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Distribution and Significance of Oxygen Isotope in CO_2 of Natural Gas

Li Jin[1,2], Li Zhisheng[1,2], Li Jian[1,2], Wang Dongliang[1,2], Zhang Ying[1,2]

[1]Research Institute of Petroleum Exploration and Development (Langfang Branch), Petrochina, Langfang, HeBei, China

[2]The Key Laboratory of Gas Formation and Development, Petrochina, Langfang, China

The natural gas containing CO_2 is distributed throughout the world, but that with high content of CO_2 is mainly distributed in mantle uplifts, volcanic magma activity areas, crustal activity areas with quite developed fault systems, carbonate distribution areas with geothermal anomaly, oil and gas enrichment areas and coal-bearing basins. Currently, the natural gas with high content of CO_2 is discovered mainly in Pacific Rim countries and regions. CO_2 gas reservoirs in China are mainly distributed in the eastern fault basins, where more than 30 CO_2 gas reservoirs (fields) have been found primarily in Hailar Basin of Inner Mongolia, Songliao Basin, Bohai Bay Basin, Subei Basin, Sanshui Basin of Guangdong, Pearl River Mouth Basin, Yingge Sea Basin of South China Sea and Fushan Depression of Beibu Gulf. Especially in recent years, a number of pure CO_2 gas fields have been drilled in Songliao Basin.

The CO_2-rich natural gas causes huge risks and engineering technical problems to exploration and development of subsurface hydrocarbon gas. In terms of natural gas exploration and geosciences research, CO_2 in natural gas is an excellent indicator for geologists to understand nature. CO_2 with various origins makes different contributions to crustal fluids, which directly affects the objective understanding on research targets. Therefore, studies conducted by many domestic and foreign geologists focus on CO_2 origins and its identification indices. In the identification of CO_2 origins, the geochemical methods, such as the abundance of noble gases and isotope ratios, are used and combined with geological conditions of gas accumulation to investigate CO_2 origins by domestic and foreign scholars. As viewed from the research achievements, the identification methods of CO_2 origins mainly include the identification method of CO_2 component content, the ratio method of stable carbon isotope $\delta^{13}C_{CO2}$, and the identification methods of $^3He/^4He$ ratio and $CO_2/^3He$ ratio.

In geological bodies, $\delta^{18}O$ value of oxygen in atmosphere is fairly constant as 23.5‰(PDB) (Kroopnick and Craig, 1972). The compositions of carbon and oxygen elements in carbonates of sediments, bio-organic matters and natural waters are closely related to the formation of oil and gas. The carbon and oxygen isotopes of marine and lacustrine carbonates are mainly distributed

from -37‰ to -6‰ (PDB) and from -10‰ to 10‰ (PDB) respectively (Galimov, 1968; Verzer et al., 1976, 1980). Those of bio-organic matters are distributed from -37‰ to -6‰ (PDB) and from 14‰ to 30‰ (PDB) respectively (Deines, 1980; Chen Tuo et al., 1999). The carbon (in dissolved bicarbonate) and oxygen isotopes of natural waters (ocean water, river water and lake water) are distributed from -12‰ to 1.5‰ (PDB) -1 to 5 and from -9‰ to 0‰ (SMOW) respectively (Mook, 1970). The studies on carbon and oxygen isotopes of CO_2 in natural gas are expected to provide a new approach for determining CO_2 origins in natural gas. Moreover, no reports are available currently investigating CO_2 origins with carbon and oxygen isotope compositions of CO_2 in natural gas. By using the technology of gas chromatography linked to isotope mass spectrometry, the carbon and oxygen isotopes of CO_2 in natural gas of Songliao Basin, Tarim Basin and Sichuan Basin were studied and a new identification method of CO_2 origins in natural gas was proposed in this study.

The CO_2 samples were collected from Xujiaweizi depression of northern Songliao Basin and Changling depression of southern basin, where CO_2 in natural gas was closely related to deep and large faults, showing a typical origin of inorganic mantle source (Tan Ying et al., 2006, Dai Jinxing et al., 2007). The contents of non-hydrocarbon components in natural gas of Sichuan Basin are low, and non-hydrocarbon / hydrocarbon ratios are generally below 0.05. In non-hydrocarbon gases, the contents of helium and argon are low, the order of magnitude of $^3He/^4He$ is 10^{-8} and that of $^{40}Ar/^{36}Ar$ is generally between 500 and 1870, showing the characteristics of crustal material sources (Dai Jinxing et al., 2003). The CO_2 in natural gas collected from Tarim Basin shows organic origin. The Ordovician natural gas in central Tarim Basin shows the origin of crude oil cracking, and the Carboniferous gas has both kerogen-cracking gas and oil cracking gas. The natural gas in AKemomu gas field of western Tarim Basin is mainly derived from Carboniferous Type –II source rocks (Wang Zhaoming et al., 2005). The natural gas in Lunnan area is dominated by methane, mainly as the oil cracking gas derived from high - over maturity Mid - Lower Cambrian source rocks (Wang Xiaomei et al., 2008). The natural gas in Hetianhe gas field is dominated by hydrocarbon gases with high non-hydrocarbon gas content generally between 10% and 25%, which was considered as sapropelic gas derived from Cambrian source rocks by Zhao Mengjun (2002).

