Combination of Inorganic and Organic Geochemistry to Study Mechanism of Carbon Isotope Anomalies of Natural Gas

Introduction

In general, the carbon isotope value of natural gas increases gradually with the carbon number, which is called the positive carbon isotope sequence ($\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4$). Most of the organic genetic natural gas has a positive carbon isotope sequence; however, the inorganic genetic natural gas generally has a negative carbon isotope sequence ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3 > \delta^{13}C_4$) (Galimov, 2006). If the carbon isotope value shows a disorderly sequence with increasing carbon number, it is referred to as a carbon isotope anomaly.

The Ordos Basin is an important natural gas production area in China. The total proven reserves of natural gas are $4.3461.89 \times 10^8$ m$^3$, accounting for 1/3 of the accumulative proven reserves of China. Natural gas is stored mainly in two sets of reservoirs: the Upper Palaeozoic terrestrial clastic rock reservoir and the Lower Palaeozoic marine carbonate reservoir. The central gas field is stored in the marine Ordovician Majiagou Formation dolomite (OMFD). Except for the central gas field, other gas fields are stored in the Upper Palaeozoic terrestrial clastic rock reservoirs, and the source rocks are Carboniferous–Permian humic coal measures.

Most of the natural gas stored in the Upper Palaeozoic does not show a carbon isotope anomaly. However, the central gas field does possess a carbon isotope anomaly, which leads to controversy about the source and genetic type of the natural gas.

Previous studies have focused mainly on organic geochemical characteristics, such as natural gas composition, carbon and hydrogen isotopes, and source rock evaluation. However, very few scholars have studied the inorganic geochemical characteristics of the OMFD to illustrate the carbon isotope anomalies. Thus, this study took the inorganic geochemical characteristics of the OMFD as a breakthrough point and combined inorganic geochemical parameters with organic geochemical responses. On this basis, the causes of natural gas carbon isotope anomalies have been studied.

Samples and Methods

Twenty-five dolomite core samples were collected from the Ordovician fifth member of Majiagou Formation of the Ordos Basin ($O_1 m_5$). Inorganic parameters including oxygen isotopes, carbon isotopes, strontium isotopes, order degree, and REEs were analysed. Natural gas samples from the 25 corresponding wells were collected and analysed for organic geochemical parameters, including composition and carbon isotopes.

Results

Organic geochemical data of natural gas: Hydrocarbon gases, ranging from 85.6 to 99.2% with the average value of 94.8%, dominate the central gas field. The hydrocarbon gas is mainly methane, and the dryness coefficient is distributed between 93.7 and 99.9%. Non-hydrocarbon gases include mainly CO$_2$ and N$_2$. The $\delta^{13}C_1$ vary from $-39.1$ to $-30.7$‰, with a mean value of $-34.2$‰. The $\delta^{13}C_2$ fluctuate greatly and have the widest distribution interval ($-37.1$ to $-23.4$‰). The carbon isotope values of propane and butane do not show obvious anomalies. A carbon isotope anomaly appeared in some wells in the central gas field ($\delta^{13}C_1 > \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4$), i.e., the $\delta^{13}C_2$ value is the lightest value.

Inorganic geochemical data of dolomite: The oxygen isotope values range from $-11.9$ to $-5.8$‰, with an average value of $-8.4$‰. The carbon isotope values vary from $-12.5$ to $1.1$‰, with a mean value of $-2.1$‰. The strontium isotope values distribute between 0.7088 and 0.7369, with an average value of 0.7173. The OMFD has a large order degree, ranging from 0.72 to 0.98, with an average of 0.89.

Discussion
Inorganic Oxygen and carbon isotopes: The δ¹⁸O value of some of the OMFD samples was more depleted than that of Ordovician seawater. When dolomitization occurs under burial conditions, temperatures are higher than near surface conditions. Due to thermal isotope fractionation, relatively heavy oxygen isotopes enter the metasomatic fluids while relatively light oxygen isotopes enter the dolomite lattice. Therefore, the buried dolomite acquires a more depleted δ¹⁸O than the Ordovician seawater. Most of the OMFD samples plotted into the high-temperature dolomite group, indicating that the dolomitization of the Ordovician Majiagou Formation occurred in a high-temperature environment (Figure 1).

**Figure 1** Cross-plots between δ¹³C and δ¹⁸O of dolomite from the Ordovician Majiagou Formation in the Ordos Basin, China.

Wang et al. (2009) studied the average homogenization temperature of fluid inclusions in the OMFD and the δ¹⁸O value (Figure 2). The δ¹⁸O values are basically consistent with the result of this study, and most of the values distribute between −10 and −6‰. The δ¹⁸O value of the diagenetic fluid (water) varies from +4 to +12‰, with an average value of +8‰, which is more positive than the Ordovician seawater. Smith (2006) stated that if the fluid composition does not change much (compared to + 8‰ in Figure 2a), then the formation temperature can be estimated accurately from the figure. From Figure 2, it was estimated that the temperature during formation of the OMFD was at least 130 °C, which further confirmed that the OMFD is high-temperature buried dolomite. Zhang et al. (2019) studied the homogenization temperature of fluid inclusions in the OMFD, which ranged from 120 °C to 163 °C, with an average value of 140 °C (Figure 2b). This result further shows that the OMFD was formed at a relatively high temperature, indicating a high-temperature buried dolomite.

