



Isotopic reversals with respect to maturity trends due to mixing of primary and secondary products in source rocks

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ABSTRACT

Carbon isotopic composition ($\delta^{13}\text{C}$) reversals with respect to maturity trends have been reported for ethane and propane in Barnett Shale gas in the Fort Worth Basin, U.S.A. This trend also exists in some conventional gas reservoirs, such as in the Ordos Basin, China and Appalachian Basin, U.S.A. Fractionation during mass transport is unlikely to be a significant mechanism, because its effect is minor under geological conditions, it would have caused more obvious reversal for methane than for ethane and propane, and mass transport can not account for the occurrence of the trend both inside and outside source rocks. This paper demonstrates that the reversal may result from mixing of indigenous primary gas (generated directly from kerogen) and secondary gas (generated from oil and condensate) within source rocks, and presents deconvolution results using end-members derived from a kinetic isotope fractionation model. The results, including the wetness and mixing ratio of primary and secondary gases, are consistent with geological conditions. Condensates may be the major precursor of the secondary gas in shale when the reversal occurs. A complete trend of $\delta^{13}\text{C}$ variations in methane and ethane with maturity is proposed that is based on the indigenous mixing mechanism.

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1. Introduction

The recent accelerated exploration of shale gas provides an unprecedented opportunity to understand the geochemical processes in oil and gas source rocks. Detailed distributions and compositions of oil, gas and other organic matter in source rocks have been investigated by organic and gas isotopic geochemistry, especially the analysis of carbon isotopic compositions ($\delta^{13}\text{C}$) of alkanes, which are among the few geochemical indices of natural gas. Interestingly, abnormal trends in $\delta^{13}\text{C}$ values are revealed by the shale gas data (Zumberge et al., 2009, 2012).

Normal trends of alkane $\delta^{13}\text{C}$ values in natural gas are fundamentally determined by the kinetic process of natural gas generation from precursors (kerogen, bitumen, oil and condensates). Specifically, the trends are determined by a kinetic isotope effect (KIE) resulting from differences in energy required for cleavage of $^{12}\text{C}-^{12}\text{C}$ and $^{12}\text{C}-^{13}\text{C}$ bonds in the precursors (Tang et al., 2000). KIE brings about a more positive carbon isotopic composition in the hydrocarbon at higher maturity. KIE is more profound for smaller molecules due to the increasing relative differences of molecular weights between their isotopologues. Therefore, two normal trends are expected:

- 1) $\delta^{13}\text{C}$ values of each gaseous hydrocarbon component become more positive with increasing maturity (Stahl and Carey, 1975;

- 2) $\delta^{13}\text{C}$ values are more positive with increasing carbon number from methane ($\delta^{13}\text{C}_1$), ethane ($\delta^{13}\text{C}_2$) to propane ($\delta^{13}\text{C}_3$) at identical maturity ($\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3$).

While much of the conventional and shale gas geochemical data follows the above trends (for shale gas examples see Hill et al., 2007), reversed isotopic trends are common. $\delta^{13}\text{C}$ reversals with respect to carbon number ($\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2$ and/or $\delta^{13}\text{C}_2 > \delta^{13}\text{C}_3$) have been found in some shale gas plays in the U.S. (Zumberge et al., 2012). This trend is not unique in shale gas; it has also been found in conventional reservoirs in the U.S. (Jenden and Drazan, 1993; Burruss and Laughrey, 2010), China (Xia et al. 1999, Dai et al., 2004), and Canada (Tilley et al., 2011). The other reversed trend, $\delta^{13}\text{C}$ with respect to maturity, is remarkable for ethane and propane in some shale gas plays (Zumberge et al., 2009, 2012) and has drawn much attention due to its relation to gas productivity (Brown, 2010). The $\delta^{13}\text{C}_2$ reversal with respect to maturity trends was also found in some conventional reservoirs, such as in the Ordos Basin in China (Xia et al., 1999).

