How sulfate-driven anaerobic oxidation of methane affects the sulfur isotopic composition of pyrite: A SIMS study from the South China Sea

Zhiyong Lin [a,c,d], Xiaoming Sun [a,b,c,e,*], Jörn Peckmann [f,g], Yang Lu [b,c], Li Xu [b,c], Harald Strauss [d], Haoyang Zhou [a], Junli Gong [a], Hongfeng Lu [h], Barbara M.A. Teichert [d]

[a] School of Earth Science and Geological Engineering, Sun Yat-sen University, Guangzhou 510275, China
[b] School of Marine Sciences, Sun Yat-sen University, Guangzhou 510006, China
[c] Guangdong Provincial Key Laboratory of Marine Resources and Coastal Engineering, Guangzhou 510006, China
[d] Institut für Geologie und Paläontologie, Westfälische Wilhelms-Universität Münster, Münster, Germany
[e] South China Sea Bio-Resource Exploitation and Utilization Collaborative Innovation Center, Guangzhou 510006, China
[f] Institut für Geologie, Universität Hamburg, Hamburg 20146, Germany
[g] Department für Geodynamik und Sedimentologie, Universität Wien, 1090 Wien, Austria
[h] Guangzhou Marine Geological Survey, Guangzhou 510760, China

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ABSTRACT

Sulfate-driven anaerobic oxidation of methane (SO$_4$-AOM) in marine sediments commonly leads to the precipitation of pyrite. It is, however, frequently challenging to unequivocally unravel the entire history of pyritization, because of the common coexistence of SO$_4$-AOM derived pyrite with pyrite resulting from organiclastic sulfate reduction (OSR). To better understand how SO$_4$-AOM affects pyritization in methane-bearing sediments and how this can be identified, we applied secondary ion mass spectroscopy (SIMS) to analyze the sulfur isotope composition (δ^{34}S) of authigenic pyrite in addition to sulfur isotope measurements of bulk sulfide and hand-picked pyrite aggregates from the two seafloor sites, HS148 and HS217, in the Shenhu seepage area, South China Sea. Authigenic, mostly tubular pyrite aggregates from these sites consist of three types of pyrite: framboids, zoned aggregates with radial overgrowths surrounding a framboidal core, and euhedral pyrite crystals. Framboids with low SIMS δ^{34}S values (as low as −41.6‰ at HS148, and −38.8‰ at HS217) are dispersed throughout the cores, but are especially abundant in the shallow part of the sedimentary column (i.e. above 483 cmbsf in HS148; above 670 cmbsf in HS217). These patterns are interpreted to reflect the dominance of OSR during early diagenetic processes in the shallow sediments. With increasing depth, both δ^{34}S values of bulk sulfide minerals and hand-picked pyrite aggregates increase sharply at 483 cmbsf in core HS148, and at 700 cmbsf in core HS217, respectively. Radial pyrite overgrowths and euhedral crystals become abundant at depth typified by high δ^{34}S values for hand-picked pyrite. Moreover, SIMS analysis reveals an extreme variability of δ^{34}S values for the three pyrite types on a small scale in these zones. Besides some moderately ^{34}S enriched framboids, most of the overgrowths and euhedral crystals display extremely high SIMS δ^{34}S values (as high as +114.8‰ at HS148, and +74.3‰ at HS217), representing the heaviest stable sulfur isotope composition of pyrite ever reported to the best of our knowledge. Such an abrupt and extreme increase in δ^{34}S$_{pyrite}$ values with depth is best explained by an enrichment of ^{34}S in the pool of dissolved sulfide caused by SO$_4$-AOM in the sulfate methane transition zone (SMTZ). The increase in δ^{34}S values from framboidal cores to overgrowth layers and euhedral crystals indicates continuous, and finally near to complete exhaustion of dissolved sulfate at the SMTZ following a Rayleigh distillation process. SO$_4$-AOM allowed for subsequent growth of later stage pyrite over the initial framboids, part of which formed earlier and at shallower depth by OSR. The combination of a detailed petrographic study of authigenic pyrite with SIMS analysis of stable sulfur isotopes in organic-rich strata proves to be a powerful tool for reconstructing the dynamics of sulfur cycling in modern and, potentially, ancient sedimentary sequences.

