Variations of natural gas carbon isotope-type curves and their interpretation – A case study

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Received 20 June 2006; received in revised form 1 March 2007; accepted 8 March 2007
Available online 16 March 2007

Abstract

Natural gas is dominated by low-molecular weight gaseous hydrocarbons (C1–C3) whose genetic and diagenetic information is mainly obtained from stable carbon isotope compositions. Ordos Basin is one of the largest natural gas provinces in China. By means of examining the carbon isotope compositions of the Ordos basin gases, altered patterns of the isotope-type curves due to secondary cracking, thermochemical sulphate reduction (TSR) and mixing of gases generated from different sources are recognized and discussed. A typical carbon isotope-type curve is nearly linear on the natural gas plot [Chung, H.M., Gormly, J.R., Squires, R.M., 1988. Origin of gaseous hydrocarbons in subsurface environments: theoretical considerations of carbon isotope distribution. Chemical Geology 71, 97–103]. Our results show that the isotope-type curve pattern of TSR and gas secondary cracking in coal is convex due to catalysis, while the isotope-type curve of gas secondary cracking in reservoirs is concave. The natural gas of Yulin, Suligemiao and Wushenqi gas fields is coal-derived gas; both coal-derived gas and mixed gas from oil- and gas-prone sources exist in the Ordovician reservoirs of the Jingbian gas field, depending on the borehole locations. In the Ordovician carbonate reservoirs TSR is recorded but uncommon, whereas secondary cracking in reservoirs is often observed.

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1. Introduction

Most of the natural gases accumulated in subsurface reservoirs are generated from thermal degradation of sedimentary organic matter, the origin of which is closely related to diagenetic and thermal alteration of organic matter (Schoell, 1980, 1983).

Natural gas, dominated by a few low-molecular weight gaseous hydrocarbons, is compositionally and isotopically simple. As a result of limited molecular complexity, important genetic and post-genetic information is commonly obtained from stable carbon and hydrogen isotope compositions of the hydrocarbons.

Stable carbon isotopic and chemical compositions of natural gases have been used to identify their source organic matter (Schoell, 1980, 1983; Mattavelli et al., 1983; Faber and Stahl, 1984;
Whiticar, 1999), the maturity of their source rocks (Stahl and Carey, 1975; Stahl, 1977; Schoell, 1983; Clayton, 1991; James, 1983), their post-generation alteration (Prinzhofer and Huc, 1995; Prinzhofer and Pernaton, 1997; Lorant et al., 1998; Prinzhofer et al., 2000) and reservoir accumulation/loss histories (Tang et al., 2000; Cramer et al., 2001; Zou et al., 2005).

The ‘natural gas plot’ to identify the origin and mixing of natural gas was proposed originally by Chung et al. (1988). A supplement to this ‘natural gas plot’ and the potentially altered patterns are provided in this paper.


Tarim Basin, located in NW China, is one of the largest oil- and gas-bearing basins in China. Natural gases in this basin originated both from marine source rocks and coal measures. Statistical results (Jia et al., 2000) for the stable carbon isotope composition of natural gases show that the methane carbon isotope composition has a wide range, from $-52.0_{\text{oo}}$ to $-22.0_{\text{oo}}$ (PDB standard), and a large overlap zone between coal-derived and oil-associated gases (Fig. 1). A trend evident from Fig. 1 is that the carbon isotope values of gaseous hydrocarbons become heavier with increasing carbon number, which is in agreement with Chung et al. (1988). The overlap zone of the isotope values of the C$_2$–C$_4$ hydrocarbons from the two sources is relatively narrow, from $-26.0_{\text{oo}}$ to $-28.0_{\text{oo}}$. Dai (1999) reported the stable carbon isotope ranges of gaseous hydrocarbons that discriminate coal-derived from oil-associated gases. For oil-associated gases, the methane carbon isotope compositions range from $-55.0_{\text{oo}}$ to $-30.0_{\text{oo}}$; ethane isotope values are lighter than $-29.0_{\text{oo}}$, and propane isotope ratios lighter than $-27.0_{\text{oo}}$. For the coal-derived gases the methane carbon isotope compositions are between $-43.0_{\text{oo}}$ and $-10.0_{\text{oo}}$; ethane heavier than $-27.5_{\text{oo}}$ and propane heavier than $-25.5_{\text{oo}}$.

