Thermochemical oxidation of hydrocarbon induced by high-valence metal oxides in the deep sedimentary basin

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We present the first geological case of thermochemical oxidation of hydrocarbon (TOH) induced by high-valence metal oxides in sedimentary basins. The study was conducted in the Lower Triassic 3200–4000 m deep sandy conglomerate strata in Junggar Basin, NW China. Oil and gas accumulate differentially in the strata, with the extensive occurrence of authigenic calcites. SIMS *in situ* stable carbon and oxygen isotopes, major elements as well as fluid inclusion Th were carried out on calcites, and the composition and carbon isotopes of oil and gas were analyzed. Results show that calcites are extremely depleted ^{13}C with the $\delta^{13}C$ as light as -92.9 ‰ VPDB (average = -52.9 ‰), far below the $\delta^{13}C$ value of CH_4 (-39.3 ~ -46.8 ‰), indicating hydrocarbons especially CH_4 were oxidized.

Anaerobic oxidation of methane and thermochemical sulfate reduction (TSR), are common geological processes resulting in precipitation of extremely ^{13}C-depleted authigenic carbonates, in which sulfate and high-valence metal oxides, such as Fe_2O_3 or MnO_2, act as electron acceptor [1, 2, 3]. However, the possibility of microbial oxidation and TSR can completely be ruled ou in the study area. The calcites are rich Mn (average Mn = 9 mol %). Meanwhile, the $\delta^{13}C$ value of undissolved calcites decreases with the increasing Mn content, presenting good negative correlation. Th of aqueous inclusions in calcites concentrates in 85–100 ºC and 105–135 ºC. All the evidences indicate that TOH was mainly induced by high-valence Mn oxide.

Therefore, TOH induced by high-valence Mn oxides can occur in relatively low temperature (>85 ºC) in sedimentary basins, which is much lower than that in laboratory simulation (>300 °C) [4, 5]. This reaction does not only affect petroleum accumulation, but also might act as a major CH_4 sink in the deep crustal carbon cycle.

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