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1. Introduction

Seepage of methane-rich fluids out of the sediment is a widely observed phenomenon along continental margins worldwide (e.g., Judd et al., 2002; Johnson et al., 2003; Judd, 2003; Suess, 2014). The amount

* Corresponding author at: School of Earth Science and Geological Engineering, Sun Yat-sen University, Guangzhou 510275, China.
E-mail address: eessxm@mail.sysu.edu.cn (X. Sun).

of methane released from the sediment has been considered as an important factor in global climate change on geologic time scales (Paull et al., 1991, 1996; Judd, 2003; Peckmann et al., 2009; Panieri et al., 2014). In areas of diffusive seepage, however, methane is mostly oxidized in the sediments at the expense of sulfate by a biogeochemical process known as sulfate-driven anaerobic oxidation of methane (hereafter SO₄-AOM). This is a process mediated by a consortium of methanotrophic archaea and sulfate-reducing bacteria according to Eq. (1) (Hinrichs et al., 1999; Boetius et al., 2000; Orphan et al., 2001; McGlynn et al., 2015; Wegener et al., 2015).

$$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O \tag{1}$$

Most of the upward-diffusing methane is consumed at the expense of sulfate within the so called sulfate-methane transition zone (SMTZ), where pore water sulfate and methane are depleted to near-zero concentrations (e.g., Jørgensen et al., 2004; Yoshinaga et al., 2014). At the same time, the SMTZ exhibits the maximum accumulation of dissolved hydrogen sulfide (Boetius et al., 2000; Jørgensen et al., 2004; Reeburgh, 2007). The localized formation of hydrogen sulfide commonly results in the precipitation of iron monosulfide minerals (e.g., mackinawite), or iron polysulfide minerals (e.g., greigite); altogether unstable minerals that convert into diagenetically stable pyrite eventually (Neretin et al., 2004; Rickard and Luther, 2007; Taylor and Macquaker, 2011). Besides, laboratory studies have shown that pyrite can form directly without any iron monosulfide precursor (e.g., Harmandas et al., 1998).

Pyrite formation, however, can also result from organiclastic sulfate reduction (OSR) that occurs during early sediment diagenesis, using organic matter and seawater sulfate as substrate and also yielding hydrogen sulfide (e.g., Berner, 1980; Gieskes, 1981; Jørgensen, 1982; Canfield, 1991; Mazumdar et al., 2012; Eq. (2)).

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \tag{2}$$

The preferential microbial turnover of $^{32}SO_4$ results in a ^{34}S depleted sulfur isotopic composition for the resulting sulfide (e.g., Canfield, 2001a,b) and leaves behind a complementary ^{34}S enrichment in the dissolved sulfate pool. Thus, sulfide in the sedimentary record will display a $\delta^{34}S$ value that is generally lower than the respective $\delta^{34}S$ value of the parental sulfate. In turn, negative $\delta^{34}S$ values for pyrite in modern and ancient sediments have been taken as a proxy for identifying its biogenic origin (Canfield, 2001a,b).

Many studies, however, revealed ^{34}S enriched authigenic sulfides in seepage areas. Moreover, such positive $\delta^{34}S$ values were interpreted to reflect enhanced SO₄-AOM occurring at the SMTZ (e.g., Jørgensen et al., 2004; Neretin et al., 2004; Peketi et al., 2012, 2015; Pirlet et al., 2012; Borowski et al., 2013; Wang et al., 2015; Lin et al., 2016a,b). Jørgensen et al. (2004) presented a compelling model, explaining how SO₄-AOM, when combined with a deep hydrogen sulfide sink, can lead to isotopically heavy pyrite. Peketi et al. (2012) observed that ^{34}S enriched sulfide minerals coincided locally with increased pyrite contents, recording past SO₄-AOM activity (Paleo-SMTZ). Borowski et al. (2013) noted that ^{34}S enriched sulfide minerals typically occur at the SMTZ and postulated that ^{34}S enrichment is a consequence of high proportions of SO₄-AOM. Due to a variable methane flux over time, leading to the vertical movement of the SMTZ, multiple pyrite generations may form in the sediment at different depths and times. Consequently, separating pyritization resulting from OSR and/or SO₄-AOM on the basis of bulk sulfur isotope measurements of sedimentary pyrite bears a high potential but represents a challenge at the same time.

