Geological Characteristics of Lower Paleozoic Shale Gas Accumulation in the Yuxi Region, Southern Sichuan Basin: In View of High-Density Methane Inclusions

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1. INTRODUCTION

China has great potential for unconventional resource development, among which shale gas is the mainstay of natural gas. Currently, several sets of shale gas formations have been discovered in the Sichuan Basin, among which the Upper Ordovician Wufeng Formation-Lower Silurian Longmaxi Formation is the main field of shale gas exploration and development in China. Shale gas demonstration areas such as Changning, Weiyuan, Puling, and Zhaotong have been successively established to realize economies of scale development in medium and shallow layers with a burial depth of 2000–3500 m. The deep Wufeng-Longmaxi Formation in the southern Sichuan Basin (burial depth at 3500–4500 m) has the characteristics of a wide area and large resource potential. As a target area for deep shale gas exploration and development, the Yuxi Region has obtained industrial gas flow.

Under the multicycle tectonic background of the Sichuan Basin, the Wufeng-Longmaxi shales in the southern Sichuan Basin have undergone an early deep burial and late strong uplift process. During the deep burial stage, the organic matter reached a high maturity stage and generated large amounts of methane, while in the uplift stage, the hydrocarbon generation of organic matter stopped and the late gas reservoir was adjusted, which made the shale gas enrichment mechanism different in different regions. However, it is undeniable that the preservation degree of shale gas is directly related to over-pressure. Most of the high-yield wells in the basin are strongly overpressured. Overpressure and shale gas preservation and enrichment have become hot issues in global research.

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Previous research has studied shale gas enrichment from the perspectives of shale organic matter enrichment, pore evolution, and methane adsorption capacity.\textsuperscript{1,2,4,6}

As the carrier of the original information of geological fluids, fluid inclusions have become an important means to study paleotemperature and pressure, paleofluid properties, and oil and gas fluid tracing. As a special hydrocarbon inclusion, methane inclusion can not only calculate the density of methane inclusion through Raman spectroscopy and microtemperature measurement, then calculate the captured pressure, and restore the paleotemperature and pressure of the formation in the geological history period but also indicate the shale sealing degree to a certain extent.\textsuperscript{18−21} Predecessors have found a large number of high-density methane inclusions in the Puguang gas field in the northeastern Sichuan Basin, the Anyue gas field in the central Sichuan Basin, the Fuling shale gas field in the eastern Sichuan Basin, and the Ningxi shale gas field in the southern Sichuan Basin,\textsuperscript{11,12,21,22} which provides not only a theoretical basis for overpressure in the formation of gas reservoirs but also a certain theoretical basis for shale gas enrichment. However, the tectonic evolution in the Yuxi Region, southern Sichuan is relatively complex, and research on this area is also relatively weak.

Herein, the trapped temperature, trapped pressure, and trapping time of high-density methane inclusions were analyzed under the multi-stage tectonic evolution of the Wufeng-Longmaxi shales in the Yuxi Region, southern Sichuan Basin by means of core slice observation, carbon and oxygen isotope analysis, simultaneous aqueous inclusion temperature measurement, and Raman tests. Further, the activity characteristics of hydrocarbon fluids were analyzed and their impact on the enrichment and preservation of shale gas were clarified in order to provide a theoretical basis for the exploration and development of shale gas.

2. GEOLOGICAL SETTING

The Sichuan Basin is located on the northwest side of the Upper Yangtze paraplatform and is a secondary structural unit of the Yangtze paraplatform. The Yuxi Region is in the south of the Huaying Mountain fault zone and on the low-steep tectonic belt in the southern Sichuan Basin (Figure 1a,b). The study area is scattered in a broom shape from northeast to southwest, showing a structural pattern of “alternating graben and horst”, with multiple gentle synclines and low steep anticlines forming, and the strength of tectonic folds gradually weakens from northeast to southwest.\textsuperscript{7}

Due to the superposition of multi-stage and multi-directional intracontinental compression deformation from Yanshanian to Himalayan, the present multi-stage wide-gentle structural styles of near east-west, north-south, and northeast were formed, and the Paleogene and Neogene strata were missing.\textsuperscript{23} Triassic Cretaceous strata were mostly exposed on the surface (Figures 1a and 2b).
Deep-water shelf facies shale was mainly formed in the Wufeng shales and the early Longmaxi shales in the southern Sichuan Basin, with high organic carbon contents (>3%), organic pore existence, high gas contents, and overpressure, with pressure coefficient ranges from 1.76 to 2.26 (Figure 2b). The current burial depth of the Yuxi Region exceeds 3500 m, and the maximum paleo-burial depth can reach 7000 m. The degree of thermal evolution is in the stage of high and over maturity, experiencing complex thermal evolution processes such as oil generation, oil cracking gas, and kerogen cracking gas.8

3. SAMPLES AND METHODS

Well H201, located on an anticline, well H202, located on a slope between a syncline and anticline, and well Z202, located on a fault anticline, which formed the fracture veins, were selected (Figure 1c). Eighteen core samples of the Wufeng-Longmaxi shale fracture veins from wells H201, H202, and Z202 in the southern Sichuan Basin at depths ranging from 3852.00 to 4126.28 m were tested. Of these samples screened, only 12 samples contained fluid inclusions with more than 3 μm size for microtemperature and Raman microprobe analyses. The details of these 12 samples are shown in Table 1. Fluid inclusion analysis was performed after the shale fracture vein samples was double-section polished, and the character-
istics, types, and occurrence of minerals with different
generations of fluid inclusions were observed by transmission
polarized light microscopy, cathode luminescence microscopy,
and Raman spectroscopy. All experiments were conducted in the
Experimental Research Center, School of Geosciences, Yangtze
University, Wuhan, China.

