

## AUTHIGENIC PYRITES AND THEIR STABLE SULFUR ISOTOPES IN SEDIMENTS FROM IODP 311 ON CASCADIA MARGIN, NORTHEASTERN PACIFIC

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### ABSTRACT

In order to understand the response of authigenic minerals to the gas hydrate geo-system, various authigenic pyrites were picked out under Zeiss Microscope and their S isotopes were analyzed later from 652 sediments samples at intervals of about 1.5m recovered from all 5 sites of Integrated Ocean Drilling Program (IODP) Expedition 311 on Cascadia Margin, northeastern Pacific. SEM photos of picked pyrites exhibit various aggregation features mainly in forms of strawberry, pillar/rod and dumbbell in sizes from 200  $\mu\text{m}$  to 1000 $\mu\text{m}$ . Typical cubic pyrite crystals could be seen under smaller scale SEM photos. Most  $\delta^{34}\text{S}$  values in Site U1325 at the west deeper water location of IODP 311 show negative values low to -33.964‰ CDT, distinctly contrasted to the  $\delta^{34}\text{S}$  in Site U1329 at the east shallower location having much more positive values up to 28.29‰ CDT. At the cold venting position assigned as Site U1328 the  $\delta^{34}\text{S}$  values show strong negative values in the upper part of sediments column above 135 mbsf (meter below sea floor), increasing gradually with the depth from -35.83‰ CDT to -1.32‰ CDT, and then display many positive excursions up to 32.49‰ CDT below 135 mbsf, which is significantly distinguished from the values in nearby non-cold venting Site U1327 having much less positive excursions in the lower part of column below 110 mbsf. In all sites a general negative  $\delta^{34}\text{S}$  excursion occur in the upper part of sediments columns above 30~35 mbsf except in Site U1328 having more depth, indicating the potential current sulfate methane interface (SMI) activity zones. Distinct positive  $\delta^{34}\text{S}$  excursions up to the highest  $\delta^{34}\text{S}$  value 53.65‰ CDT from strawberry pyrites aggregations might indicate that sulfide products by AOM probably inherit completely the sulfate having high  $\delta^{34}\text{S}$  value and no sulfate was left after AOM at a high methane flux under gas hydrate geological background.

*Keywords:* authigenic pyrite, sulfur isotope, sediments, IODP 311

### INTRODUCTION

Gas hydrate is an ice-like solid substance composed of water and natural gas (mainly methane) (Kvenvolden et al., 2001), usually stable in condition of low temperature and high pressure within sediments mainly in marine continental slope and onshore Arctic permafrost environments. The natural gases (mainly methane) in hydrate are produced usually from organic materials in sediments by anaerobic bacterial and thermal decomposition (Paull et al., 1994), and ascend and encounter the water molecules in pore water within sediments to form solid gas hydrates in sediment column (Hyndman et al., 1992; Kastner,

2001). The ascending methane, partially derived from the below hydrate dissociation and free gas zone through the conduits within sediments, will encounter sulfate from the downward seawater in the upper part of sediment column to thrive the chemical reaction of anaerobic oxidation of methane (AOM) at the sulfate-methane interface (SMI) near the boundary between seawater and sediments (Elvert et al., 2001), resulting in the precipitation of various authigenic minerals such as carbonates, barites, gypsums and pyrites etc (Bohrmann et al., 1998; Greinert et al., 2002; Wang et al., 2002, 2004; Torres et al., 2003; Chen et al., 2006).

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Pyrite recognized as the synergistic metabolism of methane oxidizing archaea (MOA) and sulfate reducing bacteria (SRB) at SMI occurs widely at the cold seeps in gas hydrate geological system (Chen et al., 2006), characterized by the distinct crystal aggregations and stable sulfur isotopic fractionation (Jorgensen et al., 2004). Here we report the authigenic pyrites and their sulfur isotopes in sediments recovered from Integrated Ocean Drilling Program (IODP) Expedition 311 on Cascadia margin, northeastern Pacific. The primary research shows that various pyrites were precipitated by both bacterial fossilization and inorganic crystallization, having a wide range of stable sulfur isotopic values. In generally, the sulfur isotopes of pyrites separated from the sediments in deep water sites are generally slight more negative than those in shallow water sites, while the sulfur isotopes of pyrites at the cold vent site show a vertical increase with the depth, possibly caused by the reusing of remained sulfate after early AOM. Thus, this research will have significant meaning for understanding the marine sulfur cycles and for interpreting the sulfur isotopic parameters in modern and ancient gas hydrate geological system.

