Intermediate Hydrocarbon Species Identified in Naturally Matured Marine Source Rocks by Programmed Temperature Pyrolysis with Multivariate Curve Resolution

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Abstract

Immature petroleum source rocks often contain a mixture of organic matter (OM) types that can be identified using petrographic evaluation of macerals or molecular analysis of biomarker compounds. As source rocks are thermally altered during burial, different OM types may mature and generate mobile hydrocarbon (HC) phases at different stages of catagenesis. Alternatively, they can be converted to other immobile, intermediate organic phases (e.g., solid bitumen, micrinite) that are retained within the rock matrix until further cracking leads to further generation of expelled oil and gas. Parameters from programmed temperature pyrolysis (PTP) can also indicate the presence of multiple OM types, albeit with less certainty. However, the influence of different types of OM in source rocks on petroleum generation can be more specifically evaluated and potentially quantified by analyzing PTP pyrograms using multivariate curve resolution (MCR). This approach allows for components contributing to the peaks representing free HCs (S1) and those derived from kerogen cracking (S2) to be separated and quantified. Previous work on immature source rocks from a variety of marine and lacustrine sources has shown that distributions of kerogen components are generally consistent with what has been interpreted from petrographic and biomarker analysis. In this study, results for naturally-matured marine source rocks were evaluated to determine how MCR-generated components evolve with increasing thermal maturity. Cuttings samples from the Lower Cretaceous Mowry Shale (Wind River Basin, WY) and Upper Cretaceous Niobrara Formation (Bighorn Basin, WY) along with core samples from the Mississippian Barnett Shale (Fort Worth Basin, TX) and the Mississippian-Devonian Bakken Shale (Williston Basin, ND and MT) were analyzed and pyrograms were processed using the MCR algorithm. The results show that for all four marine source rocks, two S1 and three S2 components are generated by MCR modeling and similar shifts in the distribution of components contributing to the S1 and S2 peaks are observed. Some variation in component pyrogram Tmax values was determined for the different formations. This is attributed to factors not related to thermal maturation, but instead differences regarding source rock formation. One of the S2 components generated appears to represent an intermediate kerogen phase, with a Tmax that is between the most thermally labile and refractory components. It is interpreted as a thermally altered product of early maturation that cracks to generate oil and gas at higher maturities. These results show that PTP can provide information on the thermal properties of OM components in immature source rocks and can track the conversion of thermally labile components to intermediate phases during maturation, a finding that is consistent with petrographic observation of macerals representing altered solid OM phases due to thermal evolution in petroleum systems.