The experimental equipment used for transmission polar-
zation was a Nikon Eclipse 80i dual channel fluorescence-
transmission light microscope. The equipment used for cathode
luminescence was a CL8200 MK5 cathode luminometer. Under
the conditions of $14^{-15}$ kV and $300^{-350}$ mA, it emitted light
on the thin section to determine the formation period of the
veins. For the gas inclusions in these samples, a LabRAM HR800
laser Raman spectrometer with a YAG solid-state laser at a
wavelength of 532 nm was used for non-destructive character-
zation of individual inclusions larger than 1 $\mu$m to verify the gas-
phase components. Different periods of aqueous inclusions were
selected to determine the homogenization temperature ($T_h$),
and the measured minimum $T_h$ of the associated fluid inclusion
assemblages (FIA) was used to approximate the formation
temperature at the time of oil and gas inclusion trapping. Based
on the homogeneous method and the freezing method, the $T_h$
and the ice melting temperatures ($T_m$) were determined by
using a Linkam THMSG600 microscope cold-heat table, and
the error of the temperature measurement results was controlled
to about $\pm0.1$ $^\circ$C. The $T_h$ of methane inclusions can be
determined by rapidly cooling the inclusions to the phase change
point using liquid nitrogen, continuously cooling the inclusions
to observe bubble changes, and then increasing the temperature
to reach a homogeneous phase of the methane inclusions, and
the $T_h$ was recorded.

The carbon–oxygen isotopic composition of the samples was
analyzed by the 100% phosphoric acid method, in which
fracture vein samples were drilled and ground to powder using a
microdrill at the hand specimen scale, and the detection
equipment was an isotope ratio mass spectrometer DELTA V
Advantage SN09017D. The samples were chemically reacted
with pure phosphoric acid at a laboratory temperature of 25 $^\circ$C
and 60% humidity. After the complete reaction for 12 h, the
released $CO_2$ was subjected to carbon and oxygen isotope
measurements on an Isoprime dual-entry stable isotope ratio
mass spectrometer. International standards NBS-18 and NBS-

Figure 3. Petrography characteristics of shale fracture veins under transmitted light and cathode light: (a) horizontal veins on the core (Sample H1-1, Longmaxi Formation, at a depth of 4085.9 m), (b) vertical veins on the core (Sample H2-5-1, Longmaxi Formation, at a depth of 4080.1 m), (c) vertical conjugate X-type veins on the core (Sample H2-5-2, Longmaxi Formation, at a depth of 4080.1 m), (d) quartz cementation is later than calcite
cementation in veins under transmitted light (Sample H1-1), (e and f) formation characteristics of calcite veins under transmitted light (Samples H2-5-1
and H2-5-2), (g) calcite emits bright cathode light, while quartz does not emit cathode light under cathode light (Sample H1-1), (h and i) Calcite
emits dark cathode light, while mineral edge and cleavage emit bright cathode light under cathode light (Samples H2-5-1 and H2-5-2).
were used to calibrate the analytical precision of the isotope mass spectrometer and carbonates. The allowable deviation of carbon isotopes is $\leq \pm 0.2\%_e$, and that of oxygen isotopes is $\leq \pm 0.3\%_e$.

4. RESULTS

4.1. Petrography Characteristics of Veins and Fluid Inclusions. The Wufeng-Longmaxi shales are mostly buried at depths greater than 3500 m in the Yuxi Region, with a large amount of natural fractures visible on core observations. It is found that shale fractures are denser from shallow to deep by observing nearly 300 m cores of the three wells in the study area.
The natural shale fracture veins are mainly formed vertically and horizontally according to their fracture morphology (Figure 3a−c), with widths ranging from 0.8 to 8 mm. The orientation of vertical veins mostly occurs in groups, part of them formed in conjugate X-type (Figure 3c). Overall, the fracture veins of the Wufeng-Longmaxi shales in the Yuxi Region has obvious penetration and cutting relationships, strong fluid activity, and multistage characteristics.

Based on macroscopy observation, microscopy petrographic observation on veins was carried out to clarify the mineral composition, symbiotic relationship, formation stage, and other information within the veins. The detection results of transmitted light and cathodoluminescence show that the minerals in the fracture veins are mainly calcite, partly dissolved by quartz (Figure 3d−f). Calcite mainly emits dark and bright cathode light, mineral edge and cleavage emit bright cathode light, and quartz does not emit cathode light (Figure 3g−i). In accordance with the mineral growth relationship under transmitted light and cathode light, the filling period of minerals was established: calcite crystals were filled early, and some quartz particles dissolved the calcite crystals with emitting cathode light at the later stage, forming the phenomenon of suspending on the calcite.

In general, natural gas inclusions containing methane and other components are gray-black with low transparency under a transmission light microscope, while methane inclusions with high density are relatively uniform translucent-transparent single-phase inclusions,21,26 which generally can be effectively identified by freezing determination micro-Raman spectroscopy. Therefore, further identification and analysis of the inclusions are needed based on petrographic observation. The inclusions trapped within the fracture vein of the Wufeng-Longmaxi shales in the Yuxi Region mainly include single liquid phase inclusions, gas−liquid two-phase inclusions (aqueous inclusions with irregular bubble motion and gas-rich inclusions), pure gas phase inclusions (methane inclusions), solid−gas two-phase inclusions (methane-bearing bituminous inclusions), and pure solid phase inclusions (bituminous inclusions) (Figures 4 and 5). Methane inclusions are mainly found in quartz and large calcite crystals in elongated, elliptical, and irregular shapes, with sizes of 3−30 μm, which appear grayish black and grayish white under transmitted light, with a brighter center (Figure 4a,d,e). Bituminous inclusions and methane inclusions have similar morphological characteristic distribution, which appear gray-black and black in transmitted light, and some inclusions have black lines (Figure 4b,c,f). Gas−liquid two-phase aqueous inclusions and single liquid phase aqueous inclusions were distributed in rectangular, elliptical, and irregular shapes, which formed within calcite and quartz (Figure 4d−f).

