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Coupled pyrite concentration and sulfur isotopic insight into the paleo sulfate–methane transition zone (SMTZ) in the northern South China Sea

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ABSTRACT

The sulfate–methane transition zone (SMTZ) is an important diagenetic redox boundary within marine sediments where the anaerobic oxidation of methane (AOM), coupled with bacterial sulfate reduction, can promote sulfur isotopic enrichments in several solid phase minerals including pyrite (FeS_2). Authigenic pyrite can form in concentrated abundances within the SMTZ and as such, can be used as a proxy to identify paleo-SMTZs. This study uses enrichments in ^{34}S and anomalously high abundances of authigenic pyrites in 287 samples from the northern South China Sea (SCS) to determine the paleo-SMTZ. The pyrite samples were collected from sediment cores acquired at three sites, each of which are known to be located in natural gas hydrate-bearing regions. We assess the relative abundances of authigenic pyrites, the types of pyrite morphologies recovered in the cored sediments, and the sulfur isotopic values of recovered pyrite samples using two methods: (1) handpicked sample analysis using a binocular microscope, and (2) the chromium reduction method. Our results show that pyrite concentrations and sulfur isotopic compositions exhibit synchronous fluctuations, particularly from 6.8 m below seafloor (mbsf) to 8.4 mbsf at all three study sites. There is a significant increase in the occurrence of rod-like pyrite morphology within this key interval. We define the position of the paleo-SMTZ by the presence of anomalously high accumulations of pyrites at greater than 5.0 wt.% using the handpicking method or greater than 0.5 wt.% via the chromium reduction method, along with positive $\Delta\delta^{34}S$ excursions greater than 10.0‰ VCDT. We discovered a regional paleo-SMTZ that is shallower than the modern SMTZ, suggesting a previous period of elevated methane flux from depth, possibly related to widespread gas hydrate dissociation.

1. Introduction

Methane is a potent greenhouse gas and a significant energy resource. An enormous amount of methane is locked up in methane hydrate reservoirs along continental margins worldwide (Kvenvolden, 1993, 2002; Kvenvolden and Rogers, 2005). Understanding the long-term stability of these hydrate reservoirs is important for climate models, carbon budgets, gas in place resource estimates, and for developing production strategies (Dickens et al., 1995; Kennett et al., 2000; Wang et al., 2008; Burwicz et al., 2011). During the geological evolution of a continental margins, sedimentary and tectonic activity can lead to shifts in the thickness of the gas hydrate stability zone (GHSZ), and potentially trigger methane seep events. The upward flux of methane from gas hydrate dissociation can result in the depletion of pore water sulfate and subsequently affect the depth of the sulfate–methane transition zone (SMTZ) (Borowski et al., 1996, 1999; Niewöhner et al., 1998; Dickens 2001; Wegener and Boetius, 2009). While sulfate contributions from seawater and local sedimentation rates can also influence the location of the SMTZ (Garming et al., 2005; Riedinger et al., 2005; März et al., 2008), numerous studies have shown that the depth of the SMTZ can migrate upward or downward in marine sediments in response to temporal variations in advective methane fluxes over geological time (Jørgensen et al., 2004; Lim et al., 2011; Peketi et al., 2012; Borowski et al., 2013; Hong et al., 2014). Thus, we hypothesize that shifts in the depth of the SMTZ may provide insight into the occurrence, magnitude and extent of gas hydrate dissociation events.

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Because of its important role as a fundamental redox driven diagenetic boundary, the SMTZ has received significant attention across fields including mineralogy, geochemistry and microbiology. Within the SMTZ, the anaerobic oxidation of methane (AOM), coupled with bacterial sulfate reduction (Hinrichs et al., 1999; Boetius et al., 2000; Orphan et al., 2001) can leave a significant imprint on not only the interstitial water chemistry (e.g., H_2S concentration, pH value and alkalinity), but also on the solid phase mineral compositions (e.g., pyrite, barite and carbonates).

Various authigenic minerals can form within the SMTZ, and if preserved, these minerals can be used as proxies for the position of past SMTZs. For example, the enrichment of authigenic barite has been proposed to record the locations of the SMTZs in regions where the intensity of methane seepage has been highly variable over time (Torres et al., 1996; Dickens, 2001; Riedinger et al., 2006). The conversion of iron (oxyhydr-) oxides (such as magnetite) to iron sulfides (such as pyrite and greigite) during the AOM could result in an abnormal magnetostratigraphy, which could also record the location of the SMTZ (Novosel et al., 2005; Garming et al., 2005; Riedinger et al., 2005; März et al., 2008; Dewangan et al., 2013). Similarly, ^{34}S enrichments in sulfide minerals (FeS_2, FeS) have been used to identify previous occurrence of AOM and the location of paleo, or "fossil", SMTZs (Dickens, 2001; Jørgensen et al., 2004; Peketi et al., 2012; Borowski et al., 2013). However, it is important to note that the range of sulfur isotopic fractionation can be influenced by various factors such as: (1) the rate of sulfate reduction, (2) the microbial sulfur disproportionation, (3) open or closed system conditions, (4) the types of sulfate reducing microbes present (Canfield et al., 2010; Sim et al., 2011a, b; Formolo and Lyons, 2013; Leavitt et al., 2013; Deusner et al., 2014).