### SAMPLES AND ANALYTICAL METHODS

All sediments samples were collected personally by the authors from the all 5 sites of Integrated Ocean Drilling Program (IODP) Expedition 311 on Cascadia margin, northeastern Pacific (Fig. 1). The research area of recovered sediments is located at the accretionary prism of the Cascadia subduction zone at the present subduction rate of ~45 mm/y (Riedel et al., 2005, 2006, 2007). The sediments in the Cascadia basin consist mainly of pre-Pleistocene hemipelagic depositions overlain by Pleistocene turbidites for a total thickness of ~2500 m (Riedel et al., 2007). Deformation and faulting developed through the entire sediment column. Five sites of U1326, U1325, U1327, U1329 and U1328 (cold vent site) were drilled during the IODP 311 Expedition from west to east in different seawater depth of about 900 m to 2200 m (Fig. 1), and 1217.76 m length sediment cores were recovered from the seafloor sediments to the beneath sediments deep to about 350 mbsf (meter below sea floor). A lot of gas hydrate samples and hydrate-bearing sediments were recovered and collected, during which different authigenic minerals including carbonate and iron sulfide

concentrations were recognized when the cores were cut and split.

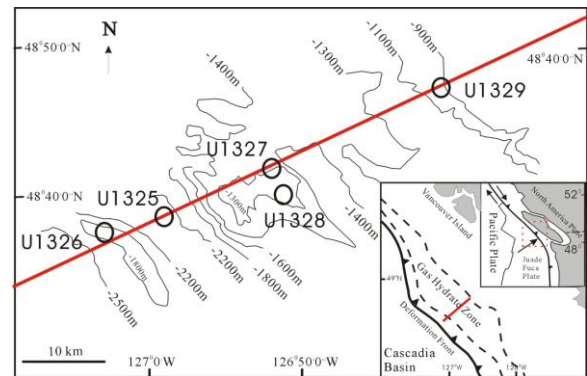


Fig. 1 Location of IODP 311 and Sites distribution along the drilling transect across accretionary prism offshore Vancouver Island with bathymetry (Inset: General tectonic location of drilling transect) (modified from Riedel et al., 2007)

Total 625 sediments samples at intervals of about 1.5m for this research were collected from the all recovered sites during the IODP 311 Expedition. About 10 cc (cubic centimeter) sediments separated from the each collected sample were then rinsed by distilled water for several times, sieved by 240 and 500  $\mu$ m sifters respectively and dried finally for at least 24 hours in air-dried equipment at temperature 50°C. All particles more than 63.5  $\mu$ m size were recollected from the tried sediments, from which authigenic minerals and *Foraminifera* were picked up carefully under the Zeiss Microscope, classified and weighed in details. Recent researches show that gas hydrates were generally constrained by the coarse grains more than 31 $\mu$ m size and authigenic carbonates and pyrites occurred in sediments (Wang et al, 2006, 2007). The main mineral components of picked pyrites were then investigated by XRD and microstructures by SEM. The stable sulfur isotopes of picked pyrites were preformed by a mass-spectrometer finally at the State Key Laboratory of Geological Processes and Mineral Resources in China University of Geoscience (Wuhan). All SEM samples for pyrite surface features were coated with gold and SEM photographs were taken by JSM-35CF operating under the condition of 0-39 kV, 15-39 mm working distance and 6 nm resolving power. The XRD analyses were completed by X' Pert Pro DY 2198 equipment. The sulfur isotope analyses were

finally preformed by MAT-251 EM mass-spectrometer with CDT (Vienna Canyon Diablo Troilite) as the standard reference (Beaudoin et al., 1994). The replicates of sulfur isotopic analyses agreed within  $\pm 0.2\%$ .

## RESULTS AND DISCUSSIONS

XRD patterns show that the picked pyrites aggregations have typical peaks of very pure pyrite, mixed with few quartz and feldspar. SEM photographs show that there are two main types of pyrites in sediments: spherical microbial fossilized aggregations and cubic inorganic crystallized aggregations (Fig. 2).

Microbial fossilized aggregations show various appearances including single spheroid (Fig. 2 A, B) and strawberry-like or framboid aggregations (Fig. 2 C, D), composed of numerous smaller spheroids within each aggregation. These spheroid pyrites are usually recognized as precipitation by bacterial fossilized processes (Chen et al., 2006), identical to the reported bloom of methane oxidizing archaea and sulfate reducing bacteria in Cascadia margin (Riedel et al., 2007). The occurrence of microbial fossilized pyrites indicates that archaea and bacteria were involved in pyrite precipitation at the gas vent and hydrate sites. The bacteria colonies contribute to the conversion of sulfate into  $H_2S$  and of ascending methane into  $CO_2$  near the sulfate methane interface (SMI) (Elvert et al., 2001), resulting in pyrite precipitation finally by the reaction of  $H_2S$  and iron minerals in sediments (Chen et al., 2006). The archaea and bacteria would be fossilized by the pyrite precipitation and their spherical appearance could be remained.

