



# Transition from melting to carbonization of naphthalene, anthracene, pyrene and coronene at high pressure



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## ABSTRACT

We have examined the decomposition of naphthalene, anthracene, pyrene and coronene at high pressures and temperatures. Experiments were performed using *in situ* X-ray diffraction in multianvil apparatus at the SPring-8 synchrotron radiation facility. In the pressure range of 1.5–3.7 GPa decomposition of studied polycyclic aromatic hydrocarbons (PAHs) was detected at 773–973 K. Melting was identified only for naphthalene at 727–730 K and 1.5 GPa. Quenched products analyzed by Raman spectroscopy consist of nano- and microcrystalline graphite. The triple points between solid, liquid and carbonized (decomposed) PAHs were placed at 1–2 GPa and 800–850 K. Analyses of *P-V-T* data indicate that anthracene and coronene possess very low thermal expansion at 1.3–4.2 GPa. The obtained melting and decomposition parameters for PAH restrict *PT*-conditions of their formation by local impacts during early planetary history, as well as provide evidences for secondary origin of PAH inclusions in natural mantle minerals from kimberlites.

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## 1. Introduction

High-pressure study of polycyclic aromatic hydrocarbons (PAHs) is important for basic organic chemistry, Earth and planetary sciences, and meteoritics. PAHs are believed to be the most abundant organic molecules in the Universe (d'Hendecourt and Ehrenfreund, 1997; Ehrenfreund and Charnley, 2000; Hudgins et al., 2005; Puget and Leger, 1989; Tielens, 2008) possibly due to electron delocalization over their carbon skeleton, which makes them remarkably stable (Ehrenfreund and Charnley, 2000).

PAHs appears in the terrestrial rocks of different genesis. PAHs were identified in pyrogenic (Nasdala and Pekov, 1993; Žáček, 1989), hydrothermal (Echigo et al., 2007; Echigo and Kimata, 2010) and metamorphic rocks (Sawada et al., 2008). In metamorphic rocks PAHs could be formed via successive heating and degradation of kerogen in the parent metapelites (Sawada et al., 2008). Moreover, PAHs have been identified as inclusions in garnet, olivine, and diamond from mantle xenoliths in kimberlite pipes

(Botkunov et al., 1985; Garanin et al., 2011; Kulakova et al., 1982; Tomilenko et al., 2016a,b). These inclusions contain naphthalene, phenanthrene, pyrene, benzopyrene, and benzoperylene (Kulakova et al., 1982).

PAHs were identified in many meteorites. For example, in carbonaceous chondrites, such as Murchison (Krishnamurthy et al., 1992; Oro et al., 1971) and in Martian meteorites (Becker et al., 1997). PAHs-bearing carbonaceous chondrites could contribute to the delivery of extraterrestrial organic prebiotic materials to the early Earth during the period of heavy bombardment of the inner Solar System bodies from 4.5 to 3.8 Ga ago. (Anders, 1989; Chyba and Sagan, 1992; Chyba et al., 1990).

Some authors suggest that PAHs can be an important component of C—O—H fluid in the deep Earth. These fluids influence most of the geologic processes in the Earth's mantle, such as mantle metasomatism, magma generation, and diamond formation (Jones et al., 2013; Litasov, 2011; Lobanov et al., 2013; Shirey et al., 2013; Sverjensky et al., 2014 b). Moreover, deep-seated fluids can significantly affect the physical properties of the mantle: viscosity, seismic wave velocities, and electrical conductivity (Dasgupta et al., 2013; Jacobsen and Smyth, 2006; Jung and Karato, 2001; Kiseeva et al., 2013; Litasov and Ohtani, 2010; Mei and Kohlstedt, 2000; Wang et al., 2006).

