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Origins of natural gases from marine strata in Northeastern Sichuan Basin (China) from carbon molecular moieties and isotopic data

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ABSTRACT

To determine the origin, maturity, formation mechanism and secondary process of marine natural gases in Northeastern Sichuan area, molecular moieties and carbon isotopic data of the Carboniferous and Triassic gases have been analyzed. Typical samples of marine gas precursors including low-maturity kerogen, dispersed liquid hydrocarbons (DLHs) in source rocks, residual kerogen and oil have been examined in a closed system, and several published geochemical diagrams of gas origins have been calibrated by using laboratory data. Results show that both Carboniferous and Triassic gases in the study area have a thermogenic origin. Migration leads to stronger compositional and weak isotopic fractionation, and is path dependent. Carboniferous gases and low-H_2S gases are mainly formed by secondary cracking of oil, whereas high-H_2S gases are clearly related to the TSR (Thermal Sulfate Reduction) process. Gases in NE Sichuan show a mixture of heavy (^{13}C-enriched) methane in comparison to the lower maturated ethane of Triassic gas samples, suggesting a similar source and maturity for ethane and propane of Carboniferous gases, and a mixture of heavy ethane to the propane for Triassic gases. Based on the data plotted in the diagram of Chung et al. (1988), the residual kerogen from Silurian marine shale and palaeo oil reservoirs are the main source for Carboniferous gases, and that the residual kerogen from Silurian and Permian marine rocks and Permian paleao oil reservoirs constitute the principal source of Triassic gases.

1. Introduction

The Sichuan Basin is the largest basin in China with the largest natural gas reserves and production, especially in the marine strata in the northeastern areas (Xie et al., 2000). Marine gas reserves account for 70% of the production in the whole basin (Zhang and Zhu, 2006). Gases have been discovered in marine strata from Silurian to Jurassic, but most gas reservoirs are found in the Carboniferous *Huanglong* formation, Permian *Changxing* formation, and Lower Triassic *Feixianguan* formation. Currently, seven large gas fields with gas reserves larger than 30 billion cubic meters have been discovered in marine strata of Northeastern Sichuan (Table 1), the *Wolonghe*, *Wubaiti*, *Shapingchang*, *Luojiazhai*, *Dukouhe*, *Tieshanpo* and *Puguang* gas fields (Dai et al., 2008). Wang et al. (2004) recognized that the natural gases of marine strata in eastern Sichuan originated from secondary cracking of previously formed oil, though some studies argue different viewpoints (Zhao et al., 2006; Ma et al., 2008). Besides oil cracking, highly maturated residual kerogen is regarded as another very important source for natural gases in the Carboniferous strata in Eastern areas whereas TSR (Thermal Sulfate Reduction) is considered to be very important for the formation of highly maturated methane in Triassic strata in the Northeastern areas (Zhao et al., 2006; Ma et al., 2008). Analysis of the carbon molecular moieties and isotopic composition of gas samples indicates that most Carboniferous and Triassic natural gasses show extensive mixing (Wang et al., 2008). Because of the high maturity of both gases and source rocks, the origin and formation mechanism of marine natural gases in NE Sichuan area are complicated and less studied. Compared to secondary cracking of oil, the contribution of primary cracking of highly-maturated residual kerogen and roles of TSR and other post-reservoir alternation process such as migration and mixing are still not well understood. In addition, there exist multiple layers of source rocks overlaying each other, making the petroleum reservoir systems complex, and the post-Triassic transition from marine to terrestrial deposition adjusted source-reservoir layout (Ma et al., 2008). It is therefore of significance to study the origin of marine natural gases and characterize the impact of secondary processes. In this study, carbon molecular moieties and isotopic data of Carboniferous and Triassic gases as well as some molecular and isotopic diagrams were constructed to identify gas origin, to estimate gas maturity, and probe the impact of late stage of tectonic evolution.

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Table 1
List of seven large (>30 billion m^3) gas fields (Dai et al., 2008; Ma et al., 2008).

Gas field	Strata symbol the reservoir rock	Gas reserves (Billion M^3)
Wolonghe	C, P_1, P_2, T_1	44.6
Wubaiti	C, P	58.7
Shapingchang	C, P_1, P_2, T_1	39.7
Luojiazhai	T_{1f}, T_{1j}	72.1
Dukouhe		35.9
Tieshanpo		37.4
Puguang	T_{1f}	356

2. Geological setting and method

The Sichuan Basin is situated in the southwestern part of China (Fig. 1). The marine deposits in Northeastern Sichuan dating from Sinian of later Proterozoic to earlier Carboniferous are mainly carbonate (Fig. 2), among which the lower Silurian strata (S_1) consisting mainly of dark shale deposited on a wide shelf with TOC = 0.6–1.6% (Hu, 1997). The whole area uplifted during the Caledonian orogeny, and the Devonian and early Carboniferous strata have been abraded. During late stage Caledonian movement, the whole NE Sichuan experienced a transgression as manifested by a sequence of mudflat carbonates (C_{2h}, *Huanglong* Formation) with 40–50 m residual depth. At the end of the Carboniferous, the area was uplifted again and the top part of C_{2h}, i.e., the Upper Carboniferous, was strongly weathered forming abundant secondary pores becoming important reservoir rocks in eastern Sichuan. From Permian to Triassic, the area experienced a new deposition cycle including Permian reef carbonates, slope clastics, and thin coal seams followed by earlier Triassic oolitic carbonates in the northeastern area, forming another important reservoir rock in NE Sichuan.