The carbon isotope compositions of a large number of individual samples of two kerogen types, oil-prone kerogen collected from the Middle-Upper Proterozoic in North China (Wang and Chen, 2004) and the Jurassic gas-prone kerogen from Kuqa depression in the Tarim Basin, are illustrated in Fig. 2. The carbon isotope compositions for oil-prone kerogens and coaly kerogens range from $-34.0_{\text{oo}}$ to $-26.0_{\text{oo}}$ and $-27.0_{\text{oo}}$ to $-22.0_{\text{oo}}$, respectively. Duan (1995) investigated the carbon isotope composition of 123 coal samples all around China; the results show that the carbon isotope values range from $-22.5_{\text{oo}}$ to $-25.5_{\text{oo}}$ for humic coals and from $-28.0_{\text{oo}}$ to $-35.0_{\text{oo}}$ for sapropelic coals.
The carbon isotope data mentioned above are summarized in Table 1, which suggest that there is a carbon isotope composition boundary between the oil- and coal-associated gases as well as between the oil- and the gas-prone kerogens that can be used to identify the origin and post-genetic alteration of the gases.

### 3. Experimental evidence

Pyrolysis techniques are frequently used to simulate hydrocarbon generation and maturation of organic matter. Different techniques have been employed: open system pyrolysis, closed system pyrolysis, and confined system pyrolysis are often reported in the literature. Numerous studies suggest that the gases generated by laboratory simulation of source rock maturation can be compared with field data, and that evidence for organic matter type as well as source rock maturity can be obtained.

In this study, pyrolysis of a type III kerogen isolated from a late Paleozoic coal collected from the Ordos Basin, North China, was performed in a confined system at 20 °C/h. The geochemical characteristics of the coal sample are presented in Table 2. The procedure of the confined pyrolysis was described in detail by Behar et al. (1997). Stable carbon isotope compositions of methane, ethane and propane are presented in Table 3. The carbon isotope data of gases generated during closed system pyrolysis of a Jurassic coal (Liu et al., 2002, 2003) and a calcareous shale (Type I kerogen, Huang et al., 1999) are also listed for comparison. Our results indicate that the gases are enriched in $^{13}C$ with higher pyrolysis temperatures (maturity increasing) and that the range of carbon isotope values is narrowed with increasing hydrocarbon carbon number. These observations indicate that the lower the carbon numbers of gases, the greater the isotopic fractionation between source rock and generated gases, and the higher the maturity, the less the isotopic fractionation between kerogen and the gases generated. The trends are consistent with previous studies (James, 1983; Schoell, 1983; Chung et al., 1988).

Berner et al. (1995) performed pyrolysis experiments on algal kerogen and land plant material in an open-system. Hydrous pyrolysis on coal and type II kerogen was carried out by Andresen et al. (1995). Isothermal (24 h) pyrolysis experiments on Type II kerogen in a confined system were carried out by Lorant et al. (1998). Huang et al. (1999) chose a calcareous shale (Type I) and Liu et al. (2003) employed a coal for isothermal (24 h) simulation experiments in a dry, closed-system and Gaschnitz et al. (2001) used coals for the non-isothermal pyrolysines in a dry, open-system. These results of carbon isotope analysis for the generated gases show a trend that gaseous hydrocarbons become enriched in $^{13}C$ as pyrolysis

### Table 1
Carbon isotope ranges of different materials and origins

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon isotope range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>$-55.0_{%}$ to $-30.0_{%}$</td>
<td>Dai (1999)</td>
</tr>
<tr>
<td>Ethane</td>
<td>$&lt;-29.0_{%}$ to $&gt;27.5_{%}$</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>$&lt;-27.0_{%}$ to $&gt;-25.5_{%}$</td>
<td></td>
</tr>
<tr>
<td>Kerogen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil-prone</td>
<td>$-34.0_{%}$ to $-27.0_{%}$</td>
<td>Wang and Chen (2004)</td>
</tr>
<tr>
<td>Gas-prone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sapropetic</td>
<td>$-35.0_{%}$ to $-25.5_{%}$</td>
<td>Duan (1995)</td>
</tr>
<tr>
<td>Humic</td>
<td>$-28.0_{%}$ to $-22.5_{%}$</td>
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</table>

