

Evolutionary characteristics of aromatics under high pressure and temperature of deep lithosphere

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Pyrolysis of lignite in closed systems was conducted at temperatures from 400 to 700°C and pressure from 1 to 3 GPa in order to investigate the evolutionary characteristics of aromatics and the effects of pressure and temperature on the maturation of organic matter under the extreme conditions. The total yield of liquid hydrocarbons decreased with increasing pressure and the aromatics shows more mature with increasing temperature at a given pressure. The data indicate that high pressure significantly suppresses the thermal evolution of geological organic matter especially at lower temperature, but favors the cyclization, polymerization and aromatization of pyrolysate. The pressure effect on maturation of organic matter is nonlinear. Therefore, it can be inferred that sediment organic-matters in the subducted slab could be retained in the deep lithosphere, and the results are also significant for understanding the accumulation and preservation of petroleum in deep reservoirs.

high pressure and high temperature, lignite, aromatic hydrocarbon, maturation, isomerization, petroleum in deep reservoirs

More than 180 overpressure basins have been discovered in the world at present. Overpressure not only affects the assessment of oil and gas resources in the superpressure basins, but also closely relates to the accumulation and preservation of petroleum in deep reservoirs^[1]. Three conflicting opinions have been proposed based on the experiments about pressure effect on evolution of organic matter: (1) increasing pressure has no detectable effect on organic-matter maturation; (2) increasing pressure enhances the hydrocarbon thermal destruction; and (3) increasing pressure significantly retards the maturation of organic matter and hydrocarbon generation^[2,3]. Some hydrocarbons and organic matters have been found in mantle and meteorite. However, their source and stability are still ambiguous^[4,5]. The mantle fluids in the supercritical state, enriched in H₂ and heat energy, are important carrier transporting matter and energy in the earth's interior and provide the ample hydrogen and heat energy for hydrocarbon generation^[6].

Aromatic hydrocarbon is more complex and stable, which could be widely used in many research aspects, such as oil-source rock correlation, thermal maturities of source rocks and oils, sedimentary environment and primary migration^[7]. Aromatic hydrocarbons display more effective objects for tracing maturation evaluation because they have much wider extension of chemical kinetics for maturity parameters than that of terpanes and steranes. However, the correlative research at high pressure is still in the early stage. In this paper, the geochemical characteristics of aromatic hydrocarbons produced by pyrolysis of lignite under the conditions of 400–700°C and 1–3 GPa (equivalent to about 30–100 km deep in lithosphere) are reported, and the gen-

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eration, preservation and evolution of organic matter are also discussed.

1 Samples and analysis methods

Lignite samples were collected from the Eogene coal-bearing strata in the Nanning Basin, Guangxi Zhuang Autonomous Region, China. The total organic carbon (TOC) of the sample is 26.32%. Microscopic analyses showed that the lignite typically contains about 77% huminite, 1.6% inertinite, 18% clay minerals, 2% quartz and 1.4% others^[8].

High temperature and pressure (HPT) pyrolysis was conducted with a YT-3000t press in a closed system at temperatures of 400, 500, 600, and 700°C and pressures of 1 and 3 GPa for 120 min. The detailed experimental procedure was described by Du et al.^[8]. The extraction, fractionation and analysis with gas chromatography-mass spectrometry (GC/MS) were performed at Lanzhou Institute of Geology, Chinese Academy of Sciences. The solvent-extracted for 48 h fractions of pyrolysates were separated on silica gel/alumina column chromatograph, and saturated, aromatic hydrocarbons, nonhydrocarbon and asphaltene were eluted. Then the aromatics hydrocarbons were analyzed on a Hewlett-Packard 6890 gas chromatograph interfaced with a

Hewlett-Packard 5973 mass-selective detector made by Agilent^[8,9].