Inorganic crystallized pyrites aggregations also show various appearances including rod, tree-like, dumbbell and other un-regular features (Fig. 2 E, F, G and H), composed of numerous cubic pyrite crystals within each aggregation. The crystallized pyrites are recently interpreted as inorganic precipitation by replacement of the out layers of bacterial fossilized pyrite framboids during the anaerobic oxidation of methane (AOM) (Chen et al., 2006). However, some large worm-like pyrite rods and tree-like pillars more than 1 mm length occurred widely in recovered sediments of IODP 311, which means most likely that these pyrite rods and pillars probably were the crystallized micro conduits, by which methane and fluids ascended at the gas and fluid diffusion in sediments column. Similar observations of pyrite aggregations were also found in cored sediments

from the gas hydrate potential area of offshore southwestern Taiwan (Jiang et al., 2006). So, our observations document the microbial activities and pyrite precipitations in gas hydrate geological system, which suggest that pyrite precipitation could develop by different mechanisms including

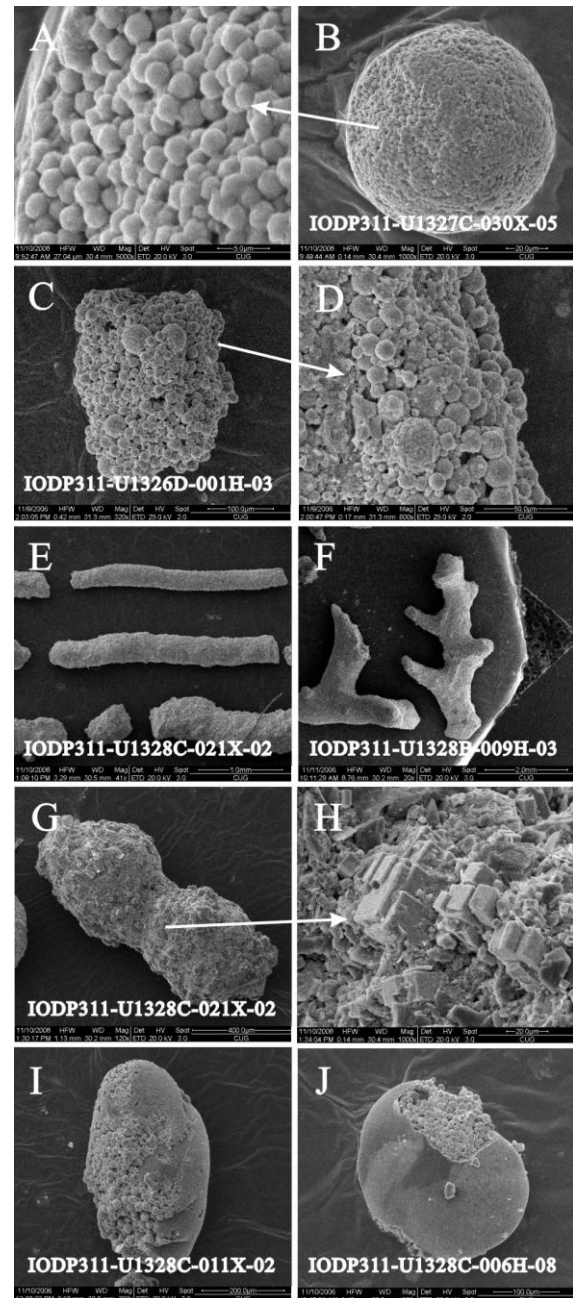


Fig. 2 SEM photos of authigenic pyrites from the recovered sediments during IODP 311 on Cascadia basin offshore, northeastern Pacific. A-D: spherical microbial fossilized pyrites; E-H: Inorganic crystallized pyrites; I-J: Foraminiferal pyrite aggregations.

bacterial fossilized ways and inorganic crystallized ones. The large pyrite rods and pillars most likely represent the crystallized conduits by which methane and fluid convection developed in sediments column.

In addition, some foraminiferal pyrite aggregations were found in sediments, filled by numerous spheroid pyrites in the room (Fig.2 I, J), indicative of some microbial crusts fossilized by the pyrite replacement during diagenesis.