### Table 2
Geochemical characteristics of coal sample used in confined system pyrolysis experiments

<table>
<thead>
<tr>
<th>Age code</th>
<th>$R_o$ (%)</th>
<th>Maceral (vol%)</th>
<th>Element (%)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Vitrinite</td>
<td>Exinite</td>
</tr>
<tr>
<td>C$_{3t}$</td>
<td>0.66</td>
<td>55</td>
<td>15</td>
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### Table 3
Carbon isotope compositions of hydrocarbon gases from pyrolysis experiments on coal and marine kerogen

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>Methane</th>
<th>Ethane</th>
<th>Propane</th>
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<tr>
<td>380</td>
<td>-33.0</td>
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<td>-26.2</td>
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<tr>
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<td>442</td>
<td>-35.8</td>
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<td>-22.5</td>
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<tr>
<td>550</td>
<td>-28.6</td>
<td>-21.3</td>
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temperature and the carbon atom number of produced gases increase, very similar to our findings.

4. Altered patterns

4.1. Established patterns

The known patterns of isotope-type curve previously reported (established) alterations of isotope-curve patterns that are mainly attributed to microbial activity. Chung et al. (1988) demonstrated that an unaltered isotope-type curve is nearly linear on the $\delta C_n$ vs. $1/n$ diagram (Fig. 3a). A classic pattern is a variation of this pattern observed for mixed (biogenic–thermogenic) gas, as demonstrated by Chung et al. (1988), Katz et al. (2002), Burruss et al. (2003), Sassen et al. (2003), Pohlman et al. (2005), and Hosgomez et al. (2005). This pattern shows a sharp decrease of the methane isotope value as compared to the unaltered isotope curve (Fig. 3b). Another alteration pattern related to microbial activity is bacterial oxidation, which results in a $^{13}$C enrichment of the higher molecular-weight hydrocarbon gases ($C_2^+$, especially propane) and a depletion of the methane (Fig. 3c), such as the cases given by

Fig. 3. The known patterns of the carbon isotope-type curves altered. (a) Unaltered; (b) mixed with biogenic gas; (c) bacterial oxidation; (d) methane leakage/diffusion.
Pallasser (2000) and Burruss et al. (2003). Gas leakage/diffusion has also been proposed to alter the isotope-type curve. Generally, the carbon isotope values of remaining methane becomes less negative, the residual gas would be enriched in $^{13}$C with increasing diffusion time in proportion to the progress of the diffusive leakage process (Fig. 3d), as illustrated by Clayton et al. (1997) and Prinzhofer and Pernaton (1997).

4.2. New characteristic patterns

Based on the statistical and experimental data, an improved interpretation of the “natural gas plot” is proposed in this paper. The potential examples for characteristic deviations from the established patterns of the ‘natural gas plot’ of Chung et al. (1988) and carbon isotope range boundaries of the gases generated from different kerogen types are given in order to identify the gas origins and their post-genetic alteration.

The two potentially systematic variations of the isotope-type curve patterns are related to the thermal stress that gases experienced in their source rock or gas reservoir, i.e. hydrocarbon gas cracking (secondary cracking) and thermochemical sulphate reduction (TSR). When the gases continue to undergo thermal stress after formation, the isotope-type curves patterns may change. We performed several pyrolysis experiments with coaly kerogen in a confined system at heating rates of 2–20 °C/h. Cracking of heavy hydrocarbon gas occurs between 450 and 480 °C, depending upon the heating rate (Table 3). Isothermal pyrolysis experiments on Type II kerogen in a confined system (Lorant et al., 1998) and on Type I kerogen in