2 Results and discussion

2.1 Variation in yield of chloroform bitumen "A" and its fractions

The chemical analysis of liquid hydrocarbons shows clearly variation tendencies (Table 1): (1) Nonhydrocarbons and asphaltenes (Non+Asp) > saturated hydrocarbons (Sat) > aromatic hydrocarbons (Aro); and (2) yields of chloroform bitumen "A" during pyrolysis of the brown coal range from 11.5 to 22.6 mg/g TOC, and the peak value of chloroform bitumen "A" increases from 400°C (1 GPa) to 600°C (3 GPa), which suggests that high pressure induces a drastic decrease of the liquid hydrocarbon yield and shifts its maximum to higher pyrolysis temperature. The results are quite different from the data reported by Xia^[10], the yield of liquid pyrolysate at normal pressure reached the maximum at 350°C and strongly decreased by 0.3 mg/g TOC at 600°C. The Sat and Aro yields show an increasing trend with increasing temperature except that of Sat at 700°C, indicating that high pressure is unfavourable for decomposing liquid hydrocarbon into gaseous products. In addition, the ratios of saturated hydrocarbon over aro-

Table 1 Variation in yield of chloroform bitumen "A" and its fractions and parameters of aromatic hydrocarbon at different temperatures and pressures

| | Sample | T (°C) | | 400 | | 500 | | 600 | | 700 | | 1 ^{b)} |
|--------------------------------------|------------------|---------|------|------|------|------|------|------|------|------|------|-----------------|
| | | P (GPa) | | 1 | 3 | 1 | 3 | 1 | 3 | 1 | 3 | |
| Chloroform bitumen "A" ^{a)} | Fractions | "A" | 19.0 | 22.6 | 18.5 | 14.8 | 22.0 | 16.1 | 24.0 | 18.5 | 11.5 | 18.8 |
| | | Sat | 2.2 | 2.8 | 2.9 | 2.9 | 3.9 | 4.2 | 5.9 | 3.4 | 2.3 | 3.6 |
| | | Aro | 1.4 | 1.2 | 2.4 | 1.5 | 3.9 | 2.2 | 3.7 | 4.5 | 4.6 | 4.8 |
| | | Sat/Aro | 1.6 | 2.3 | 1.2 | 1.9 | 1.0 | 1.9 | 1.6 | 0.8 | 0.5 | 0.8 |
| Naphthalenes | MNR | | 1.8 | 1.5 | 3.4 | 1.0 | 2.5 | 0.8 | 1.1 | 1.0 | 1.4 | 1.1 |
| | TeMN/TMN | | 0.4 | 20 | 13.7 | 7.3 | 2.6 | 0.9 | 1.8 | 1.3 | 1.4 | 1.3 |
| | 1,2,5-/1,3,6-TMN | | 0.4 | 0.7 | 1.6 | 2.6 | 1.4 | 2.5 | 1.3 | 3.1 | 0.7 | 2.9 |
| Phenanthrenes | MPI-1 | | 0.13 | 0.27 | 0.38 | 0.27 | 0.65 | 0.48 | 0.68 | 0.65 | 0.88 | 0.63 |
| | MPI-2 | | 1.64 | 1.54 | 1.02 | 1.85 | 1.73 | 1.54 | 1.76 | 1.37 | 1.95 | 1.34 |
| | MPI-3 | | 1.00 | 0.86 | 0.58 | 1.08 | 1.04 | 0.86 | 1.09 | 0.82 | 1.15 | 1.12 |
| | MPR | | 1.50 | 1.38 | 1.13 | 1.60 | 1.18 | 1.06 | 1.29 | 0.96 | 1.30 | 1.00 |
| | MP/P | | 0.34 | 0.44 | 1.27 | 0.42 | 1.41 | 1.08 | 1.53 | 2.14 | 2.25 | 2.06 |
| | Rc (%) | | 0.48 | 0.56 | 0.63 | 0.57 | 0.79 | 0.69 | 0.81 | 0.79 | 0.93 | 0.78 |
| Perylene | PER/ BFL | | 110 | 40.7 | 120 | 4.6 | 12.0 | 15.8 | 0.1 | 7.4 | 0.2 | 7.6 |
| | PER/B(e)PY | | 110 | 58.1 | 100 | 3.8 | 19.4 | 25 | 0.3 | 25.8 | 0.2 | 24.9 |

a) Data of yield of chloroform bitumen "A" and its fractions cited from Wang et al.^[9]; b) data of repeated experiments (700°C, 1 GPa). MN (methyl-naphthalene), TMN (Trimethylnaphthalene), TeMN (Tetramethylnaphthalene); P (phenanthrene), MP (methylphenanthrene); PER (perylene), BFL (benzofluranthene), B(e)PY (benzo[e]pyrene). MNR=β-MN/α-MN; MPI-1=1.5(3-MP+2-MP)/(P+9-MP+1-MP); Rc=0.6MPI₁+0.40; MPI-2=3(2-MP)/(P+9-MP+1-MP); MPI-3=(3-MP+2-MP)/(9-MP+1-MP); MPR=2-MP/1-MP.

