

## Temperature stability of polycyclic aromatic hydrocarbons at pressures of 6-20 GPa

Artem Chanyshv<sup>2</sup>, LITASOV, Konstantin<sup>1\*</sup>, SHATSKIY, Anton<sup>1</sup>, OHTANI, Eiji<sup>1</sup>

<sup>1</sup>Dept. Earth Planet. Mater. Sci., Graduate School of Science, Tohoku University, Sendai, <sup>2</sup>V.S. Sobolev Institute of Geology and Mineralogy, Novosibirsk, Russia

The origin of various deep-seated hydrocarbons was widely discussed in relation to the nature of C-O-H fluid. The estimation of  $fO_2$  conditions in the deep mantle indicate that it can be in equilibrium with reduced fluids and absolute values of  $fO_2$  in mantle rocks can be fluctuated near that for the iron-wustite buffer at the depth below 300 km. Calculations of fluid compositions at these conditions in the simple C-O-H system indicate the dominant CH<sub>4</sub>-H<sub>2</sub>O mixture, with subordinate H<sub>2</sub>, and heavier hydrocarbons. However, some theoretical calculations of equations of state for a range of hydrocarbons indicate their possible increased stability in the deep mantle. According to estimations of Chekalyuk (1967) and Zubkov (2001) some heavy alkanes, alkenes, polycyclic aromatic hydrocarbons (PAH), as well as some C-H-N and C-H-S compounds can become stable in the mantle fluids at the depths of 300-600 km and deeper. These components were found in natural samples - inclusions in deep diamonds and garnets, meteorites, as well as detected in the other planets and satellites and interstellar matters. The most stable hydrocarbons include PAHs, such as naphthalene, phenanthrene, pyrene, etc.

Experimental studies of reduced volatile species, such as hydrocarbons, and their phase relations with mantle silicates are extremely challenging and difficult. To date we have several important contributions from experimental petrology. Composition of C-O-H fluids under controlling oxygen fugacity was measured in samples quenched after piston-cylinder and multianvil experiments (Taylor and Green, 1990; Sokol et al., 2009). They reveal CH<sub>4</sub>- and H<sub>2</sub>-bearing compositions with subordinate H<sub>2</sub>O at 3-6 GPa and 1200-1600°C. Direct observation of methane formation from carbonate and methane dissociation to heavy alkanes was demonstrated in the diamond anvil cell experiments at 5-10 GPa (Scott et al., 2004; Kolesnikov et al., 2009).

We studied temperature stability and decomposition products of a range of PAHs at pressures up to 20 GPa using multianvil high-pressure apparatus and in situ X-ray diffraction at SPring-8. We successfully observed X-ray diffraction patterns of PAHs at high pressure. Disappearance of diffraction lines of PAHs was used as a detection of their decomposition. The decomposition of several PAH, ranging in atomic mass from naphthalene to pyrene and coronene was observed at 550-700°C and 6-9 GPa. Naphthalene and coronene were studied at 15 and 20 GPa and show increasing temperature stability up to about 1000°C. Our data clearly show that PAHs cannot be stable at the average PT-conditions of the upper mantle. Thus, PAHs observed as inclusions in mantle diamond and garnet (e.g. Garanin et al., 2011) must have a secondary origin and formed from lighter hydrocarbons by hydrogen loss with decreasing temperature and pressure.

Keywords: mantle, fluid, hydrocarbon, oxidation state