

Thermally-released hydrocarbons occurring on the mineral surface within shale

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Shales from the Oligocene Member Es₃^{lower} of the Zhanhua Sag in the Jiyang Depression (eastern China) and clay-sized fractions (< 2 μm) within were selected to study the occurrence characteristic of thermally released hydrocarbons on the mineral surface and elucidate the origin of the thermally released hydrocarbons in shale. Both bulk shales and clay-sized fractions were performed Rock-Eval pyrolysis to obtain TOC and the thermally released hydrocarbons (S1, free hydrocarbons; S2, thermally cracking hydrocarbons). The bulk shales and clay-sized fractions were chemically oxidized by 6 wt.% NaClO, then the raw and treated samples were performed N₂ and EGME adsorption methods to reveal their specific surface areas (SSAs). Correlations of S1 with different SSAs of raw samples are not clear in bulk shales and are negative in clay-sized fractions, while the S1 is positively correlated with mineral total/internal SSAs and is negatively correlated with mineral external SSA; for the S2 both in bulk shales and in clay-sized fractions, it is positively correlated with mineral total/internal SSAs and negatively correlated with mineral external SSA. These correlations of thermally released hydrocarbons with different SSAs indicate that the thermally released hydrocarbons (both S1 and S2) in shale are mainly adsorbed on mineral surface, particularly on the mineral internal surface.

Furthermore, the relationships among TOC, SSAs prior to and after OM removal indicate that the OM of bulk shales and clay-sized fractions mainly occur on mineral internal surface. Combining with the thermally released hydrocarbons in shale also predominantly occur on the mineral internal surface, it can be speculated that the source of thermally released hydrocarbons in shale is the OM adsorbed on the mineral internal surface, which improves the knowledge of hydrocarbon generation of kerogen.

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