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Fig. 4. The pattern of carbon isotope-type curve from oil-prone source rocks (a) and coals (b). The isotope-type curves of mature gas are nearly linear irrespective of their source rocks, whereas the curves are concave for overmature oil-associated gases and convex for overmature coal-derived gases. Solid line: isotope curve of gas generation; dashed line: isotope curve shift due to secondary cracking. (1) Type I kerogen (solid triangle, Huang et al., 1999); (2) Type II kerogen (solid square, data after Lorant et al., 1998); (3) Type III kerogen (solid circle, this study); (4) coal (open circle, Liu et al., 2003) and (5) xylite heated in open-system (open square, data after Berner et al., 1995).
a dry, closed-system (Huang et al., 1999) show that secondary cracking occurred in a similar temperature range. The typical pattern of the carbon isotope curve due to secondary cracking is illustrated in Fig. 4, which demonstrates that when the gaseous hydrocarbons are cracked, the dryness (C1/C1–5) increases (i.e. the portion of heavy hydrocarbon gases decreases) and the carbon isotope compositions of the residual C2+ gases shift towards a positive direction becoming enriched in 13C due to preferential cracking of 12C–12C bonds in C2+ alkanes. The carbon isotope composition of methane shows a small negative shift. The carbon isotope values of ethane and propane are heavier than those of their parent rocks, though the methane isotope composition is still within its isotope range. In addition, with secondary cracking a downward “concave” curve is displayed for oil-prone kerogen (Fig. 4a), whereas an upward “convex” curve is shown for gas-prone kerogen (Fig. 4b). This relationship is inferred to be associated with organic macromolecular catalysis. The pattern of the isotope-type curve may be modified by TSR in carbonate reservoirs, which will be discussed in Section 5.

Admixture of high maturity gas may also alter the isotope-type curve. Because high maturity gas is dominated by isotopically heavier methane, mixing results in a shift of methane isotopic composition towards heavier values. The characteristic patterns resulting from mixing of gases from mature type II and type III kerogen and from high maturity type II and type III kerogen are shown in Fig. 5. These data demonstrate that the mixing of gases from mature type II and type III kerogen changes the slope of the isotope-type curve, resulting mainly in a heavier methane isotope (Fig. 5a) which depends on the amount of coal-derived gas. The mixture of gases from high maturity type II and type III kerogens have relatively heavy isotope values for both methane and propane (Fig. 5b). The calculated results (Fig. 5) are similar to the cases provided by Hosgomez et al. (2005).

The mixing calculation of oil-and coal-associated gases suggests that the methane carbon isotope composition of the mixed gas mainly is

![Fig. 5. Isotope-type curves showing the patterns altered by the mixing of gas from mature type II and type III kerogen (solid line) and from overmature type II and type III kerogen (dashed line). Mixing of gases from mature type II and III kerogen changes the slope of the isotope-type curve less (a); a concave curve indicates mixing of the gas mixture from highly mature type II and type III kerogens (b). The gases components and carbon isotope compositions of pyrolysates of mature (400 °C) and high maturity (480 °C) type II kerogen are after Lorant et al. (1998), and those of high maturity (500 °C) coal are after Liu et al. (2002, 2003), respectively.](image-url)
controlled by the composition of the coal-derived gas, while the carbon isotope compositions of $C_{2+}$ hydrocarbons rely on the oil-associated gas. This is because the coal-derived gas is richer in methane and the oil-associated gas is relatively richer in $C_{2+}$ hydrocarbons. The potentially altered isotope-type curves linked to high temperature are very different from the conventional patterns mentioned above. The characteristic patterns are summarized in Fig. 6.