Based on the compositions of oxygen isotope ($\delta^{18}O_{CO2}$) in CO_2 of natural gas samples in Songliao Basin, Tarim Basin and Sichuan Basin, different CO_2 origins in the three basins were divided well by combining CO_2 content (fig.1). The CO_2 with oxygen isotopes less than 10‰ can be regarded as inorganic origin; while CO_2 content with organic origin is usually not very high. It was believed by Dai Jinxing et al. (1996) that the CO_2 with the content less than 15% or 20% mostly showed organic origin. Accordingly, the CO_2 with the content less than 25% and $\delta^{18}O_{CO2}$ greater than 10‰ was considered as organic origin. In this figure, the CO_2 in natural gas of Xushen well block in Songliao Basin is distributed in the same area to that of Sichuan Basin and Tarim Basin. Therefore, the CO_2 with the content between 0 and 5% and $\delta^{18}O_{CO2}$ between 10‰ and 15‰ was considered as the coexistence of organic and inorganic origins in this study.

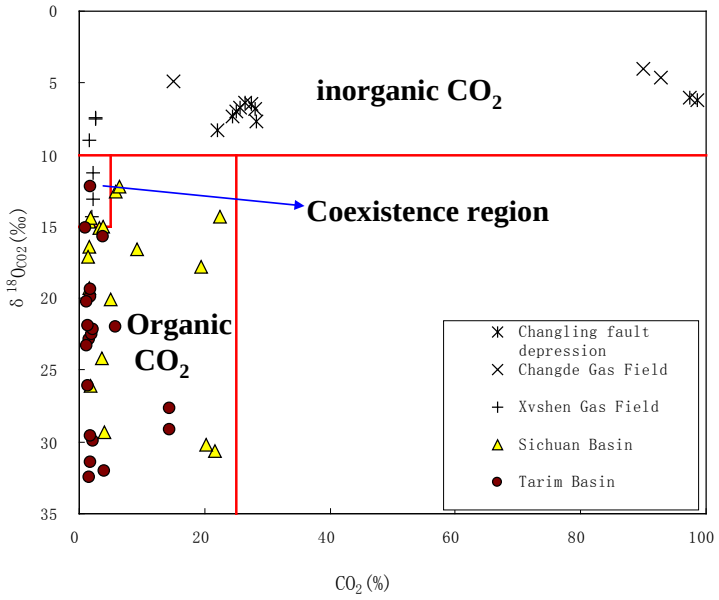

Figure 1 The relationship between CO_2 oxygen isotope and CO_2 content in natural gas

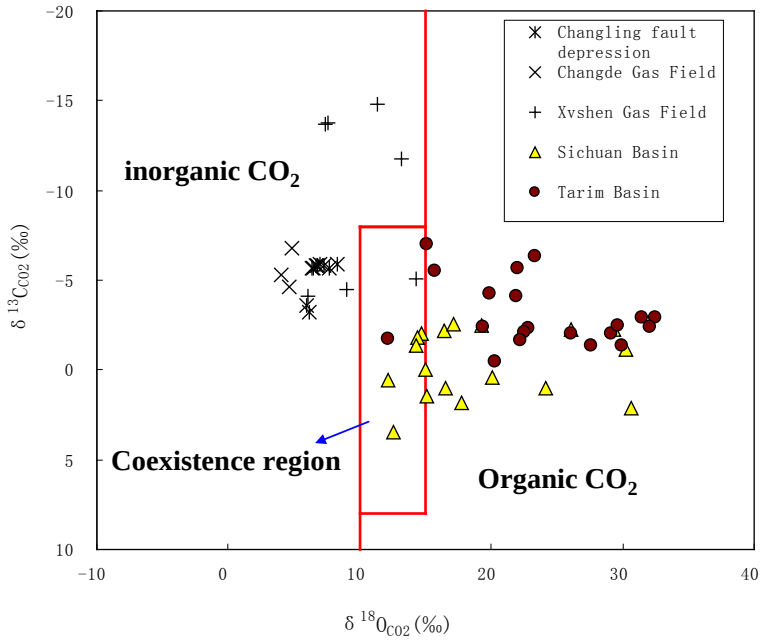

Figure 2 The relationship between CO_2 oxygen isotope and CO_2 carbon isotope in natural gas

Although $\delta^{13}C_{CO2}$ value was used to identify CO_2 with organic and inorganic origins, limitations still exist. The CO_2 with $\delta^{13}C_{CO2}$ value between -8‰ and 8‰ was considered as the coexistence of organic and inorganic origins in this study. By combining $\delta^{18}O_{CO2}$ value, CO_2 in natural gas of the three basins could also be well divided, i.e., the CO_2 with $\delta^{18}O_{CO2}$ greater than

15‰ showed organic origin; the CO_2 with $\delta^{18}O_{CO2}$ between 10‰ and 15‰ and $\delta^{13}C_{CO2}$ value between -8‰ and 8‰ was the coexistence of organic and inorganic origins; the others showed inorganic origin(fig.2).

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