4.2. Characteristics of Hydrocarbon Inclusions. 4.2.1. Raman Microprobe Characteristics of Bitumen Inclusions. The results of Raman measurement show that bituminous inclusions and methane-bearing bituminous inclusions exist in the Yuxi Region (Figure 5b,c), and the Raman spectrum shows a pair of strong carbonaceous bitumen Raman characteristic peaks, with Raman shifts near 1355 cm−1 (D-peak) and 1580 cm−1 (G-peak). According to the variation pattern of D-peak and G-peak heights in the thermal evolution of bitumen obtained by Liu et al.,27 the bituminous inclusions in the Yuxi Region belong to the carbonaceous bitumen stage, and the D-peak height is significantly lower than the G-peak height (Figure 5b,c).

Meanwhile, Raman spectrum can reflect the atomic and molecular vibration information in the structure of aromatic carbon rings of organic matter, that is, the spectral peak parameters of the Raman spectrum of organic matter have a good response relationship with the changes in the chemical structure of organic matter during thermal evolution and thus characterize the maturity.28,29 Vitrinite reflectance of kerogen is the most intuitive parameter to characterize the maturity of...
Table 2. Raman Shift of Methane Inclusions, Calculated Density, Symbiotic Aqueous Th of Micromeasurement, Trapped Pressure, and Pressure Coefficient in the Yuxi Region

| sample  | depth (m) | \( V_i \) of methane inclusions (cm\(^{-3}\)) | calculated density of methane inclusions (g/cm\(^3\)) | minimum Th of coexisting aqueous inclusions (°C) | measured number of aqueous inclusions | trapped pressure (MPa) | pressure coefficient |
|---------|-----------|---------------------------------------------|-------------------------------------------------|------------------------------------------------|--------------------------------------|----------------------|---------------------|
| H1-2    | 4111.7    | 2910.66                                     | 0.284                                           | 203.6                                          | 3                                    | 128.0                | 2.07                |
|         |           | 2911.02                                     | 0.266                                           | 192.1                                          | 4                                    | 104.6                | 1.81                |
|         |           | 2911.23                                     | 0.256                                           | 177.4                                          | 2                                    | 91.7                 | 1.88                |
|         |           | 2911.37                                     | 0.249                                           | 178.3                                          | 3                                    | 87.0                 | 1.64                |
| H1-4    | 4126.3    | 2910.62                                     | 0.286                                           | 155.9                                          | 2                                    | 109.0                | 1.91                |
|         |           | 2910.78                                     | 0.278                                           | 194.1                                          | 6                                    | 116.3                | 2                   |
| H2-1    | 4072.4    | 2911.43                                     | 0.246                                           | 171.9                                          | 3                                    | 82.9                 | 1.85                |
|         |           | 2911.26                                     | 0.254                                           | 181.8                                          | 2                                    | 91.6                 | 1.79                |
|         |           | 2910.97                                     | 0.268                                           | 184.4                                          | 5                                    | 103.7                | 1.96                |
|         |           | 2911.34                                     | 0.250                                           | 189.6                                          | 3                                    | 91                  | 1.66                |
| H2-2    | 4073.7    | 2911.38                                     | 0.269                                           | 186.3                                          | 7                                    | 105.3                | 1.95                |
| H2-4    | 4078.1    | 2910.77                                     | 0.278                                           | 190.9                                          | 5                                    | 115.1                | 1.96                |
|         |           | 2911.23                                     | 0.256                                           | 172.8                                          | 4                                    | 90.3                 | 1.94                |
|         |           | 2911.01                                     | 0.266                                           | 183.6                                          | 4                                    | 101.7                | 1.93                |
|         |           | 2911.43                                     | 0.246                                           | 178.1                                          | 4                                    | 84.7                 | 1.73                |
| H2-5-1  | 4080.1    | 2911.12                                     | 0.261                                           | 174.7                                          | 2                                    | 94.7                 | 1.98                |
|         |           | 2911.38                                     | 0.249                                           | 179.1                                          | 3                                    | 87.1                 | 1.77                |
|         |           | 2911.42                                     | 0.247                                           | 184.5                                          | 3                                    | 87.3                 | 1.65                |
|         |           | 2910.79                                     | 0.277                                           | 200.7                                          | 4                                    | 117.8                | 2.01                |
|         |           | 2910.47                                     | 0.293                                           | 214.3                                          | 4                                    | 140.1                | 2.05                |
| H2-6    | 4080.9    | 2910.56                                     | 0.289                                           | 209.6                                          | 4                                    | 133.7                | 2.07                |
|         |           | 2910.81                                     | 0.276                                           | 191.8                                          | 8                                    | 113.5                | 1.96                |
|         |           | 2911.06                                     | 0.264                                           | 180.9                                          | 5                                    | 99.2                 | 1.88                |
|         |           | 2911.16                                     | 0.259                                           | 182.3                                          | 5                                    | 95.6                 | 1.74                |
| H2-7    | 4081.5    | 2910.77                                     | 0.278                                           | 199.5                                          | 4                                    | 118.3                | 2.02                |
|         |           | 2911.38                                     | 0.249                                           | 170.8                                          | 4                                    | 84.6                 | 1.86                |

Organic matter,\(^{30}\) which is not contained in the highly mature hydrocarbon source rocks of the Lower Paleozoic and therefore cannot be used to evaluate the maturity of its hydrocarbon source rocks. However, solid bitumen is the residue left after oil cracking, and the peak spacing between G and D peaks has been proven to be the most reliable maturity index.\(^{27-29}\) Therefore, the bitumen reflectance can be converted into vitrinite reflectance to evaluate the maturity of Lower Paleozoic hydrocarbon source rocks.

According to the formula proposed by Wang et al.,\(^{31}\) we calculated the equivalent vitrinite reflectance of shale bitumen as well as bituminous inclusions in the Wufeng-Longmaxi Formation in the Yuxi Region, which ranges from 1.58 to 2.82%, with an average of 2.26%. The organic matter is in the high-over maturity stage and is dominated by thermal cracking dry gas.