Fig. 6. Schematic patterns of isotope-type curves associated with high thermal stress. (a) Oil-associated gas with high maturity; (b) coal-derived gas with high maturity; (c) mixed oil- and coal-associated gases; (d) isotope-type curve pattern of TSR.
5. Case study and discussion

5.1. Geological setting

The Ordos Basin, with an area of over 250,000 km$^2$, is the second largest sedimentary basin in China and also one of the China’s largest natural gas provinces (Fig. 7). Four giant gas fields, containing more than 100 billion cubic meters of proven gas reserves, have been discovered in the shallow Ordovician and the Carboniferous-Permian (C–P) strata in the northern part of this basin (Dai et al., 2005). A simplified stratigraphic system is shown in Table 4. Yulin, Wushenqi and Suligemiao gas fields have gas reservoirs in the Permian sandstone reservoirs, while the reservoir strata of the Jingbian gas field is mainly the Ordovician weathered carbonate (i.e. the so-called weathered crust) close to the Carboniferous/Ordovician unconformity. Tables 5 and 6 present the carbon isotope composition of natural gas.
gases collected from the four giant gas fields, integrated after Dai et al. (2005), Cai et al. (2005) and Chen and Hu (2002). Several patterns of the carbon isotope-type curve are observed, suggesting gases are not generated from a single source rock or underwent post-genetic alteration (Figs. 8–11 and 13).

5.2. Natural gas in the sandstone reservoir – the isotope curve patterns for coal-derived gas and secondary cracking

The reservoir rocks of three giant gas fields, Yulin, Wushenqi and Suligemiao gas fields, are the C-P sandstone. It has been widely accepted that the natural gases of these gas fields were generated from the Carboniferous–Permian coal measures. However, different patterns of the ‘natural gas plot’ are still observed.

In the Yulin gas field, the carbon isotope compositions of methane, ethane and propane are \(-31.6\%_{\text{oo}}\) to \(-33.7\%_{\text{oo}}\), \(-25.8\%_{\text{oo}}\) to \(-26.3\%_{\text{oo}}\) and \(-23.8\%_{\text{oo}}\) to \(-24.9\%_{\text{oo}}\), respectively. They are within the isotope range of coaly gas. The isotope-type curve shows a typical coal-derived gas (Fig. 8), which supports strongly that the natural gas is derived from the C-P coal-bearing measure.

The other two gas fields, Wushenqi and Suligemiao, have also the C-P sandstones as reservoirs.
The isotope-type curves are obviously different from that of Yulin Field. Although the methane carbon isotope compositions suggest that the gases of Wushenqi and Suligemiao fields are from the same source rock as Yulin gases, i.e. the C-P coal measure, the heavy hydrocarbon gases (ethane and...
propane) are richer in $^{13}\text{C}$ than those of the Yulin gases and their values are above the isotope range of coal-derived gas (Fig. 9).

The reasons that the heavy hydrocarbon gases become richer in $^{13}\text{C}$ are possibly: (1) microbial oxidation, suggested by Burruss et al. (2003); (2) TSR, (e.g. Krouse et al., 1988; Machel, 2001); and (3) secondary cracking, Zou et al. (2006) for instance.

Biological activity occurs below $80^\circ\text{C}$ (Head et al., 2003). The present burial depth of the C-P reservoir strata in Suligemiao and Wushenqi gas fields is generally >2500 m, mostly between 2800 and 3400 m. Since the whole basin was uplifted during late Cretaceous (97 Ma), the reservoir temperature has not been below $90^\circ\text{C}$ (Fu et al., 2003; Dai et al., 2005). In other words, the temperature has been above the temperature for microbial activity (Head et al., 2003). Therefore, the heavy carbon isotope compositions of ethane and propane are unlikely to result from microbial activity. The reservoir rocks of these two fields are the Permian sandstone and silty sandstone (Dai et al., 2005; Xiao et al., 2005); the seal rocks are the Permian lacustrine mudstone (Dai et al., 2005; Xiao et al., 2005). Although part of the reservoir is within the temperature range for TSR (100–140 $^\circ\text{C}$) to occur (Machel, 2001), it is unlikely for TSR to take place in a sandstone reservoir because of the absence of sulphate. Therefore, no evidence supports TSR in either of these two gas fields. The burial depths of the reservoirs in Wushenqi and Suligemiao gas fields are generally deeper than that of the Yulin field, but the maximum temperatures that the reservoirs were

Fig. 8. ‘Natural gas plot’ of the Yulin gas field. The carbon isotope compositions of C$_1$–C$_3$ gaseous hydrocarbons are within the coal-derived gas range and a typical isotope-type curve of coal-derived gas is shown.

