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Geochemical characteristics of liquid hydrocarbons derived from humic organic matter: Insights from semi-closed system thermal simulation experiments

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The biomarker composition and stable isotopic geochemical signatures of liquid hydrocarbons (LHCs) derived from humic organic matter (HOM) provide critical insights into the provenance, maturity, and depositional environment of the organic matter. Semi-open system thermal simulation experiments were conducted on representative low-maturity humic source rocks. The resulting LHCs were quantitatively characterized, followed by separation into compound-grouped fractions and subsequent analysis by GC-MS and stable carbon and hydrogen isotopic measurements. The results show that HOM continues to generate LHCs even at high maturity; notably, the resin and asphaltene fractions constitute a substantial proportion of the total LHCs. Concurrently, the relative abundance of saturated hydrocarbons declines progressively with increasing maturity due to thermal cracking—indicating that biomarker parameters reflecting organic matter source and depositional setting retain diagnostic utility primarily during early mature stages, whereas maturity-sensitive parameters are most robust within the oil generation window. The initial biomarker assemblage—including compound classes and their relative ratios—is fundamentally controlled by the biological precursors and depositional environment. However, progressive hydrocarbon generation and subsequent secondary cracking reactions progressively alter, and in some cases obscure, the original biomarker signals. A consistent maturity response mechanism leads to uniform evolutionary trends in related parameters. Within the experimentally constrained maturity range, the $\delta^{13}C$ values of compound-grouped fractions exceed –27‰, those of n-alkanes exceed –29‰, and δD values of n-alkanes are lighter than –140‰. The average $\delta^{13}C$ values of n-alkanes initially increase and subsequently decrease with increasing maturity, primarily governed by the kinetic isotope effect as well as the cracking of polar compounds and C_{14+} aromatic hydrocarbons. Meanwhile, δD values of n-alkanes become progressively lighter due to hydrogen isotopic exchange among the aromatic structures, unsaturated cross-linked moieties in HOM, and D-depleted formation water—a process further enhanced by free-radical reactions triggered during hydrocarbon generation and LHCs cracking. Consequently, the distinct linear distribution patterns between $\delta^{13}C$ and δD values of n-alkanes can be utilized to discriminate mixed-sourced oils and provide preliminary maturity assessment. This study provides a scientific basis for the maturity assessment and source correlation of HOM-derived LHCs.