



# Morphology and formation mechanism of pyrite induced by the anaerobic oxidation of methane from the continental slope of the NE South China Sea



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## ABSTRACT

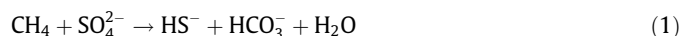
In order to understand the response of authigenic pyrite to gas hydrate geo-systems, pyrite tubes or rods at the sulfate–methane transition (SMT) zone of core GC10 from the northern continental slope of the South China Sea (SCS) were investigated. In situ X-ray diffraction (XRD) results show that the pyrite tube consists of pyrite micro-crystals with trace amount of graphite in the inner tube. Scanning electron microscope (SEM) observations of pyrite tubes indicate various aggregations in the form of framboidal, euhedral, and colloidal pyrite microcrystals. Typical framboidal pyrite is considered as packing of octahedral microcrystals. Interestingly, many framboids in the tubes consist of round or irregular microcrystals and have an outer crust that consists of secondary pyrite. The size of the framboids in the inner wall of the tube is larger than that in the middle wall or foraminifer-filled pyrite. High-resolution transmission electron microscopic (HRTEM) images show marcasite lamellae defects in the spherulitic pyrite crystals, which reveal different solution conditions during the pyrite precipitation. Nano-foil-like graphitic carbon was observed to be closely associated with the pyrite spherules. The occurrence of both marcasite layers and nano-foil-like graphitic carbon suggest that the migration of methane from deep sediment. It is suggested that the formation of pyrite serves as a catalyst during the reaction from methane to elemental carbon under the anaerobic oxidation of methane. Meanwhile, this reaction results in local acidification of the solution inside the pyrite tubes, which favors marcasite lamellae growth on the host pyrite substrate.

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## 1. Introduction

The anaerobic oxidization of methane (AOM) is the most important sink for methane in marine environments (Reeburgh, 1976, 1996; Boetius et al., 2000). More than 90% of the methane produced in anoxic marine settings is consumed by AOM before it enters the hydrosphere and atmosphere (Reeburgh, 1976; Reeburgh et al., 1993). It is the predominant process in methane-rich marine

environment (Boetius et al., 2000). Upward-moving methane, derived from the deep hydrate dissociation and free gas zone within sediments, encounters sulfate from the downward-moving seawater at the sulfate–methane transition (SMT) zone. Methane oxidation has been inferred to be coupled to the sulfate reduction operated by a consortium of archaea and sulfate-reducing bacteria (e.g., Boetius et al., 2000; Michaelis et al., 2002). A net reaction at the SMT zone can be written as the reaction:



The reaction is related to a coupled bacterial sulfate reduction and methane oxidation (Peckmann et al., 2001; Sassen et al., 2004). This reaction will increase the alkalinity, but it also slightly lowers the pH of the sea water-dominated pore fluids (Mazzullo, 2000; Pohlman et al., 2008). A linear relationship between

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alkalinity and  $\text{HS}^-$  concentration was observed in fluids from methane hydrate seep sites (Gieskes et al., 2005). The reactions result in the precipitation of various authigenic minerals such as carbonates, nano graphitic carbon, dolomite, barites, gypsums and pyrite (Bohrmann et al., 1998; Greinert et al., 2002; Wang et al., 2004; Torres et al., 2003; Chen et al., 2006; Zhang et al., 2010; Feng and Roberts, 2011).

Pyrite precipitation is a striking phenomenon that occurs at the SMT zone and maybe accompanied by carbonates in gas hydrates or cold seep settings. The production of  $\text{HS}^-$  enhances pyrite formation in sediments. Consequently, the accumulation of pyrite near the SMT could be a useful indicator in deciphering methane migration in the marine environment.

In addition, pyrites associated with methane seepage show a wide range of morphologies and mineralogical content, as well as sulfur isotopic compositions. Sassen et al. (2004) proposed that pyrite framboids formed a pseudomorphs after *Beggiatoa* and fossilized the giant filamentous bacterium in sediments. Chen et al. (2006) identified bacterial and crystal forms of pyrite scattered in the calcites crystals that collected proximal to gas vents and hydrate sites of the Gulf of Mexico and the South China Sea. Wang et al. (2008) analyzed the pyrite of an IODP 311 core sample on the Cascadia Margin. Their results show that the selected pyrites exhibit various aggregation features, mainly in the form of framboids, rods and dumbbells, and the sulfur isotopes show a vertical increase in  $\delta^{34}\text{S}$  with the depth at the cold vent site. Early studies paid little attention to crystal morphology, crystals defects, or possible formation mechanisms.

