



# Perylene degradation during gradual onset of organic matter maturation



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## ABSTRACT

Perylene and benzo[a]pyrene concentration changes during the gradual increase of thermal maturity have been analyzed for the Palaeogene Podhale flysh deposits and other Palaeozoic to Cenozoic sedimentary rock samples. Perylene is present in high relative concentration in the samples of maturation below 0.6% of the vitrinite reflectance ( $R_r$ ), while in the range of 0.6%–0.7%  $R_r$  its abundance rapidly decreased. In the case of samples with vitrinite reflectance higher than 0.7%  $R_r$ , perylene compound disappeared completely. Benzo[a]pyrene is also thermally unstable at elevated temperatures and its relative concentration is very low above vitrinite reflectance values of ca. 0.9%. Such results could have important palaeoenvironmental implications. If these five-ring polycyclic aromatic hydrocarbon compounds are characterized by low to moderate thermal stability, then their use as a wood-degrading fungi tracer in the case of perylene and palaeo-wildfire indicator in the case of benzo[a]pyrene is limited only to samples of maturation below the oil window range and below the major phase of oil generation, respectively. These results explain the scarcity of perylene in Palaeozoic sedimentary rocks, which are generally of higher maturation than the younger deposits.

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## 1. Introduction

Perylene (I – see Fig. 1) is a five-ring aromatic compound identified in recent marine and terrestrial sediments as well as in brown coals, crude oils and sedimentary rocks (summary in: Grice et al., 2009). Its origin was a long time matter of debate since it was not precisely defined. Indeed, many papers dealing with its occurrence and origin pointed out that perylene can have both an aquatic and a terrestrial source without any indication of its molecular precursor(s) (e.g. Jiang et al., 2000; Silliman et al., 2000, 2001; Venkatesan, 1988). However, a detailed review of published data clearly points out that this compound is preferentially associated to terrestrial organic matter (Aichner et al., 2007; Bechtel et al., 2007; Gocht et al., 2007; Itoh and Hanari, 2010; Jiang et al., 2000; Louda and Baker, 1984; Malawska et al., 2002; Marynowski et al., 2007, 2011; Stefanova et al., 2013; Suzuki et al., 2010; Venkatesan, 1988; Yunker et al., 1999). Louda and Baker (1984), then Jiang et al. (2000), were the first to suggest a genetic association between perylene and wood-degrading fungi. Recent studies of Holocene deposits, where high concentrations of perylene were identified, have shown that they are particularly rich in fungal spores

(Grice et al., 2009). Moreover, the obtained values of carbon isotopes  $^{13}\text{C}$  for perylene were close to the measured values for wood-degrading fungi, thereby confirming the genetic correlation between them (Grice et al., op. cit.). More recently, Itoh et al. (2012) have identified the dihydroxyl derivative of perylenequinone (DHPQ; II; Fig. 1), which is present in fungi and recent sediments, as a probable precursor of this compound. Gradual thermal transformation of DHPQ, carried out by Itoh et al. (2012), led to the formation of 3,10-perylenequinone (3,10-PQ; III; Fig. 1), before those of perylene. These authors also showed that the main source of DHPQ, in recent sediments from Lake Biwa in Japan, is *Cenococcum geophilum*, the common ectomycorrhizal fungus which has a symbiotic relationship with some tree species. Lately, Marynowski et al. (2013) confirmed the affinity of perylene and wood-degrading fungi via the molecular analysis of Mesozoic and Cenozoic fossil wood samples from the southern and central part of Poland. Indeed, these authors observed a good correlation between the abundance of perylene and selected PAHs, not associated with maturity, wood taxonomy or burning (see also Bechtel et al., 2007; Bertrand et al., 2013).

With regard to these recent findings on the origin of this particular PAH, it seems that perylene could be used as a tracer for wood-degrading fungi when its abundance is especially high, taking into account the precautions inherent to the use of any novel molecular tracer. Anyway, perylene will probably gain an increasing importance in future palaeoenvironmental reconstructions using molecular markers. In this context, it is particularly important to test the influence of other parameters on the presence/abundance of its biological precursors (i.e.

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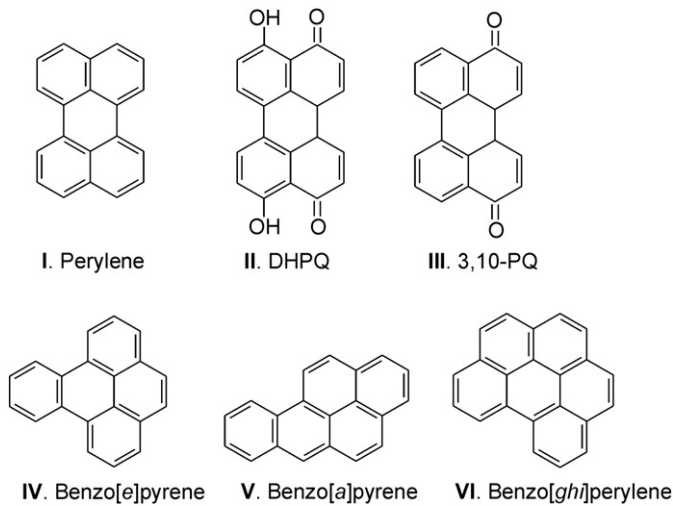


Fig. 1. Chemical structures of the aromatic compounds mentioned in the text.

wood-degrading fungi) within or close to the depositional environment. Among these other parameters, thermal maturity seems to be important since it probably influences the geosynthesis of perylene from its molecular precursors and its possible destruction by heating.

