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New insight into carbon isotopic reversals of deep gas in Songliao Basin, NE China

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The geochemistry of deep gases in Songliao Basin is characterized by heavier $\delta^{13}C_1$ values than typical coal-derived gases (Mi et al., 2010) and ^{12}C-enriched ethane (most lighter than −29‰) which used to be considered as of sapropelic origin. Partial carbon isotopic reversal (e.g. $\delta^{13}C_1>\delta^{13}C_2$ or $\delta^{13}C_2>\delta^{13}C_3$) is widespread while about half of them have complete isotopic reversal phenomenon (i.e. $\delta^{13}C_1>\delta^{13}C_2>\delta^{13}C_3>\delta^{13}C_4$). Many published works have attributed these particular geochemical characteristics especially the widespread carbon isotopic reversals to mixture of different sources of gas or inorganic origin (e.g. Huang, 2004; Dai et al., 2004; Li et al., 2009; Mi et al., 2010). However, our recent study showed that it may be mainly a result of different gas generation model or post-mature alteration other than a simple mixture model. 173 gas samples in the Lower Cretaceous Yingceng volcanic formations which are the main natural gas reservoirs in the deep Songliao Basin were compiled to review the potential origin of carbon isotopic reversals. The main results are shown in Figure 1 and Figure 2. According to current gaseous hydrocarbon generation model, gaseous alkanes' carbon isotopic values and the dryness (e.g. C_1/C_2+) will increase as maturity increases. An opposite trend was observed in our data, where $\delta^{13}C_2$ value and the dryness both decrease with depth increasing, especially below 3500m (figures are not shown in this short report). Based on James(1983) model, $\Delta(\delta^{13}C_2-\delta^{13}C_1)$ is a maturity indicator and will decrease as maturity increases. The combination of $\delta^{13}C_1$, $\delta^{13}C_2$ and $\Delta(\delta^{13}C_2-\delta^{13}C_1)$ in a single plot shows that $\delta^{13}C_1$ and $\delta^{13}C_2$ have opposite trends and the "X"-type trend in Figure 1 may indicate a different gas generation model used currently or post-mature alteration after primary gas generation. Du et al.(2003) suggested that gaseous hydrocarbon generated from organic matter (lignite) under HPT (high pressure and high temperature) conditions have completely reversed carbon isotopes and their data are shown in Figure 1 for comparison. It is obvious that carbon isotopic effect of deep gases in Songliao Basin shares some similarity with those of gas generated by HPT pyrolysis provided by Du et al.(2003) and they possibly have similar gas generation mechanism. However, as suggested by (Galimov, 2006), the increase of pressure may induce partial transformation of methane to higher homologues with heavier $\delta^{13}C_1$ value and lighter $\delta^{13}C_2$ value. In a deep basin which is usually associated with high or post-mature gases, one way to increase the pressure is in-situ wet gas cracking suggested by Ni et al.(2009) and Zumberge et al.(2009), where cracking wet gas to smaller molecules will increase the pressure enough to transform some methane to higher homologues. The decrease of both dryness(i.e. decreasing methane content) and $\delta^{13}C_2$ value with depth increasing seems to support the occurrence of methane transformation to higher homologues in the deep Songliao Basin and the "rollover" of *i*-C_4/*n*-C_4(i.e. isobutane/normal butane)in Figure 2 corroborates the

presence of in-situ wet gas cracking according to Zumberge et al.(2009). It is accordingly suggested that the carbon isotopic reversals in deep gases in Songliao Basin is most likely the result of post-mature alteration possibly associated in-situ gas cracking which increases the pressure enough to transform some methane to higher homologues and makes methane carbon isotope heavier and ethane carbon isotope more lighter. Although, more further works are needed to check our results.