Various mechanisms have been proposed to explain the two types of reversal. For $\delta^{13}\text{C}$ reversals with respect to carbon number, mixing of natural gas of different origins is regarded as the main mechanism (Jenden and Drazan, 1993; Dai et al., 2004). This mechanism seems favorable in basins having multiple source rocks containing different

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kerogens or having different maturities. For example, in the Ordos Basin, the $\delta^{13}\text{C}$ reversal with respect to carbon number has been attributed to mixing of gases from humic kerogen (more positive $\delta^{13}\text{C}$) and sapropelic kerogen (more negative $\delta^{13}\text{C}$). However, the deconvoluting results based on constant $\delta^{13}\text{C}$ values for the two end-members appears to be inconsistent with the relation between $\delta^{13}\text{C}_2$ and wetness (Xia et al., 1999, Fig. 2).

After the $\delta^{13}\text{C}_2$ reversal with respect to wetness in shale gas was discovered, a preliminary interpretation was proposed that involved mechanisms related to both generation and mass transport (Zumberge et al., 2012). A quantitative interpretation of these observations is still required to advance knowledge of the geochemical processes in source rocks and to improve natural gas resource evaluation. The main purpose of this paper is to provide a quantitative evaluation of the different mechanisms for the reversed isotope trends in shale gas and in conventional gas reservoirs, especially the mechanism of mixing gases generated from different processes. The quantitative deconvolution calculation will provide a critical evaluation of the mechanism and will improve understanding of gas generation.

2. Geological settings and geochemical data

2.1. Geological settings

Natural gas geochemical data from three basins were investigated. The $\delta^{13}\text{C}_2$ reversal was found in each basin, including the Fort Worth and Appalachian basins in the U.S. and the Ordos Basin in China. The molecular and carbon isotopic compositions of natural gas from the three basins were mainly reported by Zumberge et al. (2012), Dai et al. (2005), and Burruss and Laughrey (2010). The geological conditions of hydrocarbon generation were investigated in previous studies (Dai et al., 2005; Hill et al., 2007; Burruss and Laughrey, 2010 and references therein). Brief descriptions of the source and reservoir rocks are listed in Table 1.

These conventional and the unconventional reservoirs share several similar geological characteristics. The petroleum occurs in stratigraphic traps and the deformation of reservoir rocks is relatively gentle (though carbonates in the basins may be fractured). Major faults did not develop during the recent uplift movements after the reservoir formed. Finally, the reservoirs are vertically close to the source rocks, resulting in short migration distances.

2.2. Isotopic reversal with respect to wetness in published field data

The isotopic reversal with respect to maturity is obvious on the plot of $\delta^{13}\text{C}_2$ versus gas wetness (Zumberge et al., 2012, Fig. 2; Xia et al.,

Table 1

Source rocks and reservoirs of gas fields having isotopic reversals with respect to maturity.

	Fort Worth Basin ¹	Ordos Basin ²	Appalachian Basin ³
Reservoir	Mississippian Barnett Shale	C–P terrigenous sand; C limestone; O weathered crust	O–S tight sand, fractured carbonate and shale
Source rock	Mississippian Barnett Shale	C–P coal measures	O Utica Shale
TOC (wt %)	4.5	1–60 (coal)	1.8
Organic type	II	III	II
R_o (%)	0.8–>2.1	1.2–3 bottom Carboniferous	1–4
Thickness (m)	30–200	30–120	20–300

1 – Zumberge et al. (2012); 2 – Dai et al. (2005); 3 – Burruss and Ryder (2003), Burruss and Laughrey (2010), Repetski et al. (2008); C = Carboniferous; P = Permian; O = Ordovician; S = Silurian.

1999, Fig. 2; Burruss and Laughrey, 2010, Fig. 10). Fig. 1 summarizes data from the three basins. Note that wetness is a reliable parameter for source rock maturity. If the gas reservoir conditions and the source rock organic types are similar: wetness decreases monotonically with maturity at $R_o > 0.8\%$ (for coal-formed gas see Rice, 1993; for shale gas see Hill et al., 2007).