Fig. 9. Isotope-type curves of natural gas from Wushenqi (a) and Suligemiao gas field (b). The methane carbon isotope values are in the range of coal-derived gas; the carbon isotope values of both ethane and propane are above the range of coaly gas, suggesting secondary gas cracking.
exposed to were not more than 175 °C. Gas secondary cracking in the reservoirs is unlikely in the two gas fields. The source rock maturities of the Wushenqi and Suligemiao gas fields are relatively higher than that of the Yulin gas field. The vitrinite reflectance of the source rock for the Yulin gas field is 1.3–1.5% \( R_0 \), while the reflectance of the source rocks for the Wushenqi and Suligemiao gas fields is 1.6–2.0% \( R_0 \) (Fig. 7). Toward the south, the maturity increases to more than 2.0% \( R_0 \), covering a large area in the dry gas stage (Fig. 7). The most likely cause of the heavy ethane and propane isotope is secondary gas cracking within the source rock, which agrees with the experimental results (Fig. 4b).

5.3. Natural gas in the Ordovician carbonate reservoir – the pattern of isotope-type curve for mixing

The reservoir strata of the Jingbian gas field are mainly the Ordovician carbonates. From the end of the Ordovician to the middle Carboniferous, the whole basin was uplifted and exposed. Consequently, these strata underwent weathering and erosion, forming a 40–50 km wide weathered residue that was overlain by the C-P sequence (Cai et al., 2005). The weathered carbonate beneath the Carboniferous/Ordovician unconformity, the so-called weathered crust, became the main reservoir strata of this field. The cap rock is a bauxitic mudstone beneath the unconformity/coal measure for the top gas pools as well as argillaceous dolomite and marlstone for other gas pools. The C-P sandstone reservoir is distributed in a limited area of this field.
The origin of the gas produced from the Ordovician reservoirs remains enigmatic (Cai et al., 2005). There is no consensus on the source of the gases in the Jingbian gas field (Dai et al., 2005). The isotope-type curves of the natural gases from the Jingbian Field are complex, as demonstrated by Dai et al. (2005). In this paper, the carbon isotope data from the Jingbian Field, after Dai et al. (2005) and Cai et al. (2005), are divided into three groups according to reservoir age and sites (Table 6). The carbon isotope values of the hydrocarbon gases from fluid inclusions (Chen and Hu, 2002) are also presented in Table 6.

The patterns of the isotope plots of natural gases from the Ordovician carbonate reservoir are displayed in Fig. 10, and could provide a key to their origins. Fig. 10 illustrates the isotope-type curve of the gases around Well SC-1 in the Jingbian gas field (Fig. 10), which shows the isotope-type curve pattern of the C-P sandstone reservoir gases in the Jingbian Field (Fig. 10a) which are very similar to those of the C-P sandstone reservoirs in the Wushenqi and Suligemiao Fields (Fig. 9), suggesting both their identical origin and post-genetic alteration. In other words, all the natural gas discovered in the C-P sandstone reservoir of this basin was generated from the C-P coal measure. Interestingly, the Ordovician weathered crust gases (Fig. 10b) around this site also demonstrate the same patterns of isotope-type curve as the C-P sandstone reservoir gases (Fig. 10a), revealing a genetic relationship between the gases in the Ordovician carbonate and in the C-P sandstone reservoirs. Thus, the Ordovician weathered crust gases around Well SC-1 in the Jingbian Field appear to originate also from the C-P coal measure.

In contrast, a drastically different pattern of the isotope curve is exhibited by the Ordovician weathered crust gases far from Well SC-1 (Fig. 11), indicating the gas sources and post-genetic alterations...
are different from the C-P reservoir gases. The Ordovician weathered crust gases far from Well SC-1 have heavy propane and methane isotopes; concave isotope-type curves are observed (Fig. 11). However, the ethane isotope is still within the range of oil-associated gas. As stated above, the concave isotope-type curve may be caused by (1) gas leakage/diffusion; (2) high maturity oil-associated gas or (3) admixture of high maturity oil- and coal-associated gases.

