Origin, distribution and environmental significance of perylene in Okinawa Trough since last glaciation maximum

CrossMark

Xinyu Zhang [a], Yunping Xu [a,b,*], Jiaping Ruan [a], Su Ding [a], Xianyu Huang [c]

[a] MOE Key Laboratory for Earth Surface Processes, College of Urban & Environmental Sciences, Peking University, Beijing 100871, China
[b] Qingdao Collaborative Innovation Center of Marine Science and Technology, Qingdao 266003, China
[c] Department of Geography, Faculty of Earth Sciences, China University of Geosciences, Wuhan, Hubei 430074, China

A B S T R A C T

Perylene, a five-ring nuclear polycyclic aromatic hydrocarbon (PAH), has a different distribution pattern from anthropogenic PAHs. Its source, however, remains obscure, limiting its application as an environmental indicator. Here we examine perylene in the upper 85 m sediments of the ODP Hole 1202B from the southern Okinawa Trough. Over the past 20,000 years, the mass accumulation rate of perylene is substantially higher in the last deglaciation than the Holocene and last glacial maximum. Perylene presents a strong correlation with C_{31} *n*-alkane ($r = 0.55$; $p < 0.001$), a biomarker for terrigenous organic matter, and a weak correlation with $C_{37:2}$ alkenone ($r = -0.04$; $p = 0.23$), a biomarker for marine organic matter. The mean $\delta^{13}C$ value of perylene ($-22.8‰ \pm 0.6‰$) is substantially higher than that of long chain *n*-alkanes ($-30.7 \pm 0.4‰$), but close to that of fluvial organic matter in adjacent areas ($-24.0‰$ to $-25.0‰$). Our results strongly suggest that the perylene is of a terrigenous origin likely from soil fungi, and may be a useful tracer for soil organic carbon in marine environments.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have attracted intensive attention because of their toxic, carcinogenic and mutagenic properties. Like other PAHs, perylene ($C_{10}H_{12}$) is widely distributed in recent environments such as soils/peats (e.g., Wilcke et al., 2003; Gocht et al., 2007), lake sediments (e.g., Ishiwatari et al., 1980; Gschwend and Hites, 1981; Silliman et al., 1998, 2001; Itoh and Hanari, 2010; Fan et al., 2011) and marine sediments (e.g., Orr and Grady, 1967; Aizenshtat, 1973; Laflamme and Hites, 1978; Wakeham et al., 1979; Gschwend and Hites, 1981; Gschwend et al., 1983; Silliman et al., 2000; Soclo et al., 2000) as well as ancient deposits such as coal, oil and sedimentary rocks (e.g., Louda and Baker, 1984; Jiang et al., 2000; Grice et al., 2009). However, the distribution profile of perylene is distinctly different from that of other PAHs. Firstly, perylene is the dominant PAH in many pristine environments, but only a small amount (< 10% of total PAHs) in contaminated aerosols, soils and sediments (Baumard et al., 1998; Jiang et al., 2000; Silliman et al., 2000). Secondly, the perylene concentration usually increases with depth, whereas other PAHs dramatically decline in deeper sediments (Orr and Grady, 1967; Aizenshtat, 1973; Ishiwatari et al., 1980; Wakeham et al., 1980; Silliman et al., 1998; Fan et al., 2011). These facts suggest that perylene and other PAHs have different sources or environmental processes (Aizenshtat, 1973; Silliman et al., 2000; Itoh and Hanari, 2010).

Nowadays, it is generally accepted that perylene is mainly a diagenetic product derived from natural precursors (Aizenshtat, 1973; Venkatesan, 1988; Silliman et al., 1998, 2000; Itoh and Hanari, 2010). However, there is no consensus yet as to whether perylene is of a terrigenous or aquatic origin. Perylene has been found in marine sediments without significant terrigenous inputs, supporting an aquatic origin (e.g., diatoms) for perylene (Orr and Grady, 1967; Wakeham et al., 1979; Hites et al., 1980; Louda and Baker, 1984). In contrast, the occurrence of perylene in peats (e.g., Aizenshtat, 1973), soils (e.g., Gocht et al., 2007) and fungi-degraded woods (e.g., Marynowski et al., 2013) supports a terrigenous origin (e.g., Gocht et al., 2007; Itoh and Hanari, 2010; Marynowski et al., 2013).

