Stable Carbon Isotopes of Gaseous Hydrocarbons Revealed by Laboratory Simulation and Implications for Gas Source Recognition in Marine Sedimentary Sequences, Southern China

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There are numberous previous studies concerning the geochemical characterization, source tracers and kinetic simulation of gas generation in marine petroleum systems. A critical assessment of the earlier work reveals a large knowledge gap in the understanding of the temperature and pressure effects on gas generation from various organic precursors under a quasi-continuous geological regime, often seen in multicyclic, superimposed basins. In order to address this issue, potential gas sources (type I, II and III kerogens, condensate oil, light oil, heavy oil, primary bitumen and asphaltic sandstone) were selected to perform thermal simulation in closed system where the samples were heated to various temperatures (from 250°C to 550°C) in a high pressure vessel and under more geologically realistic conditions (Zheng et al., 2009). A detailed characterization of the pyrolysates generated under the lab simulation experiments reveals a number of compositional trends, which have significant implications for gas source recognition in Paleozoic marine sedimentary sequences in southern China.

With increasing pyrolysis temperature, the yields of methane and heavy gaseous alkanes gradually increase, but fall after the pyrolysis temperature reaches 500ºC, Although the temperature at which the gaseous alkanes display the maximum yields vary as a function of the hydrocarbon source, the fact that the temperature for the maximum methane generation is higher indicates certain lagging effect and may be related to thermal cracking of C_{2+} hydrocarbons to form methane at 450-500ºC (Ro > 1.7%). The $\delta^{13}C_{CO2}$-$\delta^{13}C_1$ values of the gaseous products derived from from dispersed soluble organic matter are greater than 20‰, while those from different types of kerogens are within 20‰, indicating more signficant isotopic fractionation for carbon dioxide and methane generation from dispersed organic matter than that from kerogen.

It is very important to observe that methane generated during the various pyrolysis experiments displays much lower $\delta^{13}C$ values than that of its source precursors, even though generally higher values are seen in pyrolysates generated in higher pyrolysis temperatures. The $\delta^{13}C$ values of gaseous alkanes are also always lower than that of the starting hydrocarbon sources. As a result, the $\delta^{13}C_1$ values of methane gas derived from the thermal degradation of

soluble organic matter turn to be lower than those of gases derived from kerogen cracking at similar maturity levels.

With increasing thermal evolution, the $\delta^{13}C$ values of the newly generated gaseous alkanes become higher, and approach that of their sources at peak gas generation. Therefore, these values can be used to trace their sources. At the high to over maturity stages (Ro > 1.5), however, the $\delta^{13}C$ values of C_{2+} alkanes derived from type II, oil-prone source rocks can be higher than those in their hydrocarbon sources and overlap with those of coal derived gases generated at low maturity levels. In this case, one must be extremely cautious if the $\delta^{13}C$ values of C_{2+} alkanes are used to distinguish gases derived from coaly and oil prone sources.

Prinzhofer (1995) indicates that gases generated from kerogen thermal degradation generally displays large variation in the ln (C_1/C_2) values with relatively constant ln (C_2/C_3) values. In contrast, gases derived from subsurface oil cracking turn to show relatively constant (C_1/C_2) values but large variation in the ln (C_2/C_3) values. In this study, we observed more significant variation in the ln (C_2/C_3) values for gaseous products derived from oil and dispersed soluble organic matter that those from kerogen degradation gas. Moreover, with increasing simulation temperature, the ln (C_2/C_3) values for gaseous products from oil and soluble increase at much larger rates than those from kerogen degradation gas (Fig.1). As the result, gases from oil cracking in the ln (C_1/C_2) – ln (C_2/C_3) plot display larger slope than that of kerogen degradation, and thus require an amendment to the commonly used empirical relationship. The revised plot and the ln(C_2/C_3) values can be used to distinguish gases derived from kerogen degradation and those from thermal cracking of crude oil or soluble organic matter. Similar applications can be also based on the cross plot of ln(C_1/C_2) and $\delta^{13}C_1$-$\delta^{13}C_2$ (Fig.2).

