Evidences for occluded hydrocarbon transfer with geomacromolecule evolution

B. Cheng[1], J. Zhao[2], C. Yang[2], Y. Tian[1], Z. Liao[1,*]
[1]*Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China*
[2] *Guangzhou Marine Geological Survey, Guangzhou, China*
(corresponding author: liaozw@gig.ac.cn)*

Inside geomacromolecule structures, such as kerogen, asphaltene, and solid bitumen, other compounds can be adsorbed and occluded as noncovalently bonded moieties. Compared with the adsorbed components present at the periphery of macromolecule, the occluded ones at the core portion of the macromolecule can be well preserved by the macromolecular structure and may retain the primary organic geochemical information.

During the general processes of oil and gas generation and evolution, kerogen can be degraded and produce oil (asphaltene), and oil (asphaltene) can be degraded and evolve into solid bitumen, showing a close origination relationship between later forming geomacromolecule and the early one. The occluded hydrocarbons inside geomacromolecules will be transferred steadily through the carrier of macromolecule fragments during the evolution process of kerogen → asphaltene → solid bitumen. There are some evidences based on the geomacromolecule structure properties, sources, and stable carbon isotope characteristics of the occluded hydrocarbons from recent studies to support this view, with details as follow: (1) Asphaltene is derived from kerogen, and can be treated as the soluble fragment of kerogen in crude oils, while solid bitumen is mainly evolved from crude oil (containing asphaltene) and enriches asphaltene components. (2) The three geomacromolecules all can accommodate some small molecules noncovalent bonding in their macromolecule skeleton because they have similar microporous structural units. (3) Plenty of common biomarkers, such as *n*-alkanes, terpanes, steranes, and so on, which were closely associated with their parent biomass, were detected inside the geomacromolecule structure. (4) Many unusual compounds, which were closely associated with traditional biomarkers, were only detected from the occluded fraction of solid bitumen and asphaltenes, such as bicyclic terpenoid sulfides, tricyclic terpenes, hopenes, and *n*-alk-1-enes. The formation of those components was impossible later than their host geomacromolecules (asphaltene or solid bitumen). (5) The stable carbon isotopes of the organic fractions and individual hydrocarbons occluded inside the asphaltene structure were generally heavier than that of the adsorbed or free fraction. (6) A simulated experiment was carried out by using one low matured asphaltene and the target compound of deuterated paraffin *n*-$C_{20}D_{42}$ under a high pressure of 20 MPa and varying temperatures of 240 °C, 270 °C, and 290 °C (Zhao et al., 2012). The organic residue from asphaltene thermal degradation can be regarded as solid bitumen in the sense that asphaltene finally evolves into solid bitumen in theory. In that case, the detected *n*-alkanes trapped inside the residue after thermal degradation must be from the occluded fractions of the raw asphaltene.

Figure 1 is a model showing the occluded components of the geomacromolecules evolution process from kerogen → asphaltene → solid bitumen. There are many occluded molecules filling in the microporous structural units of the raw kerogen. When the kerogen skeleton is cracked and generates big soluble fragment (e.g. cracking along the blue dotted line on the Figure 1 (a), the soluble fragment or the predecessor of asphaltene broken down from kerogen will carry some occluded molecules. As the primary or early components, this portion of occluded molecules will finally be preserved inside the asphaltene or solid bitumen with the evolution of fragment → asphaltene → solid bitumen.

The later forming geomacromolecules inherit the occluded components of the earlier ones according to the above discussion, but they may occlude new small molecules during their formation and evolution processes. Firstly, the asphaltene structure may have new spaces or cracks to accommodate new small molecules when it is fractured down from kerogen. Secondly, the asphaltenes are liable to flocculate in oils to form stable aggregates which also can adsorb and even occlude other small molecules (Acevedo et al., 2009) (Figure 1 (b)).

At present, the geochemical studies on the adsorption-occlusion phenomenon inside the geomacromolecule structures have made some progress, but prior studies often focused on isolating one and ignored the association with their parent or child geomacromolecules. The occluded hydrocarbons inside geomacromolecules can be transferred steadily through the carrier of macromolecule fragments during the evolution process of kerogen → asphaltene → solid bitumen.

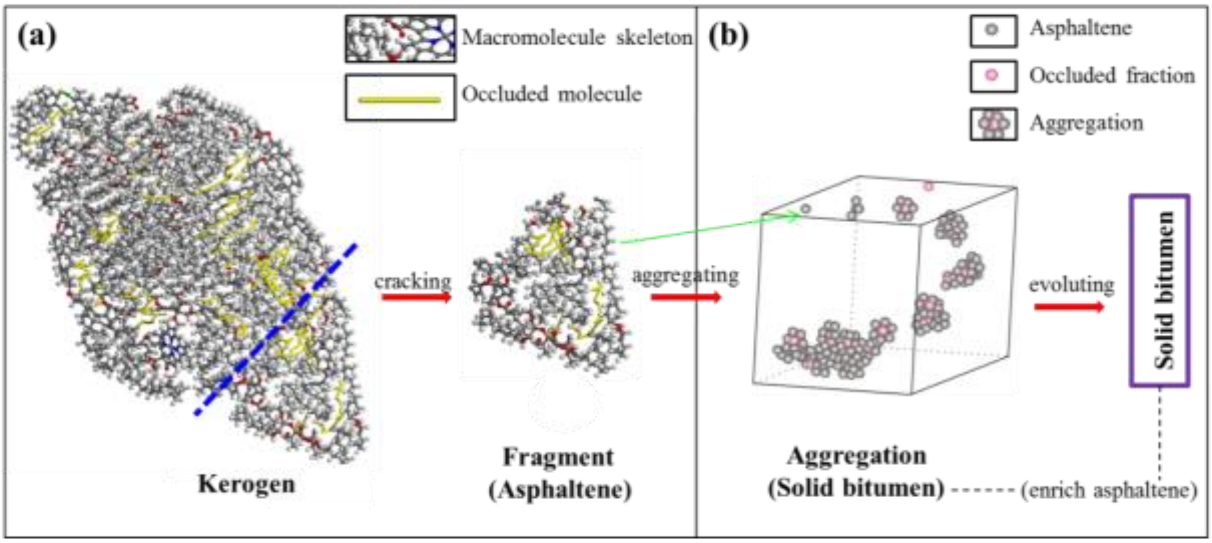

Figure 1 *Model schematic showing the primary occluded components being transferred and new ones being trapped inside geomacromolecules during the evolution of kerogen → asphaltene → solid bitumen.*

(a) The Type I-a kerogen from the Green River shale was selected to model into the 3D skeleton using software Materials Studio 7.0 in Amorphous Cell (kerogen density set as 0.95g/cm^3 for convenience). The different spheres (C-gray, H-white, O-red, N-blue, and S-yellow) connect with each other in the 3D space and represent the skeleton of the macromolecule, while the individual yellow sticks represent the occluded molecules; (b) The asphaltene aggregation was from Mercado et al. (2006), with modification.

Reference:

Acevedo, S., Cordero, T.J.M., Carrier, H., Bouyssiere, B., Lobinski, R., 2009. Trapping of paraffin and other compounds by asphaltenes detected by laser desorption ionization−time of flight mass spectrometry (LDI−TOF MS), Role of A1 and A2 asphaltene fractions in this trapping. Energy & Fuels, 23, 842–848.

Mercado, B.A., Herdes, C., Murgich, J., Muller, E.A., 2006. Mesoscopic simulation of aggregation of asphaltene and resin molecules in crude oils. Energy & Fuels, 20, 327–338.

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