxidation of methane and its impact on sedimentary environment.

In this study, we describe the behavior of the coupled C–S–Fe geochemistry and redox-sensitive elements, as well as chromium reducible sulfur (CRS) and $\delta^{34}\text{S}_{\text{CRS}}$ features in sediments collected from the cold seep area of the Dongsha on the northern continental slope of the SCS. The purpose of this study is to: 1) evaluate the dynamics of methane release over the course of sediment formation in seep environments, and 2) provide insight into impacts on the local sediment environment.

2. Background

2.1. Pyrite and pyrite sulfur isotope as a proxy of anaerobic oxidation of methane

In normal marine environment, pyrite is typically formed through sulfate reduction producing hydrogen sulfide, which reacts with reactive iron (Berner, 1970, 1984). Therefore, the sedimentary organic carbon supply is commonly the primary control on pyrite formation (Canfield, 1991; Jørgensen, 1982; Lim et al., 2011; Tribovillard et al., 2015). However, in methane-rich environment, AOM at the SMTZ could produce additional hydrogen sulfide that is ultimately fixed as sulfide minerals, such as sulfur, S^0 ; iron monosulfides, FeS ; and pyrite, FeS_2 in sediments. However, owing to the ephemeral of elemental sulfur and FeS minerals, so that it is pyrite usually survives as the main phase of the sulfide minerals (Borowski et al., 2013). Therefore, the content of sulfide minerals

near the SMTZ could indicate the historical AOM and methane migration (Lim et al., 2011). Moreover, enrichments in sulfate phases (mainly barite) based on bulk sediment Ba profiles has also been used to assess the temporal variation of methane seeping (Dickens, 2001). Owing to a small fractionation of only about 1‰ in the transfer of sulfur from dissolved sulfide into sulfide minerals, the sulfur isotope of sulfide minerals sulfur isotope values represent good estimates of the isotopic composition of pore water HS^- (Price and Shieh, 1979). Consequently, the sulfide minerals sulfur isotope values could record the AOM-induced sulfate reduction process. The high values of sulfide minerals sulfur isotope (up to +21‰) in sediment, is attributed to the isotopically-enriched HS^- pool through AOM, which was fuelled by an upward vertical methane flux (Borowski et al., 2013). Enrichment of ^{34}S in residual pore water sulfate and the HS^- is the result of higher rate of sulfate reduction than the rate of sulfate diffusion into the sediment pore water from overlying seawater in a closed system (Peketi et al., 2012). In normal marine environment, early diagenetic alteration of organic matter by sulfate reduction actually controlling the $\delta^{34}\text{S}$ composition of pore waters. Thus, ^{34}S -enriched sulfide minerals, similar to that of seawater sulfate (21‰) preserved in modern and ancient marine sediments, may identify former AOM-related processes and present-day and past locations of the SMTZ in cold seep affected sediments (Borowski et al., 2013).

2.2. Redox-sensitive elements as a proxy of aerobic oxidation of methane

Under different redox conditions, modern and ancient marine sediments are typically characterized by relative enrichment or depletion of various trace metals, such as redox-sensitive elements Mn, Mo, U, V, Cd and Re, which thus can be used as indicators of paleo-redox conditions (Warning and Brumsack, 2000; Böning et al., 2004; Tribovillard et al., 2008; Mazumdar et al., 2012b). V/Sc, U/Th, Mn/Al, Mo/Al and U/Al ratios are frequently used as indicators of oxygenation conditions of the water column (Algeo and Maynard, 2004; Tribovillard et al., 2006; Chun et al., 2010; Pålke et al., 2014). Therefore, it has been known that we can use these redox-sensitive elements as proxies for identifying past events of aerobic oxidation of methane (Chun et al., 2010; Pålke et al., 2014).

Under anoxic conditions U is preferentially taken up into the sediment, forming less soluble UO_2 , U_3O_7 , or U_3O_8 (Klinkhammer and Palmer, 1991; Morford et al., 2001) because U(VI) is reduced at the Fe(II)–Fe(III) redox boundary (Jones and Manning, 1994; Zheng et al., 2002; Tribovillard et al., 2006). In oxic settings V exists as V(V), forming soluble vanadate ionic species such as HVO_4^{2-} and H_2VO_4^- (Tribovillard et al., 2006). In anoxic environments, V(V) is reduced first to V(IV), forming vanadyl ion VO^{2+} , related hydroxyl species $\text{VO}(\text{OH})_3^-$, or insoluble hydroxides $\text{VO}(\text{OH})_2$, and under more strongly reducing environments, the presence of free H_2S causes V reduced to V(III) form insoluble oxides V_2O_3 or hydroxides $\text{V}(\text{OH})_3$ (Algeo and Maynard, 2004; Tribovillard et al., 2006). Many researches indicated that the Mo in the water column could convert to thiomolybdates under the condition of high HS^- activity, which then would be captured by iron sulfides and organic matter (Helz et al., 1996; Erickson and Helz, 2000; Tribovillard et al., 2004; Vorlicek et al., 2004). Generally, the concentration of Mo up to 20 $\mu\text{g/g}$ in bulk sediments, accompanied with low Mn content indicates anoxic conditions and free hydrogen sulfide in the pore water. Moreover, Mo concentrations up to 60 $\mu\text{g/g}$ suggest a euxinic condition (Scott and Lyons, 2012). Mn is primarily present as insoluble Mn(IV) oxides in oxic conditions (Calvert and Pedersen, 1993). Below the oxic-anoxic interface, Mn(IV) oxides are reduced to soluble Mn(II) species, and the upward diffusion of Mn^{2+} can lead to either Mn^{2+} escape to the bottom water or are reoxidized

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