In Fig. 1, at high wetness (low maturity), $\delta^{13}\text{C}_2$ values of gas from the Fort Worth Basin become more positive with decreasing wetness, which is the normal trend during gas generation. This variation is not as obvious in other two basins. When gas wetness drops to a critical point, the reversed trend is observed, not only for shale gas from the Fort Worth Basin (critical wetness of ~4%), but also for the conventional gas reservoirs in the Ordos Basin (critical wetness of ~2%) and in the Appalachian Basin (with critical wetness ~10%). The drop of $\delta^{13}\text{C}_2$ values is over 10‰ for the Ordos and Fort Worth basins. The occurrence of this reversal is independent of organic type in source rocks and of gas isotope composition ($\delta^{13}\text{C}_2$ for the Ordos Basin are the most positive and while values for the Appalachian Basin are the most negative). Interestingly, when wetness is very low (< 1 vol%), the gas from the Appalachian Basin regains the normal trend of $\delta^{13}\text{C}_2$ with respect to wetness (based on 20 samples in Fig. 1).

Similar normal and reversal trends are found for $\delta^{13}\text{C}_3$ as well (Fig. 2A); but the $\delta^{13}\text{C}_1$ values seem to increase monotonically with decreasing wetness, with some vague reversed and back-to-normal trends at wetness < 5 % (Fig. 2B). Because the reversal is stronger for $\delta^{13}\text{C}_2$ than for $\delta^{13}\text{C}_1$, when the maturity is high enough, there could be $\delta^{13}\text{C}_2 < \delta^{13}\text{C}_1$. Thus, the $\delta^{13}\text{C}$ reversals with respect to carbon number and maturity trend may result from the same mechanism.

Similar to the above isotope trends, an initial increase followed by a decrease of isobutane to *n*-butane ratio (iC_4/nC_4) with respect to maturity trend was also revealed (Fig. 3). The reverse may reflect faster generation of *n*-butane than isobutane, and/or faster decomposition of isobutane than *n*-butane at high maturity. The latter seems more probable, because isobutane is kinetically less stable than *n*-butane (the tertiary C–H bond in isobutane is more active due to stabilized tertiary radicals). Thus, the iC_4/nC_4 and $\delta^{13}\text{C}_2$ reversals may not result from the same process.

Other special trends include increased CO_2 concentrations and reversed $\delta^{13}\text{C}$ of CO_2 at higher maturity (Fig. 4 in Zumberge et al., 2012), and a methane hydrogen isotope ($\delta^2\text{H}_1$) reversal with respect to maturity trend

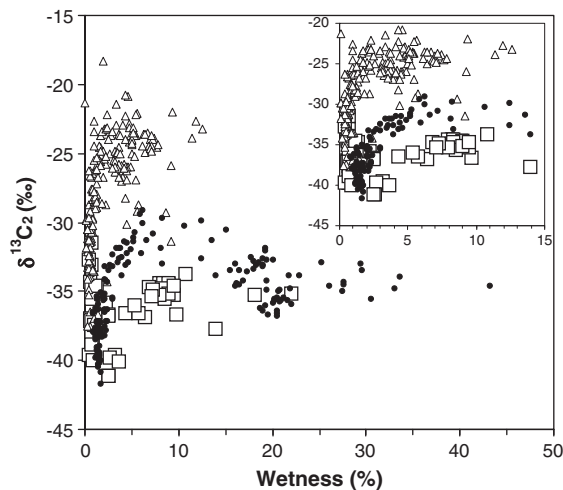


Fig. 1. Wetness-dependent variation of $\delta^{13}\text{C}_2$ (ethane) in natural gas from the Ordos Basin (triangles, Dai et al., 2005; Xia, 2000; Hu et al., 2008), the Fort Worth Basin (dots, Zumberge et al., 2012), and the Appalachian Basin (squares, Burruss and Laughrey, 2010). Wetness is defined as the volume fraction of C_{2+} gaseous hydrocarbon in total gaseous hydrocarbon. Inset shows a selected portion of the full data.

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