Generally speaking, sedimentary pyrite formation is related to decomposable organic matter, dissolved sulfate, and reactive detrital iron minerals in marine environment (Jørgensen, 1982; Berner, 1984; Canfield, 1989). Importantly, the upward delivery of methane to the SMTZ through advection intensifies the role of AOM and enhances the precipitation of the authigenic iron sulfide minerals such as pyrite (Peckmann et al., 2001; Sassen et al., 2004; Arvidson et al., 2004; Jørgensen et al., 2004; Neretin et al., 2004; Novosel et al., 2005; Lim et al., 2011; Peketi et al., 2012; Wehrmann et al., 2015; Zhang et al., 2015b). This is particularly the case in the context of methane hydrate geo-systems which have the potential to provide a source of methane from depth following perturbations to hydrate stability. Therefore, we contend that the locations of paleo-SMTZs in hydrate-bearing regions are best recognized by integrating the concentration and the ^{34}S isotopic enrichment of authigenic sulfide minerals in a manner analogous to that of authigenic carbonates (Ussler and Paull, 2008), and authigenic barites (Torres et al., 1996; Dickens, 2001) with magnetic susceptibility data (Novosel et al., 2005; Garming et al., 2005; Riedinger et al., 2005; März et al., 2008; Dewangan et al., 2013).

In this study, we collected and analyzed authigenic pyrites taken from sediment cores which were collected from three sites in the northern SCS with the aim of identifying potential paleo-SMTZs (Fig. 1). As we will show later in this research, the AOM is the dominant process affecting the SMTZ at all three study locations. Therefore, we can confidently assume any anomalous accumulations of authigenic pyrite preserved in the sedimentary record serve as a proxy for the paleo-SMTZ, and are diagnostic of a non-steady state system with enhanced methane delivery (Borowski et al., 2013) potentially related to gas hydrate destabilization.

This is the first study to couple changes in pyrite concentrations and sulfur isotopic compositions from the northern SCS. We begin with a description of the geologic context of the study region

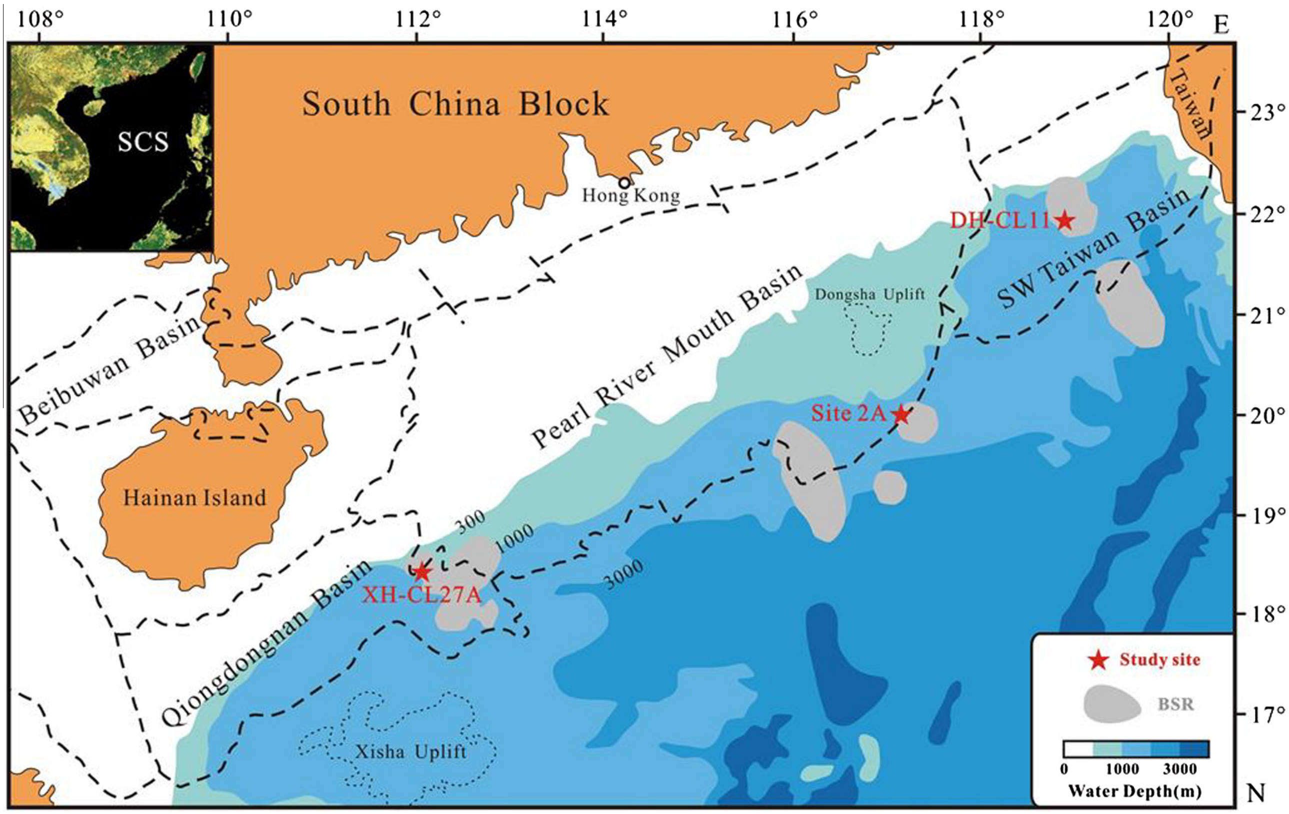

Fig. 1. Locations of the three study sites (red stars) (map modified from Sun et al., 2012. For information regarding BSRs, refer to Wang et al., 2006). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)