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Research paper

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

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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.

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 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;

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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 freeze-dried 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