According to the research performed by Clayton et al. (1997), Prinzhofer and Pernaton (1997) and Zhang and Krooss (2001), diffusive leakage may result in a $^{13}$C enrichment of the residual methane whereas the isotopic composition of propane should hardly change. In this case, isotopic composition of propane goes beyond the boundary of oil-associated gas, but ethane isotope is still within the range of oil-associated gas, which suggests that the Ordovician weathered crust gases far from Well SC-1 are affected by a diffusive leakage process. Although high maturity oil-associated gases may have heavy propane isotope isotopic compositions, exceeding the boundary of the characteristic field, the corresponding isotopic composition of methane remains usually within the range of oil-associated gas. Obviously, the weathered crust gases do not originate from one high maturity oil-prone source. Fig. 11 shows that all methane isotopes are within the range of coal-derived gas, suggesting methane origin is associated with coal measures. The most likely scenario is that the weathered crust gases far from Well SC-1 are mixtures of overmature oil- and coal-associated gases.

The bauxite seal distribution on the top of the Ordovician weathered crust reservoir is demonstrated in Fig. 12a. When the Carboniferous sequence was deposited, part of the bauxite on the Ordovician weathered crust was eroded, then filled with the Carboniferous mudstone or sandstone (Li et al., 2002), which partly replaced the bauxite as the cap rock of the Ordovician gas pool. The sealing capability of the Carboniferous sandstone/mudstone is less than that of the Ordovician bauxite, resulting in the migration of coal-derived gas of high maturity into the Ordovician reservoir of the Jingbian Field (Fig. 12b). Consequently, the carbon isotope compositions of methane in the Wushenqi, Suligemiao and Jingbian gas fields are very similar to each other (mainly $^{13}$C$_{32}$ to $^{13}$C$_{34}$), whereas the gas fractionation during expulsion and secondary migration (Snowdon, 2001) leads to predominantly methane migration into the Ordovician reservoir. Thus, the ethane and propane of the Ordovician reservoir gases keep the isotope characteristics of oil-associated gas with high maturity and the methane shows the influence of the isotope characteristics of coal-derived gas, resulting in the difference pattern of isotope-type curves from the C-P reservoir gases. The geological analysis further supports that the Ordovician weathered crust gases far from Well SC-1 are mixtures of overmature oil- and gas-prone sources. This is due to the erosion and the low seal quality of the Carboniferous strata that form a ‘window’ around Well SC-1, which...
becomes a channel for the C-P gases to enter the Ordovician reservoirs. Thus, a special scenario, in which both the C-P gases and the Ordovician gases have the same isotopic pattern, is observed. As illustrated in Fig. 12a, the coal-derived gas is limited around Well SC-1 between Hengshan and Jingbian Counties, whereas the mixed gas is distributed in a wide area far from Well SC-1.

5.4. Did TSR occur in the Ordovician carbonate reservoir?

Important information on the chemical components and isotope compositions of natural gas can be obtained from fluid inclusions in the reservoir (Thiery et al., 2000). Chen and Hu (2002) collected several samples from a calcite vein that occurred in the fractures of the Ordovician Jingbian Field reservoir. The gases in fluid inclusions were released by means of vacuum ball grinding, and then the carbon isotope compositions of the hydrocarbon gases were measured. The gases in the fluid inclusions were classified as coal-derived gas because of their heavy ethane isotope compositions (Chen and Hu, 2002). Based on the C1–C3 carbon isotope values of the gaseous hydrocarbons of these fluid inclusions, Cai et al. (2005) concluded that TSR took place in the Ordovician carbonate reservoir and resulted in the hydrocarbon gas becoming methane enriched with isotopically heavier carbon and an increasing dryness coefficient.

The isotope-type curves of the fluid inclusions are shown in Fig. 13, in which the carbon isotope range of TSR described by Machel et al. (1995) and Machel (2001) and a TSR case provided by Krouse et al. (1988) are also illustrated for comparison. Both patterns of isotope-type curves, coal-derived gas and TSR, are shown in Fig. 13.