Diagenetically stable pyrite is the crucial recorder of variations in local environmental conditions, commonly expressed by different pyrite morphologies as well as highly variable sulfur isotopic compositions (e.g., Berner, 1970, 1984; Love, 1971; Raiswell and Canfield, 1998; Grimes et al., 2002; Ono et al., 2009; Virtasalo et al., 2013; Marin-Carbonne et al., 2014). Although pyrite with various morphologies, such as framboids,

globules, crusts, pyrite overgrowths over framboidal cores, as well as euhedral crystals and distinct sulfur stable isotope patterns have been reported from seep environments (e.g., Peckmann et al., 2001, 2003; Sassen et al., 2004; Feng and Roberts, 2011; Zhang et al., 2014; Lin et al., 2016a, b), to date only one study utilized in situ sulfur isotope analysis of pyrite from seep environments to the best of our knowledge (Kohn et al., 1998).

In this study, secondary ion mass spectrometry (SIMS) is applied to analyze the sulfur isotopic compositions ($\delta^{34}S$) of different pyrite generations with various morphologic attributes from the Shenhu seepage and gas hydrate area, South China Sea. High-spatial resolution SIMS data are supplemented by results from bulk sulfur isotope measurements. Our results allow the identification of early diagenetic organiclastic sulfate reduction and superimposed effects of sulfate-driven anaerobic methane oxidation, both archived in morphologically different sedimentary pyrite at variable depth intervals.

2. Geological setting

The South China Sea is one of the largest marginal seas in the western Pacific (Wang et al., 2006). The northern slope of the South China Sea is a passive continental margin with a sedimentary sequence ranging from 1000 to 7000 m of organic-rich sediments with 0.46 to 1.90 wt.% total organic carbon (Wang et al., 2003; Wu et al., 2013). The Shenhu area is located in the middle part of the northern slope of the South China Sea (Fig. 1). To date, several prospecting regions for submarine gas hydrate with well-developed bottom simulating reflectors have been recognized (Wang et al., 2006). This margin has a high sedimentation rate, making it a favorable place for gas hydrate exploration (McDonnell et al., 2000; Jiang et al., 2008; Ge et al., 2010, 2011; Yang et al., 2010). The structural setting of the Shenhu area is controlled by complex fractures, folds, and diapirs that favor the flow of methane-rich fluids and the formation of gas hydrates (McDonnell et al., 2000; Wang et al., 2003; Paull et al., 2008). Abundant seep carbonates were discovered on the northern slope of the South China Sea, including the Shenhu area (Fig. 1; e.g., Han et al., 2008; Ge et al., 2010; Tong et al., 2013; Lu et al., 2015). In June 2007, a gas hydrate drilling campaign was implemented and gas hydrates were successfully drilled for the first time in this area (Liu et al., 2012), confirming the existence of gas hydrate in the South China Sea. These observations confirm that seepage of methane-rich fluids and gas hydrates are common phenomena in the South China Sea in general and in the Shenhu area in particular.

3. Samples and methods

Two piston cores were taken at the two sites HS148 and HS217 near the gas hydrate drilling zone in the Shenhu area during a cruise of the R/V *Haiyang Sihao* in 2006 (Fig. 1). The water depths at the two locations are 822 m and 1186 m and the lengths of the cores are 7.15 m and 8.75 m, respectively. Respective sediments mainly consist of dark-green unconsolidated clayey silt and silty clay. After retrieval, the cores were cut into sections at intervals of 0.7 m from the top to the bottom, and the top 20 cm sediments of each section were prepared for measuring headspace gas and extracting pore water onboard. The shipboard analysis of methane was performed using an Agilent Technologies-6890N gas chromatograph after gases were separated from the sediments at 40 °C. The analytical accuracy was better than 2.5%. Pore water samples were extracted on board at room temperature using a vacuum pumping method, following the operation procedures given in Cheng and Lu (2005). After extraction, the pore water was directly saved in sealed plastic bottles at 4 °C until further analysis. Pore water sulfate concentration was measured with an ion chromatograph with chemical suppression (Metrohm 790 IC), and the standard deviation (SD) of repeated measurements of sulfate concentration in standard seawater was <2% (Yang et al., 2010).

For this study, sediment samples were collected at intervals of 15 cm from the top to the bottom and packed individually in Zip-Lock plastic