Marine and Petroleum Geology 73 (2016) 181-187



Contents lists available at ScienceDirect

Marine and Petroleum Geology

journal homepage: www.elsevier.com/locate/marpetgeo



Sulfur speciation in marine sediments impacted by gas emissions in the northern part of the South China Sea





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ARTICLE INFO

Article history: Received 2 June 2015 Received in revised form 22 December 2015 Accepted 29 February 2016 Available online 2 March 2016

Keywords: Marine sediments Chemical speciation Sulfur Methane emission South China Sea

ABSTRACT

Three cores of marine sediments from the Shenhu area in the northern part of the South China Sea were analyzed by XANES analysis for sulfur speciation. The area has been investigated for the presence of hydrocarbons and potential gas hydrate formations. Cored samples of site 4B showed a specific profile of sulfur speciation with sharp and frequent variations in relative contents of sulfate and sulfide, which differed greatly from the profiles obtained for the sediments taken at sites 5B and 6A. The upper part of core 4B (of 0–95 cm) was soft and rich in pore water, containing mainly coarse silt sand. The lower part of the core (i.e., depth > 95 cm) was relatively dryer and darker in color, and dominated by silts and clay resembling sediments from mud volcanoes. The sulfur speciation results revealed that sulfate makes up almost 100 percent of all sulfur species in the upper part of the core 4B, which indicates strong oxidizing conditions, whereas the lower part of the same core has high relative contents of sulfide, sometimes close to 100% S^{2-} . In the lower part of the core, the relative content of sulfide and sulfate changes rapidly and frequently, indicating rapid changes of oxidizing and reducing conditions. On the other hand, the vertical profiles of sulfur species for the cores from sites 5B and 6A are relatively consistent with lower sulfide contents indicative of stable and weaker reducing conditions. We hypothesize that the frequent and sharp variations in the ratios of sulfide to sulfate at site 4B may indicate some intermittent eruption of methane with clay from petroleum reservoirs underneath the sea floor over a relatively short period of time.

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1. Introduction

The release of hydrocarbons from marine sediments can induce various mineralogical and geochemical anomalies, such as the presence of hydrocarbon gases in the pore water and enrich for microbes capable of degrading hydrocarbons and authigenic minerals, such as secondary carbonates (e.g. Chen et al., 2004; Hesse, 2003; Hinrichs et al., 1999; Orphan et al., 2001, 2002; Sassen et al., 2004). All of these anomalies can be considered as

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http://dx.doi.org/10.1016/j.marpetgeo.2016.02.034 0264-8172/© 2016 Elsevier Ltd. All rights reserved. meaningful indicators (either directly or indirectly) of the presence of petroleum reservoirs underneath the ocean, and even gas hydrates in shallow layers of marine sediments because the melting of the gas hydrates will result in the upward emission of methane and other gases along with ambient temperature and pressure changes (Etiope and Milkov, 2004; Hester and Brewer, 2009). Many researchers focusing on such anomalies to identify and/or explore the potential deposits of marine petroleum reservoirs (Kvenvolden, 1993, 2003) have been proven correct. For example, some authigenic pyrite and carbonates in shallow marine sediments were found as potential indicators of the occurrence of methane hydrate in submarine sediments (Aloisi et al., 2000; Bohrmann et al., 1998; Chen et al., 2006), and also the potential impact on climate change in some ancient geological times because a suddenly massive methane release from buried gas hydrate could input additional greenhouse gas to the atmosphere (Dickens et al., 1995; Campbell et al., 2002: Padden et al., 2001; Houghton et al., 2001). Some past studies using sulfur and carbon stable isotopes have discovered a close correlation between the isotopic data of the authigenic minerals and the potential occurrence of hydrocarbons in submarine sediments (Orphan et al., 2002; Wang and Suess, 2002; Xie et al., 2013).

It is a known fact that the concentration and speciation of some sedimentary elements will also be geochemically changed as a result of methane or other gas emissions, especially redox sensitive elements, such as sulfur, iron, and manganese, because their solubility and speciation are largely dependent on redox conditions which induce reduction-oxidation transformations (Takahashi et al., 2009, 2013; Zheng et al., 2010). Biological processes and/or organic-inorganic interactions along with emission of methane and other gases from petroleum reservoirs and/or gas hydrates will change the redox conditions of marine sediments. For example, the anaerobic methane oxidation (AMO) coupled to sulfate reduction (Boetius et al., 2000) can strongly influence sulfur speciation and the total concentration of sulfur in marine sediments related to hydrocarbons gas emissions. Sulfur speciation of shallow marine sediments can therefore supply additional information about the potential occurrence of petroleum deposits in some marine areas. However, separation and determination of sulfur species in solid materials such as marine sediments, is not easily done with routing methods because of their complicated speciation, mineralogy and abundance. Newly developed qualitative and quantitative X-ray absorption near edge structure (XANES) analysis is however available for redox sensitive chemical species, such as sulfur. In this study, the XANES technique was used to measure sulfur species in cored sediment samples from the Shenhu Area in the northern part of the South China Sea, where there are evidence that hydrocarbons might be present in the subsurface marine sediments (Yang et al., 2010).