The stable sulfur isotopic composition of picked pyrites seems having a wide range of  $\delta^{34}\text{S}$  values from -35.4‰ CDT to +53.6‰ CDT (Fig. 3). In generally,  $\delta^{34}\text{S}$  values of sediments from the upper part of sediments column seem having more negative values and higher sulfur isotopic fractionation than those from the lower part sediments, probably indicative of more intensive reaction of anaerobic oxidation of methane (AOM) and more seawater sulfate involvement in the upper part sediments column. In addition,  $\delta^{34}\text{S}$  values of pyrites in sediments recovered from the deep water sites show less  $^{34}\text{S}$  ( $\delta^{34}\text{S}$  values negative low to -33.96‰ CDT in west site of U1325), contrasted to positive  $\delta^{34}\text{S}$  values up to 28.29‰ CDT in east site of U1329. Moreover, in the cold vent site U1328 the  $\delta^{34}\text{S}$  values increase gradually with the depth from -35.83‰ CDT at the depth near top sediments to 32.49‰ CDT at the depth about 256 mbsf (Fig. 4), which means that much remained sulfates in the local sulfate pool within sediments after the early AOM reaction were probably reused by the later AOM reaction in the lower part of sediments column, resulting in a strong positive sulfur isotopic excursion of pyrites at a supposed unique sulfur isotopic fractionation. More positive sulfur isotopic excursions occurred in the lower part of sediments especially below the depth of 110 mbsf at the cold vent site U1328 is significantly different from the excursions at the nearby non-cold vent site U1327, strongly indicative of more active AOM reaction happened in the cold vent under the high methane and fluid flux background.

The most positive  $\delta^{34}\text{S}$  value up to 53.65‰ CDT of selected pyrites as the strawberry fossilized aggregations occurred at depth about 92 mbsf in site U1327, significantly contrasted with the just above depth of 69 mbsf with -27.97‰ CDT, having an extreme sulfur isotopic fractionation of  $\Delta\delta^{34}\text{S} \approx 80$  within around 23 m thick sediments

intervals. Such high positive isotopic excursion could be interpreted by the exhaustion of ambient sulfates in the local sulfate pool within sediments and no sulfate left after AOM reaction, leading to the produced sulfides completely inheriting the heavy isotopic values of sulfate (Shen et al., 2008). Therefore, the strong positive sulfur isotopic excursion of authigenic pyrites would probably indicate an intensive AOM under a relative closing system, especially in the situation of high methane and fluid flux in marine gas hydrate geological system.

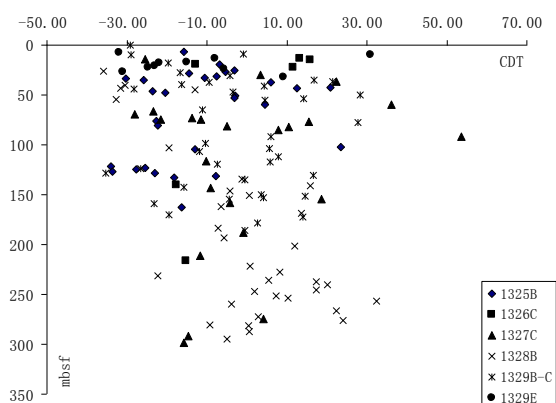


Fig.3 Sulfur isotopic composition of authigenic pyrites separated from the recovered sediments during IODP 311 on Cascadia margin, northeastern Pacific. X axis:  $\delta^{34}\text{S}$  (CDT); Y axis: depth mbsf (meter below sea floor).

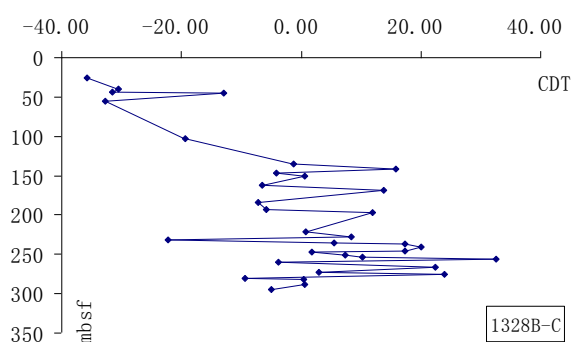


Fig.4 Sulfur isotopic values of authigenic pyrites from the recovered sediments in site U1328 increase gradually with depth, probably indicative of much remained sulfates after early AOM were reused by the later AOM. X axis:  $\delta^{34}\text{S}$  (CDT); Y axis: depth mbsf (meter below sea floor).

## CONCLUSIONS

The occurrence of authigenic pyrites separated from the recovered sediments of IODP 311 documents the reaction of anaerobic oxidation of methane (AOM) near the sulfate and methane interface (SMI) in marine sediments column. Microbial fossilized precipitation and non organic crystallization of sulfur and iron within ambient sediments would produce various kinds of pyrites aggregations including spheroid, strawberry-like, worm-like rod, dumbbell and cubic crystallized aggregations. The increasing trend of pyrite  $\delta^{34}\text{S}$  values with the depth could be caused by reusing of remained sulfate in the local sulfate pool after the early AOM. The strong positive values of pyrite  $\delta^{34}\text{S}$  with a high isotopic fractionation could be produce by the exhaustion of sulfate in the local sulfate pool within sediments column. Therefore, this research will bring a great help to understand the marine sulfur cycles and to interpret better the sulfur isotopic parameters in modern and ancient gas hydrate geological system.

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