4.2.2. Microthermometry of Methane Inclusions. Since the methane inclusion is an isovolumetric system and its thermodynamic change occurs under the isovolumetric condition, then the phase transition point Th of methane inclusion can be used to determine its density.\(^{32}\)

In the process of microtemperature measurement of methane inclusions, according to the microtemperature measurement method of methane-rich inclusions proposed by previous studies,\(^{33,34}\) the slightly larger and easily observable methane inclusion was selected under the microscope, and the methane inclusion is rapidly frozen by using liquid nitrogen. The lowest temperature that can be achieved in the test is \(-196\) °C, and the three-phase point temperature of methane is \(-182.5\) °C. Theoretically, the appearance of methane solid phase should be observed during the pure methane inclusion measurement, but this phenomenon is difficult to be observed due to the metastable state of the system.\(^{35}\) Therefore, during the microtemperature measurement of methane inclusions, the low-temperature phase transition process of methane inclusions was observed. Liquid nitrogen was used to rapidly freeze the methane inclusion; when frozen at about \(-100\) °C, a small bubble will pop out from the single-phase methane inclusion. Also, there is no other phenomenon in the methane inclusion except that the bubble volume becomes larger when cooled continuously to \(-190\) °C, which is still a gas—liquid two-phase methane inclusion. The bubbles gradually decrease until they disappear and finally homogenize into a liquid phase with a slow increase in the temperature.

Therefore, the measurement results of the Th of methane inclusions in this study revealed that the Th of methane inclusions in the Longmaxi shale fracture calcite veins in well H201 varied from \(-92.1\) to \(-88.4\) °C, that in the Wufeng-Longmaxi shales in well H202 varied from \(-94.6\) °C to \(-91.9\) °C, and no thermometric methane inclusions can be found in well Z202 (Figure 6). From the low-temperature phase transformation process of methane inclusions, most methane inclusions in fracture calcite veins in theYuxi Region can be similar to pure methane inclusions, and the Th of this kind of methane inclusion is close to that of a pure methane system (\(-82.6\) °C).\(^{35}\)

4.2.3. Density of Methane Inclusions. The density of methane inclusions can be determined by Th of methane inclusions:\(^{32}\)

\[
\rho = \frac{0.1620506}{0.288^2} \quad r = \left(1 - \frac{\text{Th} + 273.15}{190.6}\right)^{0.2857}
\]
where \( \rho \) is the density of methane inclusions (g/cm\(^3\)) and Th is the homogenization temperature of methane inclusions (°C). The calculated results show that the density of methane inclusions in the Longmaxi shale fracture calcite veins in well H201 varied from 0.257 to 0.275 g/cm\(^3\) and that of the Wufeng-Longmaxi shales in well H202 varied from 0.274 to 0.285 g/cm\(^3\). The reliable acquisition of this traditional calculation of methane inclusion density data requires the selection of methane inclusions with regular morphology and long axis lengths greater than 6 \( \mu \)m for Th testing. Moreover, the too many test steps lead to a long time, which is not applicable to all methane inclusions.

Therefore, previous studies used the Raman scattering peak \( v_1 \) of methane inclusions to calculate the density.\(^{36-39}\) The Raman scattering peak shifts of methane inclusions measured in this experiment have a wide range of displacements, between 2909.07 and 2915.49 cm\(^{-1}\). Since the Raman scattering peak of pure methane inclusion is closely related to the internal pressure, the methane Raman scattering peak that deviates to 2910.00 cm\(^{-1}\) indicates supercritical high-density inclusion and that that deviates to 2918.00 cm\(^{-1}\) usually indicates low-pressure gas-phase methane;\(^{38}\) generally, less than 2912.00 cm\(^{-1}\) is supercritical state high-density methane inclusions.\(^{40}\) Lu et al.\(^{38}\) fitted a good liner relationship between the \( v_1 \) shift of a methane Raman scattering peak and methane density, which is suitable for the density calculation of methane inclusions with a methane content of 90~100%, and the correlation coefficient is 0.9987:

\[
\rho = -5.17331 \times 10^{-5}D^3 + 5.53081 \times 10^{-4}D^2 - 3.51387 \times 10^{-2}D \tag{2}
\]

where \( \rho \) is the density of methane inclusions (g/cm\(^3\)) and \( D = v_1 - v_0 \), in which \( v_1 \) is the measured methane Raman scattering peak of methane inclusions and \( v_0 \) is the methane Raman scattering peak of methane inclusions when the pressure is close to 0. Affected by laboratory calibration methods, the value of \( v_0 \) is different in different laboratories. In this paper, the value of \( v_0 \) is calibrated by the Raman Laboratory in the Key Laboratory of the School of Geosciences, Yangtze University. Based on eq 2, the density of methane inclusions varies greatly, which can be divided into low-pressure gas-phase methane inclusions and supercritical high-density methane inclusions.

Subsequent research needs to select supercritical high-density methane inclusions, so the calculated density of well H201 according to Raman spectroscopy ranges from 0.249 to 0.286 g/cm\(^3\), with an average of 0.270 g/cm\(^3\) and that of well H202 ranges from 0.246 to 0.293 g/cm\(^3\), with an average of 0.264 g/cm\(^3\); there is no Raman reflection peak in methane inclusions observed in well Z202 (Table 2). The density of methane inclusions calculated by this method is similar to that obtained by microtemperature measurement of methane inclusions.

### 4.3. Homogenization Temperature and Salinity

Single-phase methane inclusions or bituminous inclusions are commonly found around the gas–liquid two-phase aqueous inclusions in the vein, indicating that these kinds of inclusions were formed in an immiscible two-phase system with saturated hydrocarbons. The Th and salinity of the gas–liquid two-phase aqueous inclusions represent the captured temperature and salinity of hydrocarbon inclusions. Therefore, the gas–liquid two-phase aqueous inclusions symbiotic with hydrocarbon inclusions FIA were selected for microtemperature measurement in this study. The measured Th and salinity are shown in Figure 7.

