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Heavy Sulfur Isotopic Compositions of Authigenic Pyrite in the Sediments of Shenhu Area, South China Sea

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1 Introduction

As the stable and common iron-sulfide mineral in marine, pyrite precipitates from the pore water which is supersaturated with respect to pyrite. It usually forms as pyrite framboid or euhedral crystal within the anoxic water column or below the sediments-water interface (Roberts and Turner, 1993).

Under normal marine sediments, the decomposition of organic matter can be the main reason for the precipitation of the pyrite. Thus, within CH_4-contained marine sediments, the anaerobic oxidation of methane (AOM) is the mainly microbial process whereby CH_4 is oxidized by SO_4^{2-} at the sulphate-methane transition (SMT), leading an increase in HS^- which will result in the enrichment of the pyrite (Eq.1).

$$CH_4+SO_4^{2-}\rightarrow HS^-+HCO_3^-+H_2O \quad (1)$$

During the AOM, the sulphate reduction bacteria discriminate against the heavy sulfur isotope ^{34}S, which produce the ^{34}S-riched SO_4^{2-} and ^{34}S-depleted H_2S. Therefore, the H_2S-derived pyrite reveals negative isotopic signatures in most conditions.

2 Samples and Results

This study is based on two piston core sites (HS373 with length 9.28 m and HS148 with length 7.29 m) in Shenhu Area, the South China Sea. Piston cores were collected on the Shenhu area of the South China Sea on board Ocean IV(2006) from the Guangzhou Marine Geological Survey.

These two cores mainly consisted of unconsolidated clays, besides we had found many pyrite tubes in the sediments (Fig. 1a). Such tubes were composed of pyrite framboids and euhedral octahedral microcrystals (Fig. 1b, c). Some framboids owned order structure with parallel line patterns (Fig. 1d).

The sulfur isotopic compositions of pyrite had a wide range in both of these two cores. Their trends of isotopic variation with depth were quite similar. The $\delta^{34}S$ of pyrite in HS373 ranged from about –40‰ to 40‰, and HS148 ranged from about –30‰ to 45‰ (Fig. 2). From the curves we could find that when approached to the top of the sediment, the pyrite sulfur isotope was highly depleted in ^{34}S (about –40‰), which was common in the normal marine sediments because of the bacterial disproportionation of elemental sulfur.

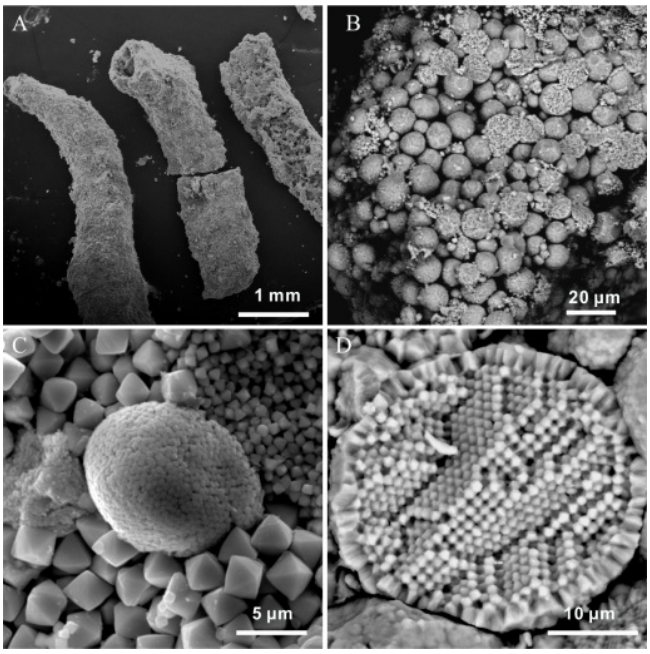

Fig. 1. (a) pyrite tubes; (b)pyrite framboids; (c) pyrite framboid and euhedral octahedral microcrystals; (d) framboid composed of order structure microcrystals.

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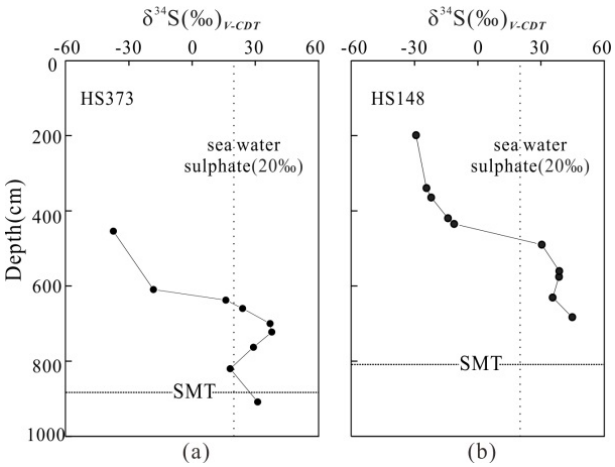

Fig. 2. The sulfur isotope variation of pyrite in the Core HS373(a) and HS148(b).

However, pyrite that formed at deeper depth in the sediments in both two cores becomed so extremely enriched in ^{34}S which was much higer than the $\delta^{34}S$ value of the sea water sulphate (20‰). Such cases were not common and reports were limited. Jørgensen et al. (2004) attributed the isotopically heavy sulfides in Black Sea sediments to the anaerobic methane oxidation and a deep H_2S sink.

3 Discussion

The locations of Core HS373 and HS148 were quite close to each other and the SMI of the two cores were very shallow. The depth of SMI in HS373 was about 900cm and HS148 was about 800 cm, which meant this area had a high methane flux from underlying gas hydrate and such two locations might be influenced by the same gas hydrate system (Wu et al., 2013).

The shallow sediments might be an open diagenesis system where fresh sulphate ($\delta^{34}S$ = 20‰) could diffuse down rather rapidly, which resulted in the formation of ^{34}S-depleted pyrite by bacterial sulphate reduction.

Most sulphate downward would be exhausted by the upward methane flux until to the SMT. Moreover, the diagenetic system would become closer with depth, which reduced the rate of downward diffusion flux of SO_4^{2-}. In such process, the remaining sulphate would become $\delta^{34}S$-riched because the lighter $^{32}SO_4^{2-}$ would be preferentially consumed during the sulphate reduction within the methane-riched sediment (Jørgensen et al., 2004). Thus, the sulphate would become isotopically heavier with depth as a result of the sulphate reduction by methane.

In such case, the H_2S produced by AOM could also be rich in $\delta^{34}S$ inherited by the $\delta^{34}S$-riched sulphate, which resulted in the heavy $\delta^{34}S$ values of pyrite in the deeper sediments.

4 Conclusions

The $\delta^{34}S$ values of pyrite had a wide range in both HS373 and HS148, and the heavy $\delta^{34}S$ values in the deep sediments were interpreted to reflect the lasting methane flux from the under hydrate system.

Acknowledgments

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