2. Study area

The Shenhu area, located in the northern part of the South China Sea, hosts marine petroleum basins that have an important potential for submarine methane hydrate exploration in China because the regional geological background is very favorable to the formation and development of petroleum systems (N.Y. Wu et al., 2009; S.G. Wu et al., 2009). The northern part of the South China Sea margin has experienced a rifting stage with lacustrine and shallow marine sediments and a post-rifting stage with shallow marine and hemipelagic deposits during the Cenozoic era (Cullen et al., 2010). In the post-rifting thermal subsidence, the deep water basins containing petroleum were formed. The marine basin sequences have been imaged from seismic data and drill wells (Yuan et al., 2009; Yu et al., 2014). Two kinds of source rocks including Paleogene lacustrine black shale and Oligocene - Early Miocene mudstone were formed in the deep-water basin whereas the deepwater reservoirs were characterized by deep sea channel fills, mass flow complexes and drowned reef carbonate platforms. Thick capping rocks are present on top of the mudstones in the post-rifting stage. Faults developing during the rifting stage provided a migration path that was favorable for the formation of the reservoirs and their petroleum accumulation.

Many cruises carried out by both domestic institutions and through international collaboration for marine petroleum methane hydrate research were performed using geophysical techniques and also geochemical methods. Numerous cores were also collected during some cruises including cores used in this study (i.e., Site 4B). The cored sites for 4B, 5B and 6A are all located in the Baiyun Sag of the Pearl River Mouth Basin, which geographically belongs to the northeast slope of the Shenhu area in the South China Sea (Fig. 1). Previous studies indicated a high deposition rate in this marine area (X. Su et al., 2005; Z. Su et al., 2005) ranging from 4000 to 7000 m of sediments during the Cenozoic era, along with high concentrations of organic matter and a 45–67.7 °C/km geothermal gradient (Wu et al., 2007). Controlled by regional tectonic movement (Lu et al., 2007), the study area is characterized by complicated geological structures. Copious amounts of geophysical data revealed that the mud diapirs or mud volcanoes were widely developed in the northern part of the south study area and possibly pierced late during the Miocene deposition. Active folds and faults (Shi et al., 2009; X. Su et al., 2005; Z. Su et al., 2005; Wang et al., 2006) are geologically developed in recent or continuing into the present and facilitate vertical gas fluid migration and the formation of gas hydrate.

3. Sample collection and analysis

Three shallow piston cores were recovered at site 4B (water depth of 970 m), site 5B (water depth 1230 m) and site 6A (water depth 1400 m) during the 2009 May–June cruise with the vessel "Ocean IV" (Fig. 1). The core taken at site 4B was 3.00 m long below the seafloor (bsf) whereas sites 5B and 6A were 8.38 m and 7.69 m in length (or bsf), respectively. The initial composition and sedimentary structures of the core sediments were only slightly damaged during recovering. The cores were sliced into two parts along the length axis in the core repository. One part was preserved under frozen condition and the other half was subdivided into various samples at a resolution of 3–5 cm intervals. A subsample was collected within 1 cm for each interval and immediately packed in a Zip-Lock plastic bag, stored (after air removed from the bag) at low temperature in an ice box and then partially freezedried using a freeze dry facility (Zheng et al., 2001, 2002).

Sulfur K-edge XANES analysis performed on the freeze-dried samples without any chemical pretreatment was done at Beamline 4B7A of the Beijing Synchrotron Radiation Facility (BSRF), Beijing, China. The beam path and the samples were placed in a vacuum to suppress X-ray scattering and absorption by air when the powder samples were exposed to the incident X-ray beam with incident angle 45°. The emitted fluorescence X-ray was measured using a solid state detector. The XANES spectra were recorded with a 0.3 eV step length (3–6 s for each point). The blank filter was also measured for comparison, and the sulfur absorption was negligible (Lin et al., 2009).