The Th values of the aqueous inclusions in Samples H1-1, H1-2, and H1-4 range from 134.6 to 177.6 °C, 135.7 to 209.8 °C, and 121.9 to 206.4 °C, respectively, those in Samples H2-1, H2-2, H2-4, H2-5-1, H2-5-2, H2-6, and H2-7 range from 142.1 to 205.9 °C, 144.4 to 195.8 °C, 172.8 to 207.5 °C, 167.8 to 224.1 °C, 143.0 to 168.9 °C, 180.9 to 226.8 °C, and 165.4 to 204.5 °C, respectively, and those in Samples Z2-2-1 and Z2-2-2 range from 115.5 to 142.1 °C and 109.3 to 148.1 °C, respectively (Figure 7a). Combining the microscopy observation and temperature measurement results, it is concluded that the Th of aqueous inclusions symbiotic with bituminous inclusions is between 109.3 and 174.1 °C and that of methane inclusions is between 137.3 and 226.8 °C. The Th above 220 °C proves that the Wufeng-Longmaxi shales have experienced deep burial. The Th distribution of each FIA for different samples is shown in Figure 7a, where the numbers marked in brackets on the diagram represent the number of measured gas–liquid two-phase

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**Figure 7.** (a) Temperature and (b) salinity distribution of 49 FIAs in wells H201, H202, and Z202. Gray areas indicate the FIAs trapped in quartz particles and the rest are those trapped in calcite crystals. The microscopic temperature measurements of the 6th, 20th, and 39th FIAs in Samples H1-2, H2-4, and H2-7 are shown in Figure 4d–f, respectively.
aqueous inclusions in each group of FIA, the box-whisker diagram of the same color represents the same vein in the same sample, the gray area in the diagram and the FIA numbers marked in red represent the FIA measured in quartz particles, and the rest are the FIA measured in calcite crystals.

Since some of the inclusions may be metastable, not all aqueous inclusions can be converted to the salinity by measuring the Tm (salinity calculation based on Bodnar41), so the salinity of the aqueous inclusions in this experiment in wells H201, H202, and Z202 ranges from 3.5 to 7.6 wt % NaCl equivalent, 1.2 to 17.2 wt % NaCl equivalent, and 1.1 to 11.9 wt % NaCl equivalent, respectively (Figure 7b). It is considered that a salinity greater than 5 wt % NaCl equivalent is a high salinity fluid. The salinity measured for most aqueous inclusions is high, which indicates a better confinement of the shale and less influence of exogenous fluids. The salinity distribution of each FIA for different samples is shown in Figure 7b.

4.4. Results of Carbon and Oxygen Isotopes. Carbon isotope is commonly used to explain the properties of diagenetic fluid, while oxygen isotope is mainly controlled by the temperature of vein-forming fluid. The mean value of δ13C_PDB of marine carbonate rocks since Phanerozoic was 0 ± 4‰ and that of δ18O_SMOW was 20–24‰; the mean value of δ13C_PDB of global sea water in the late Ordovician-early Silurian was 0 ± 1‰ to 2 ± 1.5‰ and that of δ18O_SMOW was 0 ± 1‰.42,43 The measured values of δ13C_PDB of vein in the Wufeng-Longmaxi shales in the study area have negative bias compared with those of marine carbonate rocks since Phanerozoic and global sea water in the late Ordovician-early Silurian, and the measured values of δ18O_SMOW have negative bias compared with those of marine carbonate rocks since Phanerozoic and positive bias compared with those of global sea water in the late Ordovician-early Silurian (Figure 8a).

There are two possible reasons for the negative bias of the δ13C_PDB values of veins; one is that the infiltrated surface atmospheric water is poor in 18O and rich in 12C due to the influence of CO2 in atmospheric fresh water. Therefore, the intervention of atmospheric water in the diagenetic process will make both the δ13C_PDB value and δ18O_SMOW value show negative bias. The second is the decarboxylation of organic matter, which enters the veining-forming fluid through organic acids. The positive bias of the δ18O_SMOW value may be caused by the increase in formation water with water-rock reaction time.44

with the genetic mechanism of carbonate rocks (Figure 8).45 It is found that one sample of Z202 was affected by a certain degree of atmospheric fresh water and mixed with exogenous fluids, while the rest of them mainly originated from stratigraphic water evolved under a strong water-rock reaction. Overall, the stratigraphy was well closed during the formation of the vein, mostly from endogenous fluids.

5. DISCUSSION

5.1. Methane Inclusion Trapping Conditions of Veins. According to the hydrocarbon generation model proposed by Tissot, we know that organic matter reaches the oil generation window at 60 °C, i.e., Ro = 0.5%, and reaches the gas generation window at 180 °C, i.e., Ro = 1.2%, after which oil cracking gas and kerogen cracking gas occur simultaneously. When the temperature is greater than 250 °C, i.e., Ro > 2.0%, the final stage of organic matter evolution is reached, generating dry gas and solid bitumen.46 Solid bitumen and bituminous inclusions could be observed in the samples, with black amorphous solid bitumen growing along calcite cleavage or along the edges of different calcite crystals while bituminous inclusions growing in both calcite crystals and quartz particles, and methane was also detected in some of bituminous inclusions (Figure 5c). As the solid bitumen is the final product of oil evolution, it demonstrates that the Yuxi Region has experienced deep burial and high temperatures, and part of methane was derived from oil cracking, while the early oil was metamorphosed at high temperatures to form carbonate bitumen. Also, in different crystals, the symbiotic gas—liquid two-phase aqueous inclusions were detected together, illustrating the early pore fluid saturated by hydrocarbons, and the hydrocarbon fluids exist as separate immiscible phases at the stage of fracture formation.47 Combined with the growth sequence of forming minerals in veins, it can be assumed that the formation of calcite and quartz is contemporaneous with or precedes the large-scale oil filling. The vein was formed in the early stage, as evidenced by the low Th (Figure 7a).

