Predicting the proportion of free and adsorbed gas by isotopic geochemical data: A case study from Lower Permian shale in the southern North China basin (SNCB)

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The alternating marine-terrigenous shale facies of the Lower Permian Taiyuan (P1t) formation and the Lower Permian Shanxi (P₁s) formation in the north margin of the southern North China basin (SNCB) are characterized by their high TOC values (1.76-5.09 %), types II and III organic matter, and high Ro values (> 3.0%). Geochemical parameters of 12 gas samples from the Lower Permian shale formations from well Weican-1 were analyzed in this study. The gases are dominated by methane, with small amounts of ethane, without propane and butane. Wetness of the gas is only 0.25-0.58% reflecting extremely high maturity of the source rock. The $\delta^{13}C_1$ values range from -31.6% to -26.8% and the $\delta^{13}C_2$ values range from –35.9‰ to –33.2‰, the $\delta^2 H_{CH4}$ values range from -221.1‰ to -187‰. Furthermore, carbon isotopic compositions of the alkane gases from the Lower Permian shale are characterized by $\delta^{13}C_1 >$ $\delta^{13}C_2,$ this indicates that the gases released from Permian shale are of thermogenic origin and mostly sourced from the continental shale and coal measures, with minor contribution from oil cracked gas from marine mudstones. Geochemical fractionation during the adsorption/desorption process of the shale system may play a significant part in influencing $\delta^{13}C_1$ values of shale gas. The results show that the $\delta^{13}C_1$ becomes heavier with increasing degree of gas desorption. Based on isotope fractionation during desorption of gas in shales, an equation was established to estimate the proportion of free and adsorbed gas in shales using $\delta^{13}C_1$ of shale gas. In comparison with other equations, this equation is based on the direct data of gas desorption experiment to avoid the adsorbed gas content often exhibit maxima from excess sorption isotherms experiment. This method provides efficient way to understand the gas storage behavior in shales and broaden the application of gas isotope.