matic hydrocarbon (S/A) show a decreasing trend with increasing temperature and pressure as a whole (Table 1), suggesting that pressure favors the cyclization, polymerization and aromatization of pyrolysate.

2.2 Evolutive characteristics of aromatic hydrocarbon

Various groups of aromatic compounds and their alkylated analogue, such as naphthalene, phenanthrene, fluorene, dibenzofuran, dibenzothiophene, fluoranthene, perylene, benzopyrene and biphenyl are detected in the TICs of aromatic fraction, indicating that the source rock is considered to be predominantly derived from terrigenous high plant. To provide information on maturity and source, some molecular parameters based on the distribution of naphthalene, phenanthrene, perylene and fluorine have been evaluated in detail.

(i) Distribution of naphthalenes. Identification of MN, DMN, TMN and TeMN associated with the type of organic matter and depositional environment was based on mass chromatography (m/z 142, 156, 170 and 184) and tentative assignments based on GC retention data. The methylnaphthalene ratio (MNR) (Table 1) decreases with temperature increasing from 400 to 600°C for the retarding of pressure, but shows a reverse trend at 700°C. MNR is larger at 3 GPa than at 1 GPa at the same temperature (Figure 1(a)). The alkylnaphthalenes show obvious demethylation with temperature increasing, the ratios of tetramethylnaphthalene to trimethylnaphthalene (TeMN/TMN) decrease with temperature increasing as a whole. TeMN/TMN ratios are clearly higher at 1 GPa than at 3 GPa at 400 and 500°C, but become similar at 600 and 700°C (Figure 1(b)). 1,3,6-($\alpha\beta$)-TMN and 1,3,7-($\alpha\beta$)-TMN derived from methyl rearrangement of 1,2,5-($\alpha\beta\alpha$)-TMN and 1,2,7-($\alpha\beta\alpha$)-TMN during thermal evolution, respectively, the values of which decrease with increasing maturation^[11,12]. The values of 1,2,5-TMN to 1,3,6-TMN (1,2,5-/1,3,6-TMN) of the

pyrolysate range from 0.70 to 3.10 at 1–3 GPa, showing an increasing tendency with temperature increasing from 400 to 700°C at 1 GPa, but decreasing one at 3 GPa (Figure 1(c)). This indicates that high pressure has hindered the methyl rearrangement of alkylnaphthalene. At 400°C, the ratio of 1,2,5-/1,3,6-TMN is larger at 3 GPa than at 1 GPa, which is probably due to the cracking and degradation of macromolecule asphaltene and fringe hydrocarbons of kerogen.

(ii) Distribution of phenanthrenes. Phenanthrene and its alkylated analogues are the most abundant series of aromatic compounds in the experimental samples. Detected compound accompanied with phenanthrene, is anthracene that is considered as a typical biomarker of organic matter in coal-bearing system or coal-genetic oil^[13]. The methylation, rearrangement and demethylation of phenanthrene are mainly controlled by thermodynamics. The less thermally stable α -substituted isomers shift towards more thermally stable β -substituted isomers; on the other hand, the cracking reactions of C-C bonds between substituent and benzene rings take place^[14].

