

STABLE CARBON ISOTOPIC COMPOSITION OF CYCLOALKANES AND MONOAROMATICS IN LIGHT HYDROCARBONS AS INDICATIONS OF NATURAL OIL-CRACKING

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The preservation of crude oil in the Earth's crust is limited, because most of crude oil components start to decompose to smaller compounds, and ultimately to methane and graphite with increasing temperature in deep Earth. Despite a large body of experimental evidence on oil-cracking, it is still not clear what this temperature limit is and how to assess the extent of cracking under geological conditions. Previous study showed that diamondoids can be a measure of the amount of oil destroyed by high temperatures deep in the Earth (Dahl et al., 1999). However, the concentration of diamondoids is strictly controlled by the types of minerals within source rocks and/or reservoirs, and thermal history experienced, resulting in an uncertainty as quantitative indicators of oil-cracking (Wei et al., 2006). In this paper, we try to develop new indicators to trace oil-cracking process in deep hot reservoirs.

It is well known that light hydrocarbons (LHs) are the important middle products during the course of oil-cracking. If we can differentiate oil-cracking LHs from the kerogen thermal degraded, in most cases we can identify whether the aimed oil reservoir experienced the cracking process. Theoretically, LHs from kerogen are directly degraded from macromolecular network and will migrate out of the source rock via generation and expulsion once hydrocarbon concentration reaches up to the saturated threshold of rock. There is few secondary reactions taken place. Whereas LHs from oil-cracking are formed via C-C bond cleavage of high molecular weight compounds, cyclization and aromatization, and involved an isotopic kinetic fractionation, although they will be destroyed under very high temperature. This suggests that stable carbon isotopic composition of LHs can be a measure to characterize the oil-cracking genetic and kerogen thermal degraded, further to trace the oil-cracking process. In order to verify this hypothesis, two different experiments were conducted. For source rock, an on-line pyrolysis-gas chromatography-isotope ratio-mass spectrometry was employed and the isotopic compositions of LHs from different temperature ranges were measured. For crude oil, a close-pressurized pyrolysis system under heating rate of 2°C/hr in the temperature range of 400 to 580°C was used and the isotopic compositions of LHs were off-line determined. Generally, with increasing temperature both the kerogen degraded and

oil-cracking *n*-alkanes become more positive in $\delta^{13}\text{C}$ values. However, the $\delta^{13}\text{C}$ values of cycloalkanes and monoaromatics from type I and type III organic matter, represented by vitrinite-rich and alginite-rich source rocks in Figure 1 A, were not significantly shifted with increasing maturation. For type II kerogen, the $\delta^{13}\text{C}$ values of cycloalkanes and monoaromatics were changeable because of the mixed input of organic matter, showing multiple isotopically distinct cycloalkane/monoaromatic pools within kerogen. During oil-cracking experiments, cycloalkanes and monoaromatics became more positive in $\delta^{13}\text{C}$ values with increasing temperature (Figure 1 B), indicating an isotopic fractionation accompanying cyclization and aromatization due to the difference in bond energy between ^{12}C - ^{12}C and ^{13}C - ^{13}C . Even if the LHs were decomposed under high temperature, the isotopic fractionation still followed this kinetic model. The laboratory results suggested that, for type I and III kerogen-dominated petroliferous basin, the $\delta^{13}\text{C}$ values of cycloalkanes and monoaromatics in LHs can be acted as potential indicators of natural oil cracking. A case study from the Hetianhe gasfield in Tarim basin, NW China was presented (Figure 1 C).

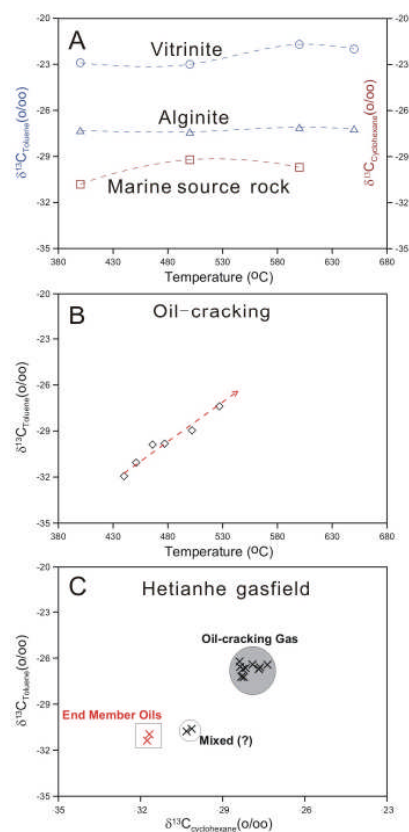


Fig 1 $\delta^{13}\text{C}$ values of cyclohexane and toluene from source rock degradation, oil-cracking, and Hetianhe gas field in tarim basin, NW China

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