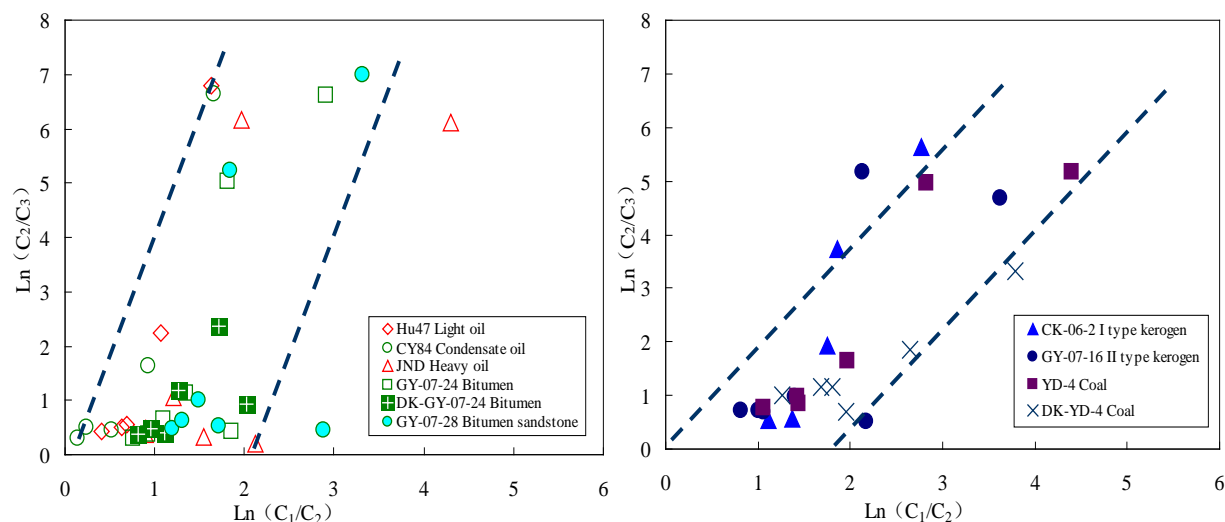Fig.1: Correlation of Ln （C_1/C_2） and Ln （C_2/C_3） for gases derived from different organic sources.
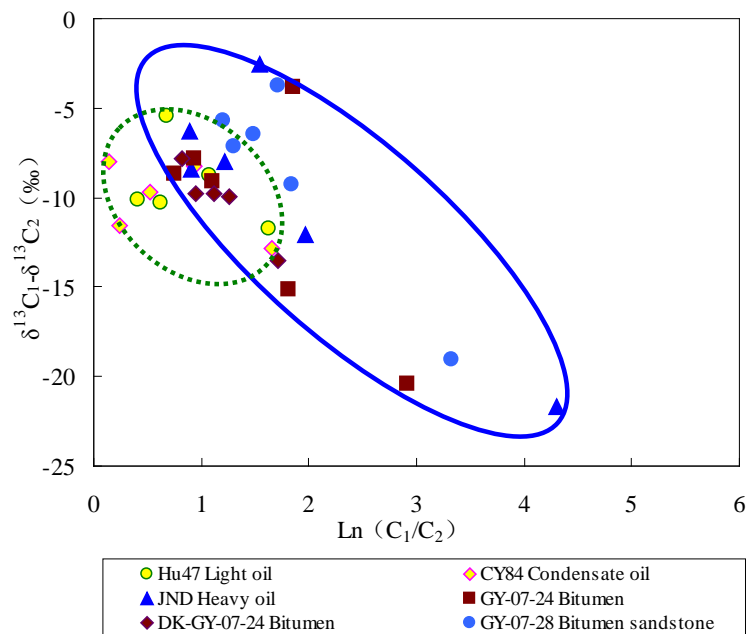
Fig.2: Cross plot of Ln (C_1/C_2) and $^{13}C_1$- δ $^{13}C_2$ values for gases from different organic sources.

References

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