All ratios of the methyl-substituted aromatics to their corresponding non-substituted aromatics increase at first and then decrease with the increasing maturation during the evolution of ingredient^[15]. Methylphenanthrene index (MPI) (Table 1) increases with maturation ($R_o < 1.5\%$) and follows a decreasing one^[16], which is probably because the demethylation predominates in the high maturation stage and the methylation and rearrangement do in the low thermal maturation stage^[17]. However, the MP/P ratios of the experimental products show an increasing trend with temperature and pressure increasing (Table 1), which suggests that increasing pressure significantly retards demethylation of methylphenanthrene, but accelerates the methylation of phenanthrene. MPI-1 is contributed by the assumptions of 2-MP and 3-MP derived from 1-MP and 9-MP by rearrangement and

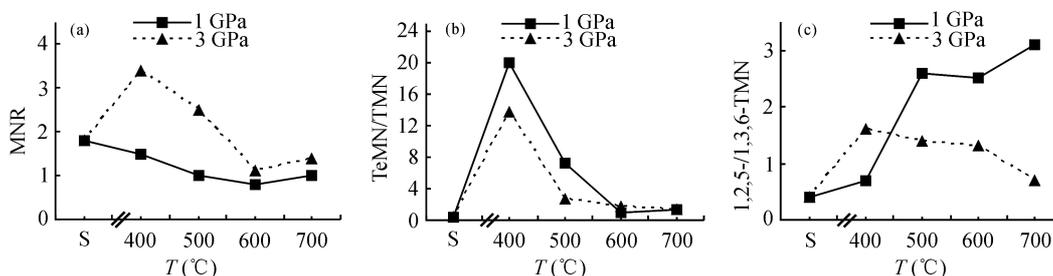


Figure 1 Parameters of naphthalene with temperature and pressure (S stands for the original sample).

from reactions of phenanthrene through methylation. Since the thermal stability of 9- and 1-substituent group of α -isomer is weaker than 3- and 2-substituent group of β -isomer, the methyl rearrangement results in the faster decomposition of 9- and 1-methyl group of α -isomer and the slower decomposition of 3- and 2-methyl group, which induce increasing MPI-1. At the given temperature, MPI-1 values at 3 GPa are larger than those at 1 GPa (Figure 2(a)). The alternative values of vitrinite reflectance (R_c) calculated by MPI-1 are the same as MPI-1 (Table 1). Our data demonstrate that the thermal evolution of geological organic matter is enhanced by the increase of temperature; and increasing pressure not only accelerates the rearrangement of MP, but also hinders its demethylation. However, values of MPI-2, MPI-3 and MPR (methylphenanthrene ratio) do not show regular trends (Figure 2(a)), suggesting that MPI-2, MPI-3 and MPR are affected by other unknown factors, MPI-1 is a better index of thermal maturation.

(iii) Distributions of perylene, benzofluoranthene and benzopyrene. The ratios of both perylene to benzofluoranthene (PER/BFL) and perylene to benzo[e]pyrene (PER/B(e)PY) (Table 1) are proposed as the very effective indexes of thermal maturity^[12,17]. With increasing pressure, temperature from 400 to 500°C, both ratios decrease sharply, and then vary to a small extent until 700°C. The values of the two indexes for the experimental products, at >400°C and 1 and 3 GPa, are much smaller than those for the original lignite (Figure 2(b), (c)). This can be explained by the facts that perylene is derived from biologic precursor during organic evolution, the relative contents of perylene in low mature sample are lower and benzofluoranthene, benzopyrene are mainly generated from cyclization and aromatization at the high mature stage^[12]. Therefore, the decrease of PER/BFL, PER/B(e)PY with temperature increasing indicates that the hydrocarbon becomes more

mature with increasing temperature at a given pressure. At 400 and 500°C, the values of the two indexes at 3 GPa are larger than those at 1 GPa, indicating that high pressures considerably hindered the thermal evolution of organic matter. The similar phenomena were observed by Jiang et al.^[18,19].