In contrast, when methane inclusions were examined, most of them were found to exist independently (Figure 4a), and only in some crystals could gas—liquid two-phase aqueous inclusions be detected (Figure 4d,e), which revealed that the pore fluid was always saturated with methane. Within the same vein, both bituminous inclusions and
methane inclusions can be observed, indicating that the fracture vein was formed in an early stage and continuously opened and closed, accompanied by the formation of crystals. When the vein is opened, methane is trapped by the crystal as a single immiscible phase under a high temperature, high pressure, and high density, forming a supercritical high-density methane inclusion. The less symbiotic aqueous inclusions may be due to the increase in burial depth and the large generation of oil cracking gas and kerogen cracking gas, resulting in the increase in gas saturation and the decrease in water saturation. As a result, the temperature and pressure state of contemporaneous aqueous inclusions with methane inclusions can represent the temperature and pressure state of the formation when methane inclusions are trapped.

The temperature and salinity variations of gas−liquid two-phase aqueous inclusions symbiotic with hydrocarbon inclusions measured in this experiment are shown in the same figure (Figure 9), and the temperature−salinity can be divided into three regions: Region I is low temperature−high salinity inclusions; Region II is medium temperature−low and high salinity inclusions; and Region III is high temperature−high salinity inclusions. Generally, low salinity (<3.5 wt % NaCl equivalent) is considered to be the influence of exogenous fluid, but since the shale is a low permeability medium, the influence of exogenous fluid is small in the process of continuous burial. The test results of carbon and oxygen isotopes above also show that the vein-forming fluid was mostly water related to hydrocarbon generation. Different degrees of water-rock reaction can reduce the salinity of pore water in the Wufeng-Longmaxi shales, so it is also reasonable that the medium temperature−low salinity is represented by Region II.

5.2. Methane Inclusion Trapping Times and Trapped Pressure. The trapping time of bituminous inclusions and methane inclusions can be estimated according to the microtemperature measurement data of fluid inclusions and the thermal history evolution of the basin model. Since the three wells are in different tectonic locations, leading to their burial−thermal history evolution being somewhat different, the burial history and thermal history of H201, H202, and Z202 wells are simulated individually. The maximum burial depth of well H201 was 7710 m at about 89 Ma, corresponding to a temperature about 227 °C; that of well H202 was 7567 m at 89 Ma, corresponding to a temperature about 228 °C; and that of well Z202 was 7615 m at 90 Ma, corresponding to a temperature about 213 °C (Figure 10).

Since the maximum difference of the symbiotic aqueous inclusion FIA Th trapped in calcite can reach 29 °C and that of quartz can reach 24 °C and the inclusions trapped in carbonate minerals are vulnerable to the later transformation, the minimum Th in each FIA was selected as the trapped temperature of hydrocarbon inclusions when estimating the trapping time. Moreover, due to the large temperature difference in the FIA, it is considered that all such inclusions were trapped before reaching the maximum burial depth. Therefore, according to the hydrocarbon generation mechanism, it is believed that the minimum Th of aqueous inclusion FIA, which is symbiotic with methane inclusions in the burial period, is usually greater than 170 or 180 °C, corresponding to the stages of oil cracking gas and kerogen cracking gas. When it is detected to be less than 170 or 180 °C, it indicates that this kind of FIA was trapped in the stage of gas dynamic adjustment in the uplift period (Figure 10). Furthermore, it is found that the trapping times of hydrocarbon inclusions in the three wells are similar when projecting FIAs' Th onto the burial−temperature history.

In order to understand the specific trapping time of bituminous inclusions and methane inclusions, we projected the time axis of the measured minimum Th of each symbiotic FIA in each sample, and the results are shown in Figure 11. The green arrow represents the trapping time of bituminous inclusions, that is, the trapping time of previous oil inclusions,
and the red arrow represents the trapping time of methane inclusions. A longitudinal comparison of 12 samples from these three wells shows that most of the bituminous inclusions were trapped in the Indianan period. The minimum Th of aqueous inclusions coeval with bituminous inclusions in wells H201 and H202 is mostly concentrated in 135 and 155 °C, and that of well Z202 is mostly concentrated in 110 and 135 °C, which are overall concentrated in 220 and 250 Ma, corresponding to burial depths of about 3000 and 3800 m, respectively. The trapping time of methane inclusions spans in a large range, with trapped temperatures during the whole gas generation stage at 170–225 °C. The corresponding trapping time is mostly concentrated in 160 and 195 Ma, corresponding to the burial depths of 5000 and 6500 m. In addition, one phase of methane inclusions was trapped in well H202 at 124 Ma when the burial depth reached 7000 m and the temperature reached 220 °C, and one phase of methane inclusions was trapped in wells H201 and Z202 at around 51 to 56 Ma during the uplift period. No aqueous inclusions were trapped in the early stage of uplift, indicating that no strong compression occurred throughout the early stage of uplift, and only strong Himalayan compression led to paleo-fluid activity. The trapped temperature and pressure of fluid inclusions record the temperature and pressure of the formation at that time. The calculation of the trapped pressure is based on the equation of state applicable for the supercritical methane system established by Duan et al.:

$$Z = \frac{PV}{RT} = \frac{P\rho_{V}}{T_{V}} = 1 + \frac{B}{V_{r}} + \frac{C}{V_{r}^{2}} + \frac{D}{V_{r}^{3}} + \frac{E}{V_{r}^{4}} + \frac{F}{V_{r}^{5}} \left( \beta + \frac{\gamma}{V_{r}} \right) \exp \left( \frac{\gamma}{V_{r}} \right)$$