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Thermodynamic calculations for garnet peridotite assemblages and experimental data for enhanced  $\text{Fe}^{3+}$  incorporation into silicates show that the redox conditions in the Earth's mantle below 250–300 km depths should be controlled by the iron-wüstite buffer (Frost and McCammon, 2008). The composition of C–O–H fluid calculated based on the equations of state of simple volatile compounds (Belonoshko and Saxena, 1992; Zhang and Duan, 2009) at these conditions corresponds to mixture of  $\text{CH}_4$  and  $\text{H}_2\text{O}$  with subordinate amount of  $\text{H}_2$  and  $\text{C}_2\text{H}_6$ . However, some theoretical calculations of equations of state for a wider range of hydrocarbons indicate possible stability of higher alkanes, alkenes, and PAHs in the deep mantle (Chekalyuk, 1967; Spanu et al., 2011; Zubkov, 2009). Recent theoretical estimations based on the Deep Earth Water (DEW) model (Sverjensky et al., 2014a) for calculating the standard Gibbs energy of aqueous species at high pressures suggested that dissolved ionic carbon can also play an important role in the upper mantle fluids (Sverjensky et al., 2014 b).

Many investigations have been devoted to the study of PAHs at ambient pressure and high temperature. Melting temperature at normal pressure conditions was defined in the range of 353–711 K for a large number of PAH from naphthalene  $\text{C}_{10}\text{H}_8$  to coronene  $\text{C}_{24}\text{H}_{12}$  (Lide and Haynes, 2009). These data indicate that heavier PAHs have generally higher melting temperature at ambient pressure (Table 1). Thermal carbonization of different PAH melts at atmospheric pressure was defined at 823–873 K (Table 1) (Johns et al., 1962; Mochida et al., 1981; Scaroni et al., 1991; Talyzin et al., 2011). Solid and molten PAHs are subjected to various modifications at high temperatures, including polymerizations, polycondensations, cracking reactions, molecular rearrangement, hydrogen transfers, etc.

Pressure effect on the behavior of many organic compounds has been also intensively studied during recent years. Pressure-induced oligomerization at room temperature was found for benzene (Fitzgibbons et al., 2015; Shinozaki et al., 2014), propene (Mugnai et al., 2004 b), butadiene (Mugnai et al., 2004a), glycine (Sugahara and Mimura, 2014) and alanine (Fujimoto et al., 2015; Ohara et al., 2007). Benzene oligomerization was explained by the overlapping of  $\pi$  bonds and decrease of the intermolecular distances (Ciabini et al., 2006; Shinozaki et al., 2014). Significant oligomerization of PAHs was observed from recovered samples after multi-anvil experiments at 7 GPa and 773–873 K (Chanyshv et al., 2015a).

The melting curves of PAHs were determined for naphthalene and benzophenone at pressures up to 3 GPa using differential thermal analysis (Akella and Kennedy, 1970). However, an important feature of PAH behavior at high pressure is a direct transition from solid state to dissociated carbon aggregates. The limited temperature stability of PAHs at pressures of 7–15.5 GPa was suggested from recent experiments by Davydov et al. (2004) and Chanyshv et al. (2015a,b). Shock-wave experiments have revealed the PAHs oligomerization and polycondensation at high pressure up to 30 GPa and estimated shock temperatures of 500–1660 K (Mimura and Toyama, 2005; Mimura et al., 2005).

The structural response of PAHs to high pressures has been intensively studied for the last 70 years. The structure of the ambient pressure phase of naphthalene, monoclinic, space group  $P2_1/a$ , first determined by (Abrahams et al., 1949), is stable at least to 13 GPa (Likhacheva et al., 2014). Similarly, monoclinic anthracene structure,  $P2_1/a$  (Mathieson et al., 1950) is stable to 22.6 GPa (Oehzelt et al., 2003). Pyrene exhibits two structures at ambient pressures, a stable form (I) and a metastable form (II), both crystallizing in space group  $P2_1/a$ . The crystal structure of pyrene form (I) was initially defined by (Robertson and White, 1947). Phase transition pyrene-I to pyrene-II occurs at 110 K (Jones et al., 1978). High-pressure study of pyrene pointed towards a phase transition at 0.3 GPa and 298 K (Fabbiani et al., 2006). The structure of high-pressure polymorph of pyrene-III was defined as  $P2_1/a$  (Fabbiani et al., 2006). Coronene ambient pressure phase possesses monoclinic symmetry with a  $P2_1/a$  space group (Fawcett and Trotter, 1966; Robertson and White, 1945). It undergoes a phase transitions at 1.5 GPa and 12.2 GPa at 298 K. High-pressure phases were identified as monoclinic and orthorhombic crystal structures with space groups of  $P2/m$  and  $Pmmm$ , respectively (Zhao et al., 2013).