As far as tectonic controls and trap properties are concerned, Carboniferous and Triassic gas pools exhibit different characteristics: Carboniferous traps are mainly anticlines whereas Triassic traps are mainly fault-controlled (Hu, 1997). The later Himalayan movement significantly influenced both Carboniferous and Triassic gas pools, reworking the Carboniferous traps into steep anticlines, and the Triassic ones into fault-sealed ones (Wang et al., 2004). In this study, we sampled Carboniferous gas from *Wubaiti*, *Shapingchang* and *Wolonghe* in eastern Sichuan area and Triassic gas from *Liujiazhai*, *Tieshanpo* and *Dukouhe* in Northeastern Sichuan area. The molecular moieties, C_1, C_2, and C_3, and carbon isotopes were analyzed in laboratory by gas chromatograph (GC) and gas chromatograph isotope ratio mass-spectrometer (GC-IRMS). The chemical and isotopic compositions of gas samples are listed in Table 2. For comparison, some published data of gas chemical and isotopic compositions were also used for plotting.

We calibrated several published geochemical diagrams of gas origins using our laboratory data in this study. Laboratory pyrolysis was carried out in a closed system on gas generated from typical samples of marine gas precursors including low-maturity kerogen, dispersed liquid hydrocarbon (DLH) in source rocks, residual kerogen, and oil. These samples included low-maturity kerogen, dispersed liquid hydrocarbon (DLH) in source rocks, residual kerogen and in-reservoir oil. Geochemical characteristics of both source rocks and oil for laboratory simulation are listed in Table 3. From these basic chemical and isotopic as well as their maturities, they can be easily classified as type II (marine origin) kerogen. The molecular moieties and isotopic compositions of pyrolysis gases from these samples were analyzed and used for diagram calibration to identify the origin of the gas, estimate gas maturity and probe the impact of secondary processes. Our pyrolysis apparatus consists of a closed, temperature-programmed (non-isothermal), gold-tube system described by Wang et al. (2006). The experiments were carried out at heating rates of 2 °C/h and 20 °C/h. Pyrolysis procedures and analysis have been described in detail by Wang et al. (2006, 2007). In a closed system, the liquid hydrocarbon and residual kerogen of marine source rocks mix together in hydrocarbon generation, making it difficult to discriminate the two types of gases. We therefore performed separate experiments for the generation of liquid hydrocarbon and residual kerogen. We first carried out kinetic experiments for low-maturity kerogen by heating to the temperature range between liquid hydrocarbon generation and cracking (390–400 °C for this sample). Next we

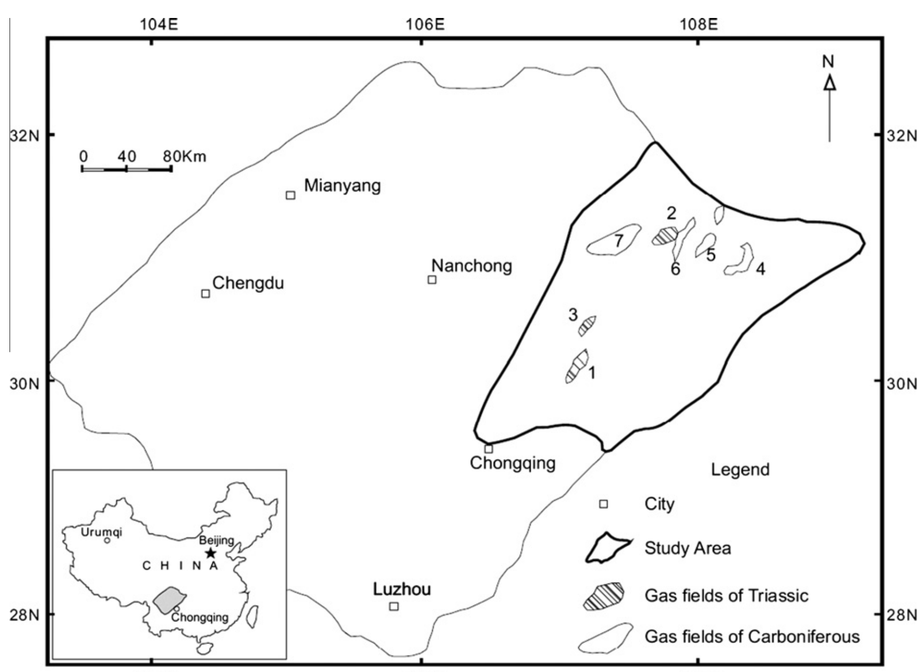

Fig. 1. Map of the Sichuan Basin showing its location in China, the study area and gas fields (1. Wolonghe; 2. Wobaiti; 3. Shapingchang; 4. Luojiazhai; 5. Dukouhe; 6. Tieshanpo; 7. Puguang. Here, C refers Carboniferous; T refers Triassic).