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Research Advances

Characteristics of Authigenic Pyrite and its Sulfur Isotopes Influenced by Methane Seep—Taking the Core A at Site 79 of the Middle Okinawa Trough as an Example

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Objective

Authigenic pyrite often develops extensively in marine sediments, which is an important product of sulfate reduction in an anoxic environment. It has a specific appearance and complicated sulfur isotopic properties, and acts as important evidence of methane seep in marine sediments. Strong AOM (anaerobic oxidation of methane) activity has developed in the Okinawa Trough. Owing to the inconvenient geochemical sampling, few studies have been conducted on the pyrite and its sulfur isotope based on an AOM-development setting. This work analyzed the characteristics of authigenic pyrite and its sulfur isotopic values with an AOM background in the middle Okinawa Trough. We discussed how the changes in the pyrite and its sulfur isotope content affect the anaerobic oxidation of methane and the methane flux.

Sampling and Methods

The sediments in this study were obtained from the cruise site 79 using gravity cores on board the R/V Kexueyihao in July 2012. The entire sample is 4.1 m in length. The samples were divided into two parts. The first part we used for the observations of pyrites at the State Key Laboratory of Geological Processes and Mineral Resources of the China University of Geosciences (Wuhan). The second part of the sample was used to extract pyrites through chromium reduction and then to determine the sulfur isotopic values and the experiments and testing were performed in the Key Laboratory of Biological Geology and Environmental Geology of China University of Geosciences (Wuhan).

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Results

(1) Appearance of pyrite

SEM observations show that the aggregate form of pyrites is very abundant and mostly has a stripy shape or foraminifera-compartment-filled shape. Furthermore, a small amount of irregular massive pyrite was found, and the lengths of the stripy pyrites are mostly in the range of 1–3 mm. Inside the stripy pyrite, we found a clear tubular layer structure. An analysis using energy-dispersive X-ray spectroscopy show that the outer layer mainly consists of clay with small amounts of pyrite, the middle layer consists of a porous cementation of pyrite, and the inner layer consists of tightly packed spherical pyrite. The chamber of foraminifera is filled with a large amount of spherical pyrites, and the microcrystalline structure is primarily octahedral with a uniform size.

(2) TOC, TS, pyrite content,and sulfur isotope

The TOC of core A shows significant differences at a depth of 270 cmbsf. Above 270 cmbsf, the TOC is relatively high, ranging from 1.68% to 1.23% (the average is 1.43%); with the increasing depth, the TOC values tend to decrease progressively. Below 270 cmbsf, the TOC values plunged, with an overall range of 0.56% to 0.86% (the average is 0.74%). The TS increases with the increasing depth and shows an abrupt increase above 100 cmbsf. The percentage of pyrites and the sulfur isotopic values of 30 sediment samples vary largely with depth. Between 0 and 100 cmbsf, the percentage of pyrites is approximately 0.55%. From 100 cmbsf to 200 cmbsf, the percentage of pyrites decreases from 0.98% to 0.30%.

However, below 240 cmbsf, the percentaget of pyrites is relatively high, with an average of 0.83%. The values of $\delta^{34}S$ above 278 cmbsf are more negative and more stable than those below 278 cmbsf, ranging from −32.73‰ to −41.20‰ V-CDT. Below 278 cmbsf, the values of $\delta^{34}S$ significantly increase, showing a gradual positive trend, ranging from −21.49‰ to +8.92‰ V-CDT.

Conclusions

Optical microscopy and SEM observations suggest that the aggregate form of pyrites is very abundant, and it is mostly of stripy shape and foraminifera-compartment-filled shape. The internal space of tubular pyrite provides a channel of upwelling methane, which forms spherical pyrites with uniform size through intense AOM activity.

At 0–278 cmbsf, which corresponds to 17.18–5.3 ka, the sulfur isotopic values of pyrite are very stable. Meanwhile, the SRZ (sulfate reduction zone) is deep, and the methane flux is very low (Fig. 1), reflecting the weak methane see. At the same time, the higher TOC and lower TS also suggest that AOM is not the main reason for the fractionation of sulfate from another side. Consequently, the $\delta^{34}S$ values are stable. Below 278 cmbsf (corresponding to 18.86–17.18 ka), sulfur isotopic values gradually increase, corresponding to the SRZ with low depth and increasing methane flux (Fig. 1). During this stage, the enrichment of ^{34}S, and the abrupt increase in pyrite content show intense AOM activity and methane seep. In particular, in 18.78 ka (370 cmbsf), the maximum sulfur isotopic value of +8.92‰ V-CDT and the maximum sulfate reduction rate occur, supported by the upward migration of methane.

AOM provides the main sulfur source for pyrite formation in the SRZ, leading to the excessive consumption of sulfate, increase in the sulfate reduction rate, and incomplete fractionation of the sulfur isotope, which is the main factor determining the positive sulfur isotopic values. It is believed that abnormally positive sulfur isotopic values can be used as a geological record of AOM, indicating methane seep and intense AOM.

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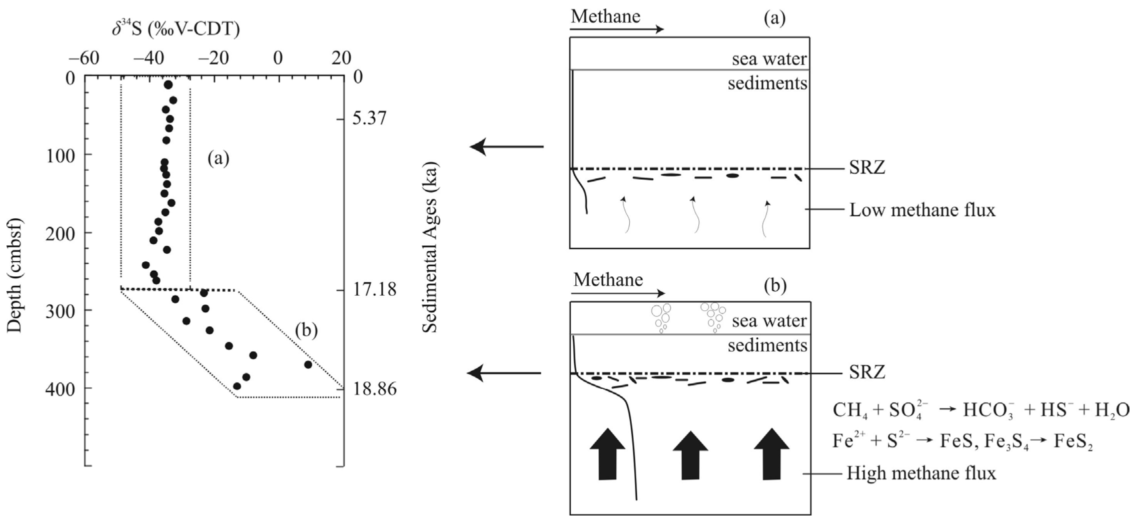

Fig. 1. Diagrams showing sulfur isotopic values and methane seep at core A of the site 79.