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The Influence of Thermochemical Sulfate Reaction on the Hydrogen Isotope Ratios of Alkane Gases

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The hydrogen isotope ratio of natural gas is controlled by paleo-climate and maturity and discussed by some authors (Schoell, 1980; Dai, 1990). But the study that the influence of secondary alteration (for example, thermochemical sulfate reaction (TSR) on the carbon and hydrogen isotope is also an interesting topic and the result is also meaningful to determine the origin, maturation and secondary alteration of natural gas. A lot of works have been done on the influences of TSR on the carbon isotopes of methane and ethane, but few works has been done on the influences of TSR on the hydrogen isotopes of natural gas.

Simple balanced reactions for alkane gases by TSR is expressed as following (Worden and Smalley, 1996).

$CH_4 + CaSO_4 \rightarrow H_2S + CaCO_3 + H_2O$
$C_2H_6 + 2CaSO_4 \rightarrow H_2S + S + 2CaCO_3 + 2H_2O$
$C_3H_8 + 3CaSO_4 \rightarrow H_2S + 2S + 3CaCO_3 + 3H_2O$
$C_nH_{2n+2} + nCaSO_4 \rightarrow H_2S + (n-1)S + nCaCO_3 + nH_2O$

All these expressions show that hydrogen element in alkane gases was involved in TSR and also confirmed by the products of H_2S and H_2O. The cracking of C-H is easier than that of C-D, so the hydrogen fraction should exist with the increasing of TSR alteration. In addition, the water solution is necessary for TSR process. The hydrogen exchange between alkane gases and water may also affect the hydrogen isotope of alkane gases.

The resource of natural gas is abundant in Sichuan basin in China and High H_2S gas distributed in marine gas reservoirs and fields widely, for examples, Puguan, Luojiazhai, Dukouhe gas fields and Leisan gas reservoir in Zhongba gas field, etc.. Most of natural gases sourced from marine sedimentary organic matter, called as oil associated gases. The distribution of high sulfur-bearing gas fields is consistent with the gypsum and interbedded with the

reservoirs. The origin of H_2S is formed by Thermochemical Sulfate Reduction based on content and isotope of H_2S and CO_2.

Based on the geochemical data of natural gases in Sichuan Basin, the influences of TSR on the hydrogen isotope of alkane gases have been studied (Fig.1). With the increasing of $\delta^{13}C_1$, δD_1 is also increasing largely. TSR has affected the carbon isotope ratio of methane sharply and with the increasing of TSR process, the remaining methane becomes isotopically heavier. Although maturation also affects the hydrogen isotope ratio of methane, the fairly well correlation between isotope ratios of carbon and hydrogen of methane implies that the hydrogen isotope ratio is also affected by TSR. The gas sourness ($H_2S*100/(H_2S+C_nH_{2n+2})$) has been proposed to determine the level of TSR. The relation between gas sourness and δD_1 is shown in Figure 1. With the gas sourness increasing, methane is getting isotopically heavier. δD_1 is changing from -156‰ to -107‰ with gas sourness from 0 to 26.5%. Methane became D-enriched as TSR proceeded. The positive relationship between δD_1 values and gas sourness leads to inference that as sulfate reduction of methane proceeded, H in methane was more easily depleted than D as a result of kinetic isotope fraction with the residual methane more enriched in D.

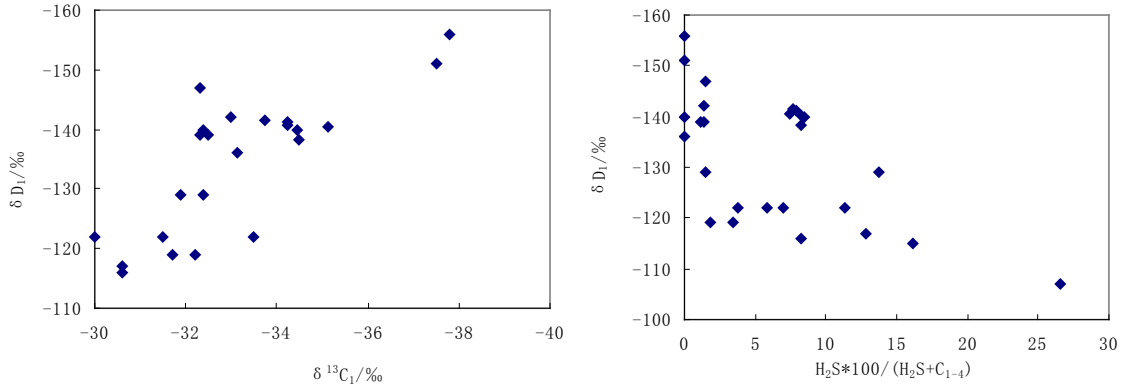

Fig.1 The relationship between isotope ratios of carbon and hydrogen of methane (Left), hydrogen isotope ratio and gas sourness (right)

Higher alkanes, such as ethane, also became D-enriched as TSR proceeded (Fig. 2). With the gas sourness increasing, ethane became isotopically heavier. δD_2 is increasing from -153‰ to -106‰ with gas sourness from 0 to 26.5%. Kinetic isotope fraction results in TSR for C-H being faster than TSR for C-D. Compared with methane, the variation range of hydrogen isotope of ethane is similar to that of methane.

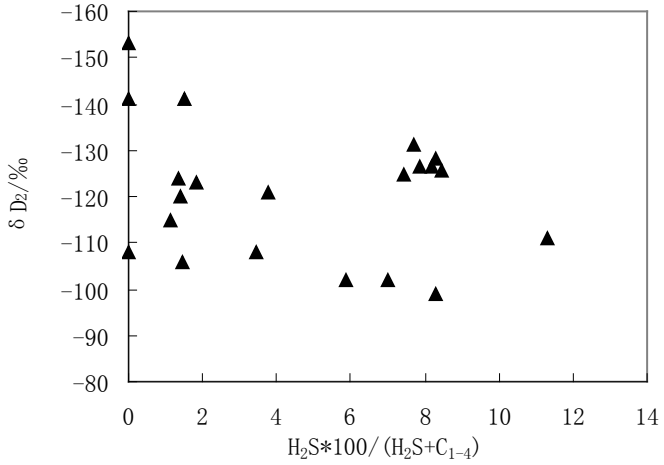

Fig. 2 The relation between gas sourness and hydrogen isotope ratio of ethane

The relationships between hydrogen isotope and carbon isotope, gas sourness show hydrogen isotopes of methane and ethane are getting heavier as TSR proceeds. The result is very helpful to determine the origin, paleo-climate and maturation of alkane gas based on hydrogen isotope of natural gas. Butt the variation range of hydrogen isotope is still unclear and should be studied strictly.

References

Schoell, M., 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. Geochimica et Cosmochimica Acta 44, 649-661.

Dai, J., 1990. Characteristics of hydrogen isotopes of paraffinic gas in China. Petroleum Exploration and Development 17(5), 27-32. (in Chinese).

Worden, R.H., Smalley, P.C., 1996. H_2S-producing reactions in deep carbonate gas reservoirs: Khuff Formation, Abu Dhabi. Chemical Geology, 133,157-171