where

- $B = a_{1} + \frac{a_{2}}{T_{m}} + \frac{a_{3}}{T_{m}^{2}}$
- $C = a_{4} + \frac{a_{5}}{T_{m}} + \frac{a_{6}}{T_{m}^{2}}$
- $D = a_{7} + \frac{a_{8}}{T_{m}} + \frac{a_{9}}{T_{m}^{2}}$
- $E = a_{10} + \frac{a_{11}}{T_{m}} + \frac{a_{12}}{T_{m}^{2}}$
- $F = \frac{a_{13}}{T_{m}^{2}}$
- $\beta = \frac{P_{r}}{P}$
- $\gamma = \frac{\rho_{V}}{\rho_{m}}$
- $T_{m} = \frac{T}{T_{0}}$
- $V_{r} = \frac{V}{V_{m}}$
- $P_{r}$ is the pressure (bar);
- $T$ is the temperature (K);
- $R$ is the gas constant (0.08314467 bar·dm$^{-3}$·K$^{-1}$·mol$^{-1}$);
- $V$ is the molar volume, which can be determined by the density of methane inclusions and molar mass (dm$^{3}$/mol);
- $Z$ is the compression factor; $P_{r}$ and $T_{m}$ are the comparative pressure and temperature, respectively, and their dimensions are 1; $P_{r}$ and $T_{m}$ are the critical pressure (46 bar) and critical temperature (190.4 K), respectively, and the unit is the same as $P$ and $T$; $a_{1} = 0.0872553928$; $a_{2} = -0.752599476$; $a_{3} = 0.375419887$; $a_{4} = 0.0107291342$; $a_{5} = 0.0054962636$; $a_{6} = -0.0184772802$; $a_{7} = 0.000318993183$; $a_{8} = 0.000211079375$; $a_{9} = 0.000201682801$; $a_{10} = -0.0000165606189$; $a_{11} = 0.000119614546$; $a_{12} = -0.000108087289$; $\alpha = 0.0448262295$; $\beta = 0.75397$; and $\gamma = 0.077167$.

The calculation of this formula requires the supercritical high-density methane inclusions. Therefore, the trapped pressure of well H201 during the deep burial period calculated by eq 3 ranges from 87.0 to 128.0 MPa, with the pressure coefficient ranges from 1.64 to 2.07; that of the uplift period is 109.0 MPa, with the pressure coefficient being 1.91. The trapped pressure of well H202 during the deep burial period ranges from 82.9 to 140.1 MPa, with the pressure coefficient ranges from 1.65 to 2.07 (Table 2).

As per the calculation results, it can be confirmed that the maximum trapped temperature in FIA of the three wells is 214.3 °C, which almost corresponds to the maximum burial depth of well H202, with the density of methane inclusion being 0.293 g/cm$^{3}$, the trapped pressure of methane inclusion being 140.1 MPa, and the corresponding pressure coefficient being 2.05. It shows that during the deep burial period, the formation was in a strong overpressure state due to the massive gas generation of organic matter. Based on this density, the formation pressure of 227 °C at the maximum burial depth was 145.3 MPa, with the corresponding pressure coefficient being 1.96. However, the measured pressure coefficient of the Wufeng-Longmaxi Formation of well H202 is 2.04, indicating that the strong overpressure was inherited from the maximum burial depth. The uplift leads to the decrease in the overlying formation pressure and the increase in the corresponding formation pressure coefficient.

### 5.3. Response of Shale Gas Accumulation

Closed fracture veins will obstruct gas seepage, while open fracture veins are the dominant channel of oil and gas migration. The formation of veins is very important to shale gas reservoirs. The trapping time of secondary inclusions represents the oil and gas activity time, while that of primary inclusions represents the vein formation time. However, in this study, no primary inclusions were detected. Therefore, the opening and closing of veins can be further clarified through secondary inclusions. Moreover, due to the multi-stage of fluid activity and different fluid properties, it is difficult to determine the gas content in the reservoir directly through the fluid activity time, and the correlation between the two can only be determined by means of inclusions.

In well H202, quartz grew later than calcite. However, the high Th of fluid inclusions trapped in quartz indicates that deep and high-temperature siliciclastic fluids may come from the nearby fracture zone during deep burial. Well H202 is located on the slope between an anticline and syncline, and faults were formed nearby, indicating that this speculation is reliable. However, since this oil and gas activity occurred before uplift, the damage to shale gas reservoirs is limited. The main paleofluid activity stages occurred during the burial period, indicating that the shale gas was well preserved, and it was supported by the high gas content and pressure coefficient (Figure 12).

In well H201, although quartz grew later than calcite, it is considered that both the calcite and quartz were formed in the
middle-shallow burial period according to the Th of fluid inclusion, which is hardly destructive to shale gas reservoirs. The fluid inclusions trapped in the uplift period confirmed that the Himalayan compression movement of Paleogene led to the opening of fracture vein and the adjustment and migration of shale gas. The early similar opening time with well H202 of fracture vein indicate that the damage degree was also similar, while the late stage opening of fracture vein led to the partial loss of shale gas. Therefore, the current pressure coefficient is close to two at deep burial, indicating that the current overpressure is inherited from the overpressure at the maximum burial depth. The earlier the fracture opening, the less the impact on shale gas accumulation, and the more the stages of fracture opening-closing, the greater the damage to shale gas accumulation.

6. CONCLUSIONS

The fracture veins of shale and fluid inclusions in minerals of the Wufeng-Longmaxi Formation in the Yuxi Region were observed and measured in this study, and the burial history was restored, leading to the following conclusions:

(1) The shale fracture veins are mainly oriented vertically and horizontally, with calcite crystals filling at an early stage and some quartz grains dissolving the calcite crystals at a later stage. The vein-forming fluids are derived from endogenous fluids. The homogeneous temperature of the aqueous inclusions contemporaneous with the bituminous inclusions range from 119.3 to 174.1 °C, which were trapped during 120 to 210 Ma. The homogeneous temperature of the aqueous inclusions contemporaneous with the methane inclusions range from 137.3 to 226.8 °C, which were trapped during 160 to 195 Ma and 51 to 56 Ma.

(2) The density of methane inclusions calculated by microthermometry and Raman spectroscopy varies between 0.257–0.265 g/cm³ and 0.246–0.293 g/cm³, showing high density characteristics. The captured pressure is between 82.9 and 140.1 MPa, with the pressure coefficient between 1.64 and 2.07. The formation pressure coefficient is close to two at deep burial, indicating that the current overpressure is inherited from the overpressure at the maximum burial depth.