The carbon isotope compositions of the C1–C3 gases in the fluid inclusions suggest that TSR took place in the Ordovician carbonate reservoir. However, the same isotope-type curve pattern is not observed in numerous wells and pool gases. In contrast, a concave isotope-type curve with light ethane isotope value is prevalent in the Ordovician carbonate reservoir (Fig. 11), which seems to indicate that the TSR is uncommon in this reservoir.

![Methane isotope vs. ethane isotope diagram](image)

Fig. 14. Methane isotope vs. ethane isotope diagram. The gases in the C-P reservoirs, the Ordovician reservoir near Well SC-1 and one fluid inclusion are coal-derived gases. The gases of the other two fluid inclusions have obviously distinctly different characteristics (TSR). The other gases in the Ordovician reservoirs of the Jingbian gas field show a trend of gradually approaching the C-P reservoir gases, indicating an increase in coaly gas in the gas mixture.
An alternative explanation for the increasing dryness coefficient is the mixing of coal-derived methane as well as C$_{2+}$ cracking in the reservoir. The methane vs. ethane isotope diagram of natural gases from different gas fields/reservoirs of the Ordos Basin is illustrated in Fig. 14, which shows three clusters among them, the gases in the C-P reservoirs, the Ordovician reservoir near Well SC-1, and one fluid inclusion have a characteristic increase of methane isotope values as ethane isotope value increase, demonstrating a maturity trend and a genetic relationship between them. The other two gases from fluid inclusions and the other gases in the Ordovician reservoirs of the Jingbian Field are far from this cluster, suggesting their different origins and/or post-genetic alterations.

6. Conclusions

On the basis of statistical and pyrolysis experimental data, the carbon isotope range and boundary of hydrocarbon gases generated from gas-prone and oil-prone source rocks are used to modify the ‘natural gas plot’ proposed originally by Chung et al. (1988). Deviation from the typical patterns may be caused by heavy hydrocarbon gas cracking, thermochemical sulphate reduction, and mixing as discussed using a case study in this paper. The following origins and post-genetic alterations of natural gas are recognized by applying these patterns to the Ordos Basin:

(1) Different isotope patterns result from secondary cracking and TSR. A convex curve with heavy ethane and propane isotope values is indicative of coal-derived gas cracking and TSR because of catalysis in reservoirs. In contrast, a concave curve with large differences between ethane and propane isotes is found when oil-associated gas secondary cracking occurred.

(2) The natural gas discovered in the Yulin gas field is a typical coal-derived gas, generated from the Carboniferous–Permian coal-bearing measures. The natural gases in the Wushenqi and Sulingemiao gas fields are highly mature coal gases. The heavy carbon isotope compositions of ethane and propane are thought to be caused by secondary cracking of C$_{2+}$ hydrocarbons.

(3) Mixing of oil-associated gas and coal-derived gas takes place in the Ordovician reservoirs of the Jingbian gas field, while the natural gas around Well SC-1, whether found in the Ordovician or in the C-P reservoirs, is mainly from the C-P coal measures. In the gas mixture, methane is mainly from the C-P coal measures and the C$_{2+}$ gaseous hydrocarbons are generated from highly mature carbonate.

(4) The isotope-type curves of the hydrocarbon gases from fluid inclusions suggest that TSR took place in the Ordovician carbonate reservoir of the Jingbian Field during its geologic history, but those of the reservoir gases show that TSR is less common in gas pools. The increasing dryness may be related to methane mixed from the C-P coal-derived gas and heavy gaseous hydrocarbon cracking in the Ordovician reservoir.

Acknowledgements

We thank Drs. J.Z. Liu and W.L. Jia for their assistance in carrying out pyrolysis experiments and isotopic analysis. This work was supported financially by the Natural Sciences Foundation of China (Grant Nos. 40572083 and 40272067). Prof. Philip A. Meyers (University of Michigan, USA) is gratefully acknowledged for his comments and language improvements. The manuscript benefited greatly from the very careful and detailed reviews of two anonymous reviewers.

Associate Editor—Maowen Li

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