4. Results and discussion

4.1. Physical description of the sediments

The core from site 4B could be divided into two parts according to the physical appearance of the sediments: the upper part at a depth of 0–95 cm was soft and rich in pore water, containing mainly coarse silt sands and mud. When the core was freshly opened, the sediments looked like deep gray sludge. The lower part below 95 cm was relatively drier and displayed a darker color; it was dominated by silts and clay. The sediments of the lower core were very sticky and difficult to separate with a knife. These features are quite similar to the sediments erupted from the Dushanzi mud volcanoes in Xinjiang, China (Zheng et al., 2010), which is a small eruptive ground structure composed of a very sticky mud deposit containing oil, gas, water. The physical characteristics of the lower portion of the core suggest that the sediments might



Fig. 1. Location of core sites (modified from Wang et al., 2006). Three separate marine exploration regions separately in the Shenhu area in the northern part of the South China Sea, where the cored samples used in this study were taken (sites 4B, 5A and 6B).

correspond to submarine mud volcanic sediments. Geophysical exploration already determined the existence of diapiric structures, high-angle fractures and vertical fissure system (N.Y. Wu et al., 2009; S.G. Wu et al., 2009), and also bottom simulating reflectors (BSR; Wu et al., 2005) that indicate the existence of gas hydrates.

The cores from sites 5B and 6A are more representative of normal marine sediments, containing mud and silts of deep gray to black colors. Some parts are bright gray and relatively sticky with typical pyrite particles (Xie et al., 2013). However, there are no sharp changes in physical properties of the cores as observed in the core 4B. There is no sludge layer similar to that observed in site 4B in these two cores, which is likely indicative of different sedimentary environments.

4.2. Sulfur speciation

Sulfur K-edge XANES spectra were obtained for all samples, but only representative ones are shown in Fig. 2. The spectra obtained for the samples were compared to those of selected sulfurcontaining reference materials, including pyrrhotite (FeS), pyrite (FeS₂), elemental sulfur (S⁰) and calcium sulfate (CaSO₄) (Zhang et al., 2013). The influence of self-absorption for the reference materials was examined by using powdered reference samples containing sulfur at various concentrations. Self-absorption effects were not observed for S < 0.5 wt%. Positions of the peaks found in the cored marine sediment samples are mainly located at two ranges of similar energy to those found in the spectra of pyrite and/ or elemental sulfur, and also sodium sulfate, indicating the main sulfur species are sulfides and sulfate, respectively. As shown in Fig. 2, the absorbing peak on the left in the range of



Fig. 2. Selected original spectra of the sulfur species in the marine sediment samples. The absorbing peak on the left with lower energy range corresponds to sulfides whereas the peak on the right with a higher energy range corresponds to sulfate.



Fig. 3. All spectra of the sulfur species in the cored samples of site 4B from the Shenhu area of the South China Sea. All spectra were normalized taking sulfate as the same height and then the height for all sulfides with their relative contents.

2.471–2.474 keV represents the S^{2-} , S_2^{2-} and probably also S^0 sulfur species, whereas the peak on the right in the range of 2.481–2.484 keV represents SO_4^{2-} species. These sulfur species were confirmed by comparing them to typical sulfur-containing reference materials selected for this study. The obtained spectra for all samples are shown in Fig. 3, in which some complex variations in various sulfur species are displaced according to their spectrum structures and the peaks that are represented as sulfides and/or sulfate, respectively.

In order to show a clear variation of sulfide to sulfate, all spectra were normalized by taking the absorbing peak for sulfate with a top peak at 2.4825 keV as the same height. The peaks for all sulfides were normalized according to their relative contents of corresponding sulfate, for which all sulfur species of S^{2-} , S_2^{2-} and also S^0 are taken as sulfide for data treatment, and then the relative contents of sulfides and sulfate are calculated based on their peak areas. The spectra for all samples measured are shown in Fig. 4 where variations of sulfide with respect to sulfate in the core are clearly shown.

4.3. Vertical variation of sulfur speciation

The cored samples from site 4B showed a specific profile of sulfur speciation with sharp and frequent variations of sulfide and



Fig. 4. Vertical profile of sulfur speciation for the cored samples of site 4B. The relative contents of sulfides to sulfate were calculated based on the absorbing peaks corresponding to sulfides on the left and sulfate on the right. The photos show surface properties of the sediments from the core taken at site 4B.

sulfate contents when compared to normal marine sediments, such as those in the cores 5B and 6A collected from different sites of the same region (Fig. 5). Core 4B was the only one to display such a unique vertical sulfur speciation. For sulfur speciation, sulfate accounts for almost 100 percent of all sulfur species in the samples from the upper part of the core (0-95 cm), which indicates strong oxidizing conditions. There is more sulfide in the lower part of the core with high relative contents, sometimes close to 100% S²⁻. The relative content of sulfide and sulfate changes rapidly and frequently, indicating frequent and strong variations of oxidizing and reducing conditions within the sediments. The vertical profiles of sulfur species for the cores from site 5B and 6A (Fig. 5) are clearly different from those of site 4B (Fig. 4), the sediments have a lower relative sulfide content indicative of stable and weaker reducing conditions (Jasinska et al., 2012). For the lower part of core 6A, there seems to be variations in the sulfur speciation patterns, but the intensity of the variations is less intense given the lower relative contents of sulfide in comparison to that of site 4B.