**Figure 2** (a). Spider graph between δ¹⁸O and the average homogenization temperature of fluid inclusions of the OMFD and saddle dolomite with cavity filling. Water value from the SMOW standard (after Smith, 2006). (b). Histogram of homogenization temperature of the OMFD.

The δ¹³C value of dolomite can be used to determine whether the diagenetic fluid experienced mixing of organic carbon. Carbon from organic sources, i.e., CO₂ from hydrocarbons, is more depleted than
that of atmospheric CO₂. These materials with more depleted δ¹³C values undergo isotope exchange with carbonate rock during diagenetic processes, which generates carbonate rock with a more depleted δ¹³C value. The δ¹³C value of a part of the OMFD is within the range of the Ordovician seawater (−2.0‰ to 0.5‰). The other part is more depleted than the δ¹³C value of the Ordovician seawater (Figure 1). This illustrates that the dolomitization fluid of part of the OMFD continued to be from the seawater. During the process of dolomitization of these OMFD, they were not affected by organic carbon. However, the other part of the OMFD was affected by organic carbon during the process of dolomitization. The mixing of organic carbon caused the metasomatic fluid to become rich in ¹²C, which caused the δ¹³C value of this part of the OMFD to be more depleted than the Ordovician seawater.

Inorganic-Strontium isotopes: The ⁸⁷Sr/⁸⁶Sr value of the OMFD is higher than that of the seawater during the same period. The dissolution of aluminosilicate minerals during burial diagenesis can provide marine carbonate with radiogenic strontium and cause an increase in the strontium isotope ratio. When subsurface brine exchanges with carbonate rocks under burial conditions, radioactive ⁸⁷Sr is mixed in, causing the ⁸⁷Sr/⁸⁶Sr value of subsurface brine to be higher than the average value of the seawater (0.70878). Therefore, the metasomatic fluid in the OMFD is likely to be subsurface brine under burial conditions. This shows that the OMFD is buried dolomite, which is consistent with the result based on the δ¹⁸O value.

Inorganic-Dolomite order degree: The order degree of the OMFD varies from 0.72 to 0.98, with an average value of 0.89, indicating that the dolomite grows slowly and has sufficient conditions to form a crystal structure close to the ideal dolomite. Thus, the OMFD has a large order degree and is buried dolomite. In addition, the order degree is also related to the crystallization temperature of dolomite. The order degree of dolomite formed at high temperature is larger than that of dolomite formed at low temperature. This indicates that the OMFD may have formed in the burial diagenesis stage with higher temperature, which is consistent with the oxygen isotope and strontium isotope results.

Inorganic-REEs: The REE content of seawater is very low, it was amplified by 10⁶ times before standardization. We proposed an identification templet that distinguishes dolomites of different genetic types according to their REE distribution patterns (Figure 3a-3d). The OMFD has the lowest REE content, there is an obvious negative Ce anomaly, and the REE distribution pattern shows fluctuating characteristics (Figure 3e). The REE distribution patterns of the OMFD are consistent with the templet of high-temperature hydrothermally altered dolomite. This shows that the OMFD was subjected to the influence of high-temperature hydrothermal alteration in the later period, which caused the carbon isotope anomaly of the natural gas stored in it.

![Figure 3 Seawater-normalized REE distribution patterns of the Ordovician Majiagou Formation dolomite. (a). Penecontemporaneous dolomite of seawater origin; (b). Atmospheric precipitation leaching dolomite; (c). Dolomite affected by diagenetic fluid; (d). High-temperature hydrothermal altered dolomite. (e). OMFD.](image)

Organic geochemical response: Although the overall quality of the OMFD is poor, there are good source rocks in some sections, which have a certain hydrocarbon generation capacity and can generate a small
amount of natural gas. The gas samples distributed in the oil-associated thermogenic gas (OA) and late mature thermogenic gas (LMT) groups (Figure 4). The OA group indicates that there was a mixture of marine sapropelic organic matter involved in the formation of the natural gas, which may have come from the OMFD. The LMT group indicates that the natural gas experienced late high temperature effects. This result is consistent with the aforementioned results based on inorganic geochemical data.

**Figure 4** $\delta^{13}C_1$ vs. $CH_4/(C_2H_6+C_3H_8)$ indicating genetic types of natural gas (after Milkov and Etiope, 2018).

**Conclusions**

Natural gas stored in the OMFD of the central gas field exhibits a carbon isotope anomaly ($\delta^{13}C_1 > \delta^{13}C_2$). Previous studies focused mainly on the organic geochemical parameters, including natural gas components, carbon and hydrocarbon isotopes, and source rock evaluation. However, there are no reports on the application of inorganic geochemical parameters to the study of the carbon isotope anomalies in the natural gas in the central gas fields. In this study, inorganic and organic geochemical parameters were combined to study the cause of the carbon isotope anomalies of the natural gas in the central gas field. Inorganic geochemical parameters, including oxygen isotopes, strontium isotopes, dolomite order degree, and REEs, indicated that the OMFD incurred a high-temperature effect during the dolomitization process. This high temperature led to the carbon isotope anomalies of the natural gas stored in the OMFD. Inorganic carbon isotopes indicated that the organic carbon was mixed in the process of dolomite formation. The organic geochemical characteristics, including source rock and natural gas composition as well as carbon isotopes, suggest that this additional organic carbon was derived from the OMFD itself. The combination of inorganic geochemical characteristics and organic geochemical response proves that the carbon isotope anomaly in the central gas field is attributable to the high-temperature effect and organic carbon mixing.

**References**