Perylenequinone pigments are present in many fungi (Weiss et al., 1987; Krohn et al., 1999; Gao et al., 2009) and occasionally in tropical termite nests (Wilcke et al., 2002). These compounds were thought to be a precursor for perylene because of structural similarities (Louda and Baker, 1984). Based on the depth profiles and $\delta^{13}C$ values of PAHs in three Upper Triassic to Middle Jurassic

sedimentary sequences, Jiang et al. (2000) suggested that fungi were a major contributor for perylene. Itoh et al. (2012) examined the Lake Biwa sediments and catchment soils, and proposed that 4,9-dihydroxyperylene-3,10-quinone (DHPQ) from the soil fungus *Cenococcum geophilum* could be transformed into perylene under natural conditions. However, perylenequinone derivatives have been also found in some marine organisms and thus, an aquatic origin of perylene is also possible (Gao et al., 2009; Kjer et al., 2010).

In this study, we examined the upper 85 m section of the Ocean Drilling Program (ODP) Hole 1202B from the southern Okinawa Trough (OT), which was dated back to the Last Glacial Maximum (LGM). The OT is an ideal venue for studying land–ocean interaction since it receives enormous amounts of continental material from the Yangtze River and other surrounding rivers. In addition, the OT is under a strong influence of the East Asian Monsoon and Kuroshio Current, both playing important roles in hydrological cycle in the densely inhabited East Asia. Our major objectives are to (1) reconstruct variability in the mass accumulation rates of perylene, $C_{37:2}$ alkenone and long chain n-alkanes in the southern OT since the LGM; and (2) identify the source of perylene in the marine environment based on the temporal distribution patterns and stable carbon isotopic compositions of perylene and other biomarkers.

2. Materials and methods

2.1. Samples and age model

The OT is a curved backarc basin located between northwestern Pacific Ocean and southeastern East China Sea (ECS; Fig. 1). It is about 1200 km long and 100–230 km wide with the mean water depth > 1000 m (Salisbury et al., 2002). The OT is subject to the strong influence of the East Asian Monsoon and Kuroshio Current.
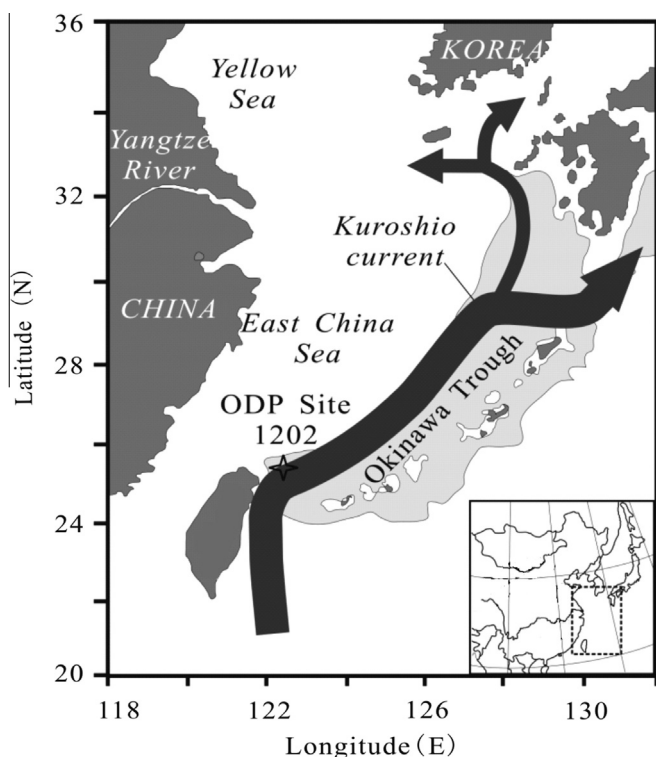

Fig. 1. Location of the ODP Site 1202 in the Okinawa Trough. Black arrows indicate the main axis of Kuroshio Current and its branches.

