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Geochemical characteristics of anaerobic degradation of petroleum hydrocarbons to methane under exogenous electron receptor stress

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In actual reservoir environments, anaerobic degradation of crude oil to generate methane typically involves two pathways: the syntrophic route and the single organism alkylotrophic pathway. Exogenous electron acceptors in reservoirs are key factors influencing methane production from crude oil degradation (crude oil biogasification). Currently, comprehensive studies on the combined effects of exogenous electron acceptors on methane-producing systems involving both pathways (more representative of real-world conditions) remain incomplete, with insufficient research on the geochemical characteristics of crude oil during this process. This study conducted anaerobic cultivation experiments using crude oil as the carbon source (involving both pathways) and added different electron acceptors (nitrate, ferric iron, and sulfate). Over a three-year cultivation period, we monitored the crude oil degradation, methane and CO2 production, electron acceptors consumption, and the microbial community structure under different electron conditions. At higher electron acceptor concentrations (20 mM), the degradation of crude oil alkanes followed the order: control (no electron acceptor) > SO_4^{2-} > Fe^{3+} > NO_3^-. Correspondingly, methane production inhibition followed the inverse order (NO_3^- > Fe^{3+} > SO_4^{2-}). Degradation of phenanthrene and naphthalene was observed under all three electron acceptor stresses. Furthermore, most geochemical indicators for saturated hydrocarbons and aromatics (e.g., carbon preference index (CPI), hopanes-related index, and methylphenanthrene index) remained largely unchanged. These findings provide insights for crude oil biogasification and the exploration and development of biodegradable oils.