The purpose of this study is to focus on the morphology and formation mechanisms of pyrite in marine sediments, in particular, the minerals formed with pyrite (e.g., marcasite domains and graphitic nano-foils) that were observed by high-resolution transmission electron microscope (HRTEM). Special emphasis is placed on utilizing these minerals as indicators of past environmental conditions and methane-rich environments.

## 2. Materials and methods

### 2.1. Geological setting and sampling

The South China Sea (SCS) is one of the largest marginal seas in the West Pacific and is located at the junction of the Eurasian, Pacific, and Indian-Australian tectonic plates. The margins of the SCS exhibit a complex, and possibly unique tectono-sedimentary framework (McDonnell et al., 2000; Wang et al., 2003). The marine sediments on the continental slope of the NE South China Sea are considered a favorable place to host gas hydrates, because the region has a high sedimentation rate, thick sediments and suitable pressure–temperature regime (McDonnell et al., 2000; Fu, 2005; Zhang et al., 2007; Jiang et al., 2008; Yang et al., 2010).

Our study site (GC10) is located in the NE South China Sea, near the bottom of the continental slope of Taiwan Island (Fig. 1). The samples were collected by a gravity piston during the SO-177 survey, which was operated by Ocean IV from the Guangzhou Marine Geological Survey and SONNE from Germany in 2004. The sampling site was 3008 m in water depth and had a 973 cm long core. During SO-177 survey, methane-fueled microbial communities and bivalves were reported by SONNE for the first time. Carbonate chimneys formed by methane vents were also observed (Huang et al., 2005). A bottom simulating reflection has also been performed and revealed the occurrence of gas hydrates (Wang et al., 2006). The core sediment contains 0.42–1.74 wt.% total organic carbon; the average is 0.81 wt.%. This amount of organic carbon can supply enough microbial methane for gas hydrates according to Paull et al. (2000). The pore water  $\text{CH}_4$ ,  $\text{SO}_4^{2-}$  and  $\text{HS}^-$  gradients in the core sediment indicate that the SMT depth of the core is between 450 and 800 cm (Fig. 2c. Wu et al., 2011). The core sediment gradients also indicate that the rate of AOM is very high, but drops dramatically away from the SMT zone (Dale et al., 2008; Knab et al., 2008).

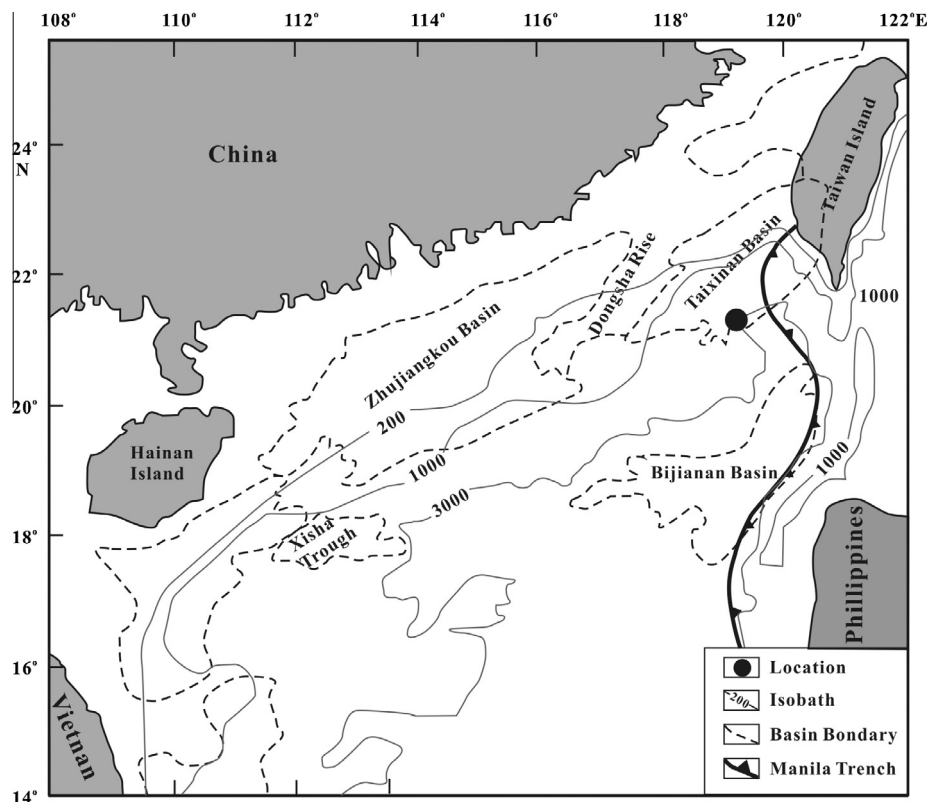


Fig. 1. Location of the studied site in the South China Sea (modified from Wu et al., 2005).

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