In parallel to the perylene, benzo[a]pyrene (V; Fig. 1) is another 5-ring PAH also recovered in sedimentary record. Its origin is clearly

less debated than those of the perylene since there is a consensus among the organic geochemical community. Benzo[a]pyrene, like many other non-substituted PAHs, is generated during natural biomass burning e.g. palaeo-forest wildfires, but other sources cannot be ruled out (Nabbefeld et al., 2010; Radke, 1987). However as for perylene, there is not much information on the influence of thermal overprint on the abundance and the occurrence of benzo[a]pyrene.

The lack of clear data on the thermal stability of perylene can cause confusion in the interpretation of palaeoenvironments and in the determination of the origin of organic matter when using this molecular marker. This paper fills this gap using a combination of an analytical approach on stratigraphic sections showing an increasing thermal maturation downward and an experimental approach based on the artificial maturation of a perylene/smectite mixture.

## 2. Materials and methods

### 2.1. Samples

The investigated samples were collected from cores and natural outcrops from the Podhale Trough area (south of Poland; Fig. 2). Samples from the following cores were analyzed: Chochołów IG1, Zakopane IG1, Furmanowa IG1, Bukowina Tatrzańska IG1, Bańska IG1, Poronin PAN1, Biały Dunajec PAN1 and outcrops along the streams: Mały Rogoźnik, Łapszanka, Kacwinianka and Antałowski Potok (Fig. 2). The detail bulk and molecular characteristics of the Palaeogene flysh samples were presented elsewhere (Marynowski et al., 2006; Poprawa and Marynowski, 2005; Śródoń et al., 2006). These sedimentary

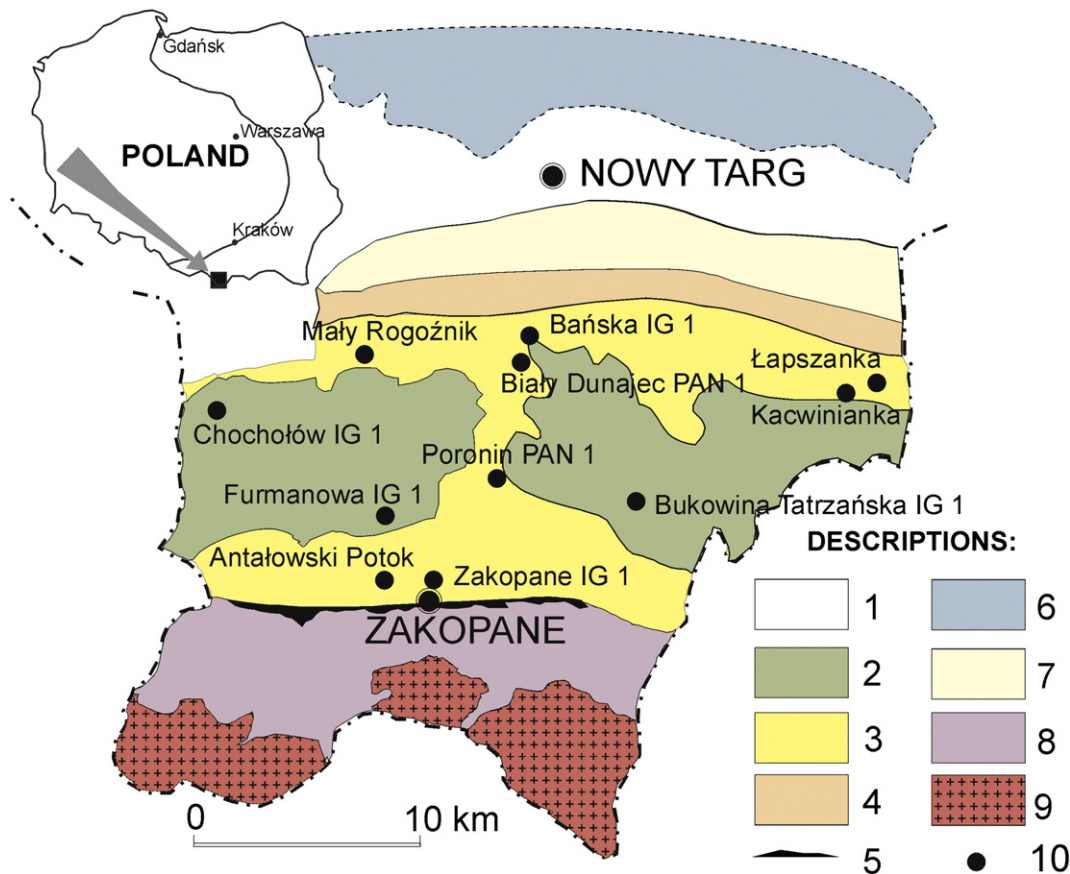


Fig. 2. Locations of sampling points. 1 – Holocene; Palaeogene, 2 – Chochołów beds, 3 – Zakopane beds, 4 – Szaflary beds, 5 – Eocene, 6 – Magura unit, 7 – Pieniny Klippen Belt, 8 – Mesozoic, 9 – Tatra crystalline rocks, 10 – cores.

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