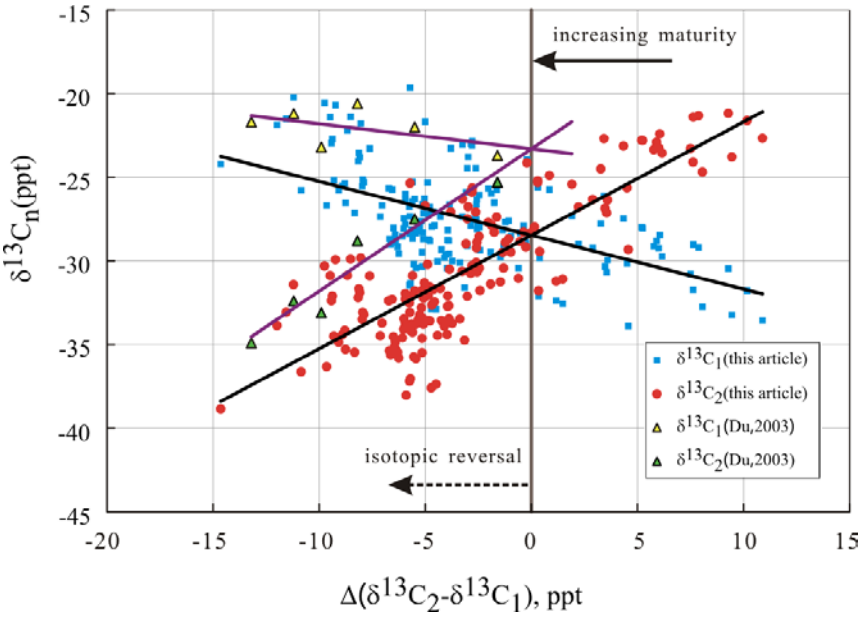

Figure 1: "X"-type carbon isotopic effect between methane and ethane. Lines are least square fits for corresponding data.

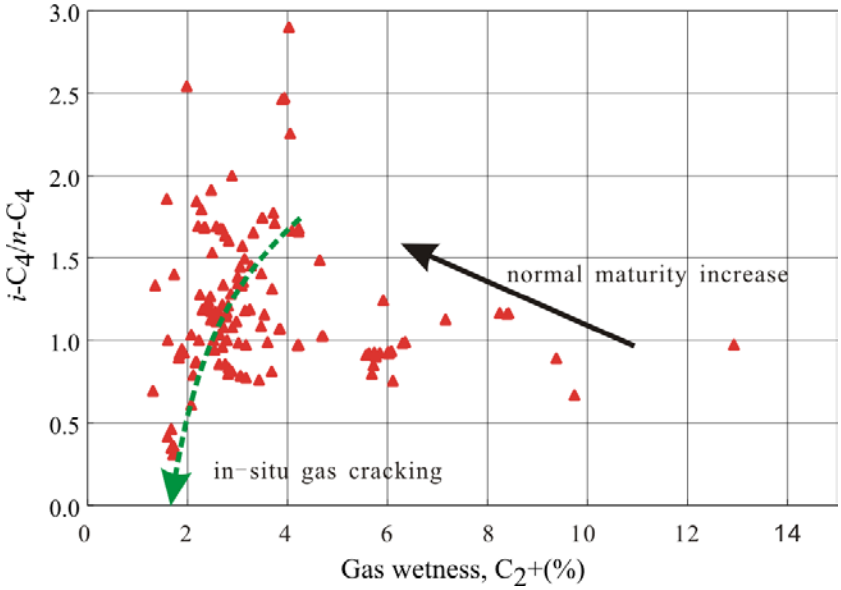

Figure 2: Evidence of in-situ gas cracking in deep gases in Songliao Basin

REFERENCES CITED

Dai, J., X. Xia, S. Qin, and J. Zhao, 2004, Origins of partially reversed alkane [delta]13C values for biogenic gases in China: Organic Geochemistry, v. 35, p. 405-411.

Du, J., Z. Jin, H. Xie, L. Bai, and W. Liu, 2003, Stable carbon isotope compositions of gaseous hydrocarbons produced from high pressure and high temperature pyrolysis of lignite: Organic Geochemistry, v. 34, p. 97-104.

Galimov, E., 2006, Isotope organic geochemistry☆: Organic Geochemistry, v. 37, p. 1200-1262.

Huang, H., 2004, Geochemistry of natural gases in deep strata of the Songliao Basin, NE China: International Journal of Coal Geology, v. 58, p. 231-244.

James, A. T., 1983, Correlation of natural gas by use of carbon isotopic distribution between hydrocarbon components: AAPG Bulletin, v. 67, p. 1176-1191.

Li, J., W. Liu, H. Zeng, and M. Li, 2009, Possible origins for inverse stable carbon isotopes of gaseous alkanes in nature: preliminary results from laboratory simulation experiments: 24th International Meeting on Organic Geochemistry, p. 130.

Mi, J., S. Zhang, G. Hu, and K. He, 2010, Geochemistry of coal-measure source rocks and natural gases in deep formations in Songliao Basin, NE China: International Journal of Coal Geology, v. 84, p. 276-285.

Ni, Y., J. Dai, X. Yang, Y. Tang, Y. Jin, and J. Chen, 2009, Kinetic modeling of post-mature gas generation: Constraints from high-pressure thermal-cracking of n-C24: Geochimica et Cosmochimica Acta, v. 73, p. A940.

Zumberge, J., K. Ferworn, and J. Curtis, 2009, Gas character anomalies found in highly productive shale gas wells: Geochimica et Cosmochimica Acta Supplement, v. 73, p. 1539.