Isotopic Kinetics of NSO Gases from Marine Shale Bitumen and Application on Deep Gas Originating

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Origin of deep gases is complicated due to multiple sources and long forming process. Here, a marine shale rock sample from Zhangjiakou, northern China is selected for simulation, and the artificial bitumen is extracted as a representation of primary oil. Hydrocarbon (saturated and aromatic HC) and NSO fractions (resin and asphaltenes) are separated from the extracts and each fraction is pyrolysized using a closed, non-isothermal pyrolysis gold-tube system. The pyrolysis temperature ranges 300-600 °C at 2°C /h and 20°C /h heating rates. The gas carbon/hydrogen isotopes are analyzed using GC-IRMS. The Rayleigh's method proposed by Rooney (1995) was used to model isotopic variation and retrieve kinetic parameters of carbon isotopes of gases [1]. Here, the methane carbon isotopic kinetic parameters are calculated as $\alpha(C^{13}/C^{12})=1.010$ with $\delta^{13}C_0 = -33.50\%$, $\alpha(C^{13}/C^{12}) = 1.0107$ with $\delta^{13}C_0 = -3.50\%$ 31.26‰, $\alpha(C^{13}/C^{12})=1.0102$ with $\delta^{13}C_0=-30.49\%$ and $\alpha(C^{13}/C^{12})=1.0092$ with $\delta^{13}C_0=-31.78\%$ for saturated HC, aromatic HC, resin and asphaltenes, respectively. Fig. 1 shows show good agreement between the modeled methane carbon isotopes and the experimental ones from four fractions. These isotopic parameters were used to calculate the real gas isotopes of Gaoshiti gas field, one deep gas accumulation in Sichuan Basin, China by integrating with accurate thermal historical data and kinetics of gas generation. The $\delta^{13}C_1$ from NSO fractions was calculated as -33.2% to -34.4% which show great agreement with real gases, implying the gases were originated from NSO fractions of retained oil. Acknowledging Strategic Program of CAS (XDB10010300) & NSFC (41372137) for grants.



Fig. 1 The experimental and modeling $\delta^{13}C_1$ of four fractions (α fractionation factor, $\delta^{13}C_0$ initial carbon isotope)

[1] Rooney et al. (1995) Chem. Geology. **126**, 219–232.