Here we aimed to determine triple points between solid, liquid and decomposed PAHs, for naphthalene ( $\text{C}_{10}\text{H}_8$ ), anthracene ( $\text{C}_{14}\text{H}_{10}$ ), pyrene ( $\text{C}_{16}\text{H}_{10}$ ), and coronene ( $\text{C}_{24}\text{H}_{12}$ ) in the experiments at 1.5–3.7 GPa using *in situ* X-ray diffraction enhanced by synchrotron radiation. Combined with previous data at 7–10 GPa and melting data at ambient pressures these data provide further constraints on the PAH phase diagrams and their systematics at high pressures.

## 2. Experiments and analyses

Experiments were carried out on PAHs from naphthalene ( $\text{C}_{10}\text{H}_8$ ) to coronene ( $\text{C}_{24}\text{H}_{12}$ ) with 99.9% purity produced by Wako Co Ltd. or Alfa Aesar. High-pressure experiments were conducted using a Kawai-type 1500-tons multianvil apparatus installed at a bending magnet beamline BL04B1 at the SPring-8 synchrotron radiation facility (Hyogo prefecture, Japan). This apparatus is equipped by an energy dispersive X-ray diffraction system with a Ge solid state detector and a CCD camera for radiographic imaging of the sample. Decomposition parameters of studied PAHs were obtained by *in-situ* X-ray diffraction measurements. The incident X-ray collimated to dimensions of 50  $\mu\text{m}$  horizontally and 200  $\mu\text{m}$  vertically was directed at the sample through the gaps between the second stage anvils. A Ge solid state detector (SSD) with a 4096-channel analyzer was used. The SSD analyzer was calibrated using the X-ray fluorescence lines of different metals before the measurements. The diffraction angle ( $2\theta$ ) was calibrated before each experiment with precision of  $0.0001^\circ$ , using  $\text{MgO}$  as the standard.

WC anvils with a truncated edge length (TEL) of 12.0 mm were used. Experimental cell contained  $\text{ZrO}_2$  pressure medium, cylindrical graphite heater, BN sample capsule, and Mo electrodes (Fig. 1) (Litasov et al., 2013; Shatskiy et al., 2011, 2013). Each charge

**Table 1**  
Melting ( $T_m$ ), boiling ( $T_b$ ), and carbonization ( $T_{\text{carb}}$ ) temperatures and crystal structure of studied PAHs at ambient conditions and vapor/liquid critical temperature ( $T_c$ ) and pressure ( $P_c$ ).

|   | $T_m$ , K | $T_b$ , K | $T_c$ , K | $P_c$ , MPa | $T_{\text{carb}}$ , K      | Space group                        |
|---|-----------|-----------|-----------|-------------|----------------------------|------------------------------------|
| Naphthalene $\text{C}_{10}\text{H}_8$   | 353       | 491       | 748       | 4.05        | 843 (Johns et al., 1962)   | $P2_1/a$ (Alt and Kalus, 1982)     |
| Anthracene $\text{C}_{14}\text{H}_{10}$ | 491       | 613       | 869       | 2.87        | 873 (Scaroni et al., 1991) | $P2_1/c$ (Hofer and Peebles, 1951) |
| Pyrene $\text{C}_{16}\text{H}_{10}$     | 420       | 677       | –         | –           | 873 (Mochida et al., 1981) | $P2_1/a$ (№ 00-024-1855)           |
| Coronene $\text{C}_{24}\text{H}_{12}$   | 711       | 798       | –         | –           | 873 (Talyzin et al., 2011) | $P2_1/a$ (Echigo et al., 2007)     |

Melting ( $T_m$ ) and boiling ( $T_b$ ) temperatures at 0.1 MPa for studied PAHs are from Lide and Haynes (2009). Vapor/liquid critical temperatures and pressures for studied PAHs are from (Poling et al., 2001).

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