4.4. Potential indicators of gas emission

The specific pattern of sulfur speciation in the core of site 4B may indicate the occurrence of petroleum reservoirs and/or even methane hydrate in the area, a process similar to methane releasing mud volcanoes (Zheng et al., 2010). The release of methane has the potential to stimulate microbial activity including methanogens and sulfate reducing bacteria (SRB). Organic matter mineralization in marine sediments has been shown to be intimately linked to the microbial reduction of sulfate (Jørgensen, 1982; Jørgensen and Boetius, 2007; Hensen et al., 2003). During the active period of mud eruption with methane and other hydrocarbons, it is likely that populations of sulfate reducing bacteria increase, which can lead to sulfide production and precipitation of metal sulfide minerals in the reduced sediments (Niemann et al., 2006). On the other

hand, at times of weaker eruption, more sulfate remains in the sediments due to a lack of electron donors (i.e., methane or hydrocarbons) for the sulfate-reducing bacteria, which can lead to less reducing conditions. Such scenario could therefore explain the frequent and sharp variations in the ratio of sulfide to sulfate in the site 4B profile. Intermittent eruption of methane with clay from the petroleum reservoirs along with possible methane hydrate formation and melting process in a relatively short period of time could lead to such unique sulfur speciation patterns. Very clear different vertical profiles of sulfur speciation in the cores from sites 5B and 6A may indicate the absence of petroleum reservoirs and/or gas hydrate in these two areas (Fig. 1), or very limited amount of hydrocarbons release during the sedimentation periods of both sites. It is however clear that further analysis of the cores is needed to fully assess the relationship between sulfur speciation and hydrocarbon presence. Such analysis should include dating of the sediments and sulfur speciation at a smaller scale, along with other mineralogical and geochemical characteristics of the marine sediments from the Shenhu area in the South China Sea, of which carbon and sulfur isotopes might be very useful and necessary (Dickens et al., 1995; Formolo and Lyons, 2013; Orphan et al., 2001).

Several layers enriched with authigenic pyrite were observed in the lower part of the same core from site 4B (Xie et al., 2013) and a potential submarine muddy volcanic environment in the area was suggested based on the relative contents of pyrite with respect to the mass of total dry sediments and their associated sulfur isotopic compositions. However, there are just three or four layers clearly distinguished from those data, of which two layers are in a bright gray color, relatively harder and dryer as shown on the left part of the photos in Fig. 4. These two layers are enriched with pyrite particles with specific surface appearance that could be easily distinguished with the naked eye when the core was cut open. These pyrite enriched sediments might have been deposited under strong reducing conditions where methane emissions had an



Fig. 5. Vertical profiles showing the sulfur speciation for the cored sediments taken at sites 5A and 6B. The calculating method is the same as in Fig. 4. The black arrows indicate a redox front typically seen in normal marine sediments. The sulfur speciation for sites 5A and 6B is clearly different from that of site 4B (Fig. 4).

important control in the study area. In the present study, several layers with strong reducing conditions in the core from site 4B were evidenced with the help of sulfur speciation analyses using the XANES technique, showing the advantage of the latter technique for hydrocarbon exploration research.

5. Conclusions

The special vertical variation patterns of sulfur species in the core from site 4B suggest sharp and frequent redox changes even though the sedimentation rate appears to be similar in both the upper and lower parts of the core (i.e., similar particle size). The distinct redox changes inferred by the sulfur speciation results may result from the emission of hydrocarbons from underneath petroleum reservoirs in the Shenhu region. It is likely that the activity of sulfate reducing bacteria is largely dependent on the supply of methane and other hydrocarbons emitted from deep layers along with the intermittent activity of submarine mud volcanoes. Such methane emissions could supply energy to sulfate reducing bacteria, which then leads to sulfide production and metal sulfide precipitation along with the submarine mud volcanic deposits. Therefore, such a very special variation pattern of vertical sulfur speciation in marine sediments could be a potential indictor of petroleum reservoirs and/or even gas hydrate deposits, which may be revealed by further investigation and research in the future.

Acknowledgments

We would like to thank Prof. Duofu Chen from Guangzhou Institute of Geochemistry CAS and Prof. Nengyou Wu from Qingdao Institute of Marine Geology CGS for their comments on this study and suggestions for this manuscript, Prof. Jiasheng Wang from the China University of Geosciences (Wuhan, China) and his students for their assistance in sampling collection, Dr. Xiangxian Ma and Miss Chengyan Ma for their assistance in sulfur species measurements. This study was jointly supported by the China National Key Basic Research and Development Program "973" (2009CB219506), the National Natural Science Foundation of China (41273112), and the CAS/SAFEA International Partnership Program for Creative Research Teams (KZCX2-YW-T10).

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