

Graphitic carbon in the pyrite rods in the sediment of South China Sea as a mineral indicator for gas hydrates

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Gas hydrates are generally considered as a potential energy resource. Most often detected by seismic means such as BSRs and the geochemical anomalies produced by dissociation of gas hydrate.

Authigenic pyrite is the end product of the microbial sulfate reduction in the sediments, which coupled to either the oxidation of methane or the mineralization of organic material. Some chemical anomalies profiles in this site show that pyrite has the connection with methane but not organic material [1]. However, we didn't have the direct evidence.

In order to find some useful evidences from pyrite, we measured pyrite rods in the sediment of South China Sea using SEM and HRTEM. It is located at the junction of the Eurasian, the Pacific and the Indian–Australian Plates. The results show that the pyrite is framboidal. Nanocrystalline graphite occurs with the pyrite. Generally, graphite can be deposited from metamorphic organic matter or natural carbon-bearing fluids such as those containing CO₂, CO and /or CH₄. Temperature has been considered as the major factor controlling the formation of fluid-deposited graphite deposits [2, 3, 4]. However, when C-O-H fluids in the systems are supersaturated and the temperature decreases, graphite can be deposited [2, 3], following the reaction: CO₂+CH₄=2C+2H₂O. Therefore, the graphite indicates that the fluids containing CO₂ and CH₄ are saturated in the sediments from which the pyrite deposited, suggesting that there is a methane source under the site.

The finding of graphite associated with pyrite suggest that there is a gas hydrate in this site of South China Sea, and graphite can be used as a mineral indicator to detect methane sources. It also has an implication for the industrial synthesis of graphite.

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[1] Lu (2007) *Ph.D dissertation*. [2] Luque *et al.* (1998) *AGS* **298**, 471–498. [3] Luque *et al.* (2009) *Geology* **37**, 275–278. [4] Pasteris (1999) *JMG* **17**, 779–787.

Origins of hydrocarbon volatiles in the Earth's mantle rocks

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Hydrocarbon volatiles trapped in the mantle-derived rocks likely record the information about their origins. Two types of fresh mantle-derived rocks: ophiolitic peridotite from Yushigou and mantle xenolith from Damaping, China have been extracted the hydrocarbon volatiles (CH₄, C₂H₆, C₃H₈ and C₄H₁₀) trapped in the minerals by ameliorative stepped-heating method. The results showed that two volatile releasing peaks at ~ 500-600°C and 900-1000°C likely correspond to two types of fluid inclusions which were trapped at different stages of mineral growth, the late-stage fluid inclusion decrepitated at lower temperature than the early-stage one. The majority of data at low temperature falls in the range of methane oxidation in the plot of δ¹³C_{CH₄} and δ¹³C_{CO₂}, suggesting that CH₄ in the late-stage fluid inclusion mainly originates from organic matter oxidation. In contrast, CH₄ in the early-stage fluid inclusion released at high temperature with δ¹³C₁ of -25.8 to -20.8‰ suggest its possible abiogenic origin. δ¹³C_∞ values of the early-stage fluid inclusion in Damaping mantle xenolith remain constant with increasing temperature, suggesting that hydrocarbons via Fischer-Tropsch (F-T) synthesis reaction from oxidized carbon compounds reduction by molecular hydrogen occurred under a static closed system at deep earth. A reverse carbon isotopic distribution patterns among CH₄-C₄H₁₀ hydrocarbons in the early-stage inclusions further supports the formation and preservation of hydrocarbons in both subcontinental lithospheric mantle and oceanic lithospheric mantle by F-T synthesis reaction.

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