Taking account of various activating energy, productivity and bulking effect, the different influence of high pressure on the constituents of pyrolysate and reaction mechanism leads to the differential retardation of various thermal maturation and maturity parameters. Considerable amounts of liquid hydrocarbons with the carbon number up to C₃₅ and the isoprenoid hydrocarbon, with relatively low thermal stability, were found at 3 GPa and 700°C, which is considered extinct exceeding the “dead line” for liquid hydrocarbon. Isomerizations at the C-22 position in hopane and at the C-20 in regular sterane have not reached the typical end-point value even at 700°C^[9,19]. The transformation of aromatics is very complicated during the maturation of organic matter, including aromatization of alkane and cyclanes, cracking and condensing reactions of aromatic hydrocarbons. Aromatic hydrocarbons may crack and demethylate alone with continuously elevated temperature at lower temperature and pressure while hydrocarbons may be converted to alkene and dialkene by strong dehydrogenation, and then converted to condensed aromatics by aggregation and cyclization at higher temperature and pressure. With temperature and pressure increasing, β -substituted isomers become more abundant than α -substituted isomers for alkylnaphthalene; and 9-MP and 1-MP are more abundant; whereas the relative contents of 3-MP and 2-MP are less. It is well known that α -substituted isomers of polynuclear aromatic systems are sterically hindered to a greater extent than the β -substituted isomers and thermodynamically less stable. The α -isomers are more abundant than β -isomers in the

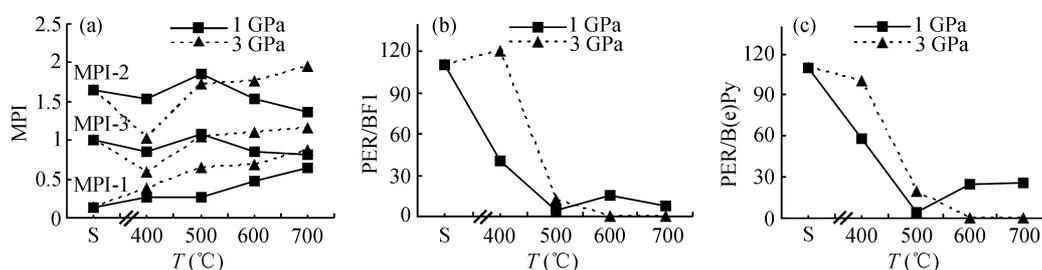


Figure 2 MPI, perylene/benzofluoranthene and perylene/benzo[e]pyrene with temperature and pressure.

early evolution of organic matter, but inverse during the later diagenesis stage. This conversion may be accelerated by pressure in some degree.

Temperature and pressure are recognized as two important interactional and interinhibitive parameters in a confined system with some complicated effects on the maturation of organic and hydrocarbon generation. Increasing temperature is believed to contribute to the transformation of organic matter into oils, strongly inducing the pressure increasing in a confined pyrolysis system; thus highly increasing collisional probability among hydrocarbon molecules in such a high pressure system. However, some heat energy will be consumed in order to overbear pressure, resulting in the maturation of organic compounds out of proportion to buried depth, and lowering strongly the total yield of gas and enhancing the yield of oils. The effect of pressure on the generation and cracking lies in restraint on volume expansion, while that on the maturation lies in demethylation and dehydrogenized aromatization^[3,20]. Water plays an important role in the evolution of organic matter and hydrocarbon generation by exchange reactions of hydrogen and oxygen with organic matter. Supercritical water ($T_c = 374^\circ\text{C}$, $P_c = 22.1\text{ MPa}$) with strong dissolubility can decrease activating energy and reduce reaction temperature, thus speeding up pyrolysis reactions of organic compounds.

3 Conclusions

Increasing temperature and pressure significantly affects organic matter metamorphism, resulting in the reduction of the S/A ratio and more abundant alkylphenanthene than phenanthrene. The mature parameters, such as MNR and MPI-1, are directly proportional to temperature, but inversely proportional to pressure. The experiments indicate that: (1) at a given pressure, organic matter maturity increases with temperature increasing; (2) increasing pressure significantly controls all aspects of organic matter metamorphism, including hydrocarbon generation, maturation and thermal destruction, especially at lower temperature. Increasing pressure hinders the thermal destruction of liquid hydrocarbon, but favours cyclization, aggregation, aromatization and rearrangement reactions of pyrolysate; and (3) high pressure affects nonlinearly the maturity of organic matter. Considerable amounts of liquid hydrocarbons with the carbon number up to C_{35} are found at 3 GPa and 700°C that exceed the upper threshold named “dead line” for liquid petroleum. This indicates that sedimental organic matter brought by the subducted slab can remain in deep lithosphere. The results are significant for highlighting the accumulation, pooling and the exploration of natural gas in the high temperature and pressure areas.

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