As the largest warm current in the northwestern Pacific, the Kuroshio Current has a depth up to 1 km and a width of 150–200 km, bringing a large volume of warm and salty water from tropical Pacific to a high latitude ocean (Salisbury et al., 2002).

The ODP Hole 1202B (24°48.24′N, 122°30′E; 1274 m water depth) was drilled during the ODP Leg 195 Expedition in 2001 (Fig. 1). The total length of the core is 140.5 m. In our study, sediments from the top 85 m were investigated. They are exclusively composed of hemipelagic mud without visible silt-sand layer. The clay mineral assemblage mainly consists of illite, chlorite and kaolinite.

The chronology was established on the basis of accelerator mass spectrometry (AMS) ^{14}C dates from Wu et al. (2012) and Wei et al. (2005) (Table 1). The raw ^{14}C dates were converted into calendar years using the CALIB program with a 400 year surface-ocean reservoir correction (Stuiver et al., 1998). The ^{14}C data showed no age reversal and that the upper 85 m of sediment spanned the past ca. 20 kyr. A linear interpolation suggested that the sedimentation rate varied from 2.2 m/kyr in the Holocene to 9.4 m/kyr in the deglaciation (Wei et al., 2005; Wu et al., 2012).

2.2. Lipid analyses

A total of 479 sediment samples were selected for lipid analyses. A detailed method has been described by Sun et al. (2011). Briefly, the sediments were freeze dried and homogenized with a mortar and pestle. About 5 g of sediments were used for lipid extractions. After addition of 3.2 μg squalane as a recovery standard, the sediments were ultrasonically extracted three times, each with 20 ml of dichloromethane:methanol (3:1 v:v) for 15 min. After centrifugation at 3000 rpm for 10 min, the supernatant liquids were concentrated by a rotary evaporator and then completely dried under a mild nitrogen stream. The dried extracts were re-dissolved in 1.0 ml hexane and separated into three fractions using a silica gel column, namely hydrocarbons (5 ml hexane: dichloromethane; 9:1 v:v), ketones (5 ml hexane:dichloromethane; 1:1 v:v) and polar compounds (5 ml dichloromethane: methanol; 1:1 v:v).

Since the coelution of perylene and C_{29} n-alkane exists on the gas chromatograph (GC), a further separation is needed to measure δ^{13}C of individual compounds. A glass column (30 cm in length, 13 mm i.d.) filled with 12 cm silica gel and 12 cm neutral Al_2O_3 was used. Hydrocarbons were separated into aliphatic hydrocarbons with 45 ml hexane and aromatic hydrocarbons with 50 ml hexane:dichloromethane (1:1 v:v). These two fractions were concentrated prior to instrumental analyses. All solvents used in our study are of the pesticide analysis grade (Dikma Corporation, Beijing, China).

2.3. Gas chromatography-mass spectrometry (GC–MS)

The identification of long chain n-alkanes (C_{25}–C_{33}), aromatic hydrocarbons and long chain alkenones were achieved on an Agilent 7890A–5975C GC–MS system. The ion source was at 250 °C and the ionization energy was 70 eV. A selected ion monitoring (SIM) mode was used with m/z 252 for perylene and m/z 85 for n-alkanes. The separation was carried out on a J&K HP-5MS column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The GC oven temperature was programmed from 60 °C (held 1 min) to 300 °C (held 20 min) at a rate of 6 °C/min. The injection volume was 1 μl in a splitless mode and injection temperature was 300 °C. Helium (> 99.999%) was the carrier gas. Data were acquired and processed with the Chemstation software. The compounds were identified by comparison of mass spectra with authentic standards and the mass library data. The perylene and long chain n-alkanes was quantified on the GC–MS using peak areas based on external