(3) The tectonic compression movement in the Himalayan period of Paleogene determines the enrichment degree of shale gas. Compared with the well H202 at the slope, wells Z202 and H201 at the anticline are more prone to fracture vein opening, which in turn has a destructive effect on the reservoir, which has a lower pressure coefficient and gas content. The earlier the fracture opening, the less the impact on shale gas accumulation, and the more the stages of fracture opening-closing, the greater the damage to shale gas accumulation.

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Notes
The authors declare no competing financial interest.

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**NOMENCLATURE**

FIA, fluid inclusion assemblages  
Th, homogenization temperature  
Tm, ice melting temperature

**REFERENCES**

(1) Lin, W.; Li, X. Z.; Yang, Z. M.; Lin, L. J.; Xiong, S. C.; Wang, Z. Y.; Wang, X. T.; Xiao, Q. H. A new improved threshold segmentation method for scanning images of reservoir rocks considering pore fractal characteristics. *Fractals* 2018, 26, 1840003.

(2) Lin, W.; Xiong, S. C.; Liu, Y.; He, Y.; Chu, S. S.; Liu, S. Y. Spontaneous imbibition in tight porous media with different wettability: Pore-scale simulation. *Phys. Fluids* 2021, 33, No. 032013.

(3) Zhao, X. L.; Liu, X. W.; Yang, Z. M.; Wang, F.; Zhang, Y. P.; Liu, G. Z.; Lin, W. Experimental study on physical modeling of flow mechanism in volumetric fracturing of tight oil reservoir. *Phys. Fluids* 2021, 33, 107118.

(4) Shen, W. J.; Ma, T. R.; Li, X. Z.; Sun, B. J.; Hu, Y. Y.; Xu, J. C. Fully coupled modeling of two-phase fluid flow and geomechanics in ultra-deep natural gas reservoir. *Phys. Fluids* 2022, 34, No. 044301.

(5) Zhang, P. Y.; Jiang, F. J.; Zhu, C. X.; Huang, R. D.; Hu, T.; Xu, T. W.; Li, W. D.; Xiong, H. Gas Generation Potential and Characteristics of Oil-Prone Shale in the Saline Lacustrine Rifting Basins: A Case Study of the Dongpu Depression, Bohai Bay Basin. *Energy Fuels* 2021, 35, 32192–32208.

(6) Shen, W. J.; Li, X. Z.; Ma, T. R.; Cai, J. C.; Lu, X. B.; Zhou, S. W. High-pressure methane adsorption behavior on deep shales: Experiments and modeling. *Phys. Fluids* 2021, 33, No. 063103.

(7) Yang, H. Z.; Zhao, S. X.; Liu, Y.; Wu, W.; Xia, Z. Q.; Wu, T. P.; Luo, C.; Fan, T. Y.; Yu, L. Y. Main Controlling Factors of Enrichment and High-Yield of Deep Shale Gas in the Luzhou Block, Southern Sichuan Basin. *Nat. Gas Ind.* 2019, 39, 55–63. (in Chinese with English abstract)

(8) Ma, X. H.; Xie, J. The Progress and Prospects of Shale Gas Exploration and Exploitation in Southern Sichuan Basin, NW China. *Pet. Explor. Dev.* 2018, 45, 161–169.

(9) Guo, T. L. Evaluation of Highly Thermally Mature Shale-Gas Reservoirs in Complex Structural Parts of the Sichuan Basin. *J. Earth Sci.* 2013, 24, 863–873.

(10) Pang, H. Q.; Xiong, L.; Wei, L. M.; Shi, H. L.; Dong, X. Z.; Zhang, T. C.; Cai, Z. L. Analysis of the Main Geological Factors for the Enrichment and High Yield of Deep Shale Gas in South Sichuan: A Case Study of Weirong Shale Gas Field. *Nat. Gas Ind.* 2019, 39, 78–84.

(11) Gao, J.; Zhang, J. K.; He, S.; Zhao, J. X.; He, Z. L.; Wo, Y. J.; Feng, Y. X.; Li, W. Overpressure Generation and Evolution in Lower Paleozoic Gas Shales of the Jiaoshiba Region, China: Implications for Shale Gas Accumulation. *Mar. Petrol. Geol.* 2019, 2, 844–859.

(12) Liu, Z.; Hao, F.; Liu, X.; Wu, W.; Quan, L.; Tian, J. Q.; Feng, Z. Q. Development Characteristics and Geological Significance of High Density Methane Inclusions in the Longmaxi Member I in the Ningxi Area, Southern Sichuan Basin. *Earth Sci.* 2021, 46, 3157–3171.

(13) Feng, Q. Q.; Qiu, N. S.; Tenger, B.; Wu, H.; Zhang, J. T.; Shen, B. J.; Wang, J. S. Tectonic evolution revealed by thermo-kinematic and its effect on shale gas preservation. *Energy* 2022, 240, 122781.

(14) Hill, D. G.; Nelson, C. R. Reservoir properties of the upper cretaceous Lewis shale, a new natural gas play in the San Juan Basin. *AAPG Bull.* 2000, 2000, 1240.

(15) Bowker, K. A. Barnett shale gas production, Fort Worth Basin: issues and discussion. *AAPG Bull.* 2007, 91, 523–533.

(16) Ambrose, R. J.; Hartman, R. C.; Diaz-Campos, M.; Akkutlu, I. Y.; Sondergeld, C. H. Shale gas-in-place calculations part I: new pore-scale considerations. *SPE J.* 2012, 17, 219–229.

(17) Liu, H.; Wang, H.; Fang, Z.; Guo, W.; Sun, S. The formation mechanism of overpressure reservoir and target screening index of the marine shale in the South China. *Earth Sci. Front.* 2016, 23, 48–54.

(18) Beeskow, B.; Rankin, A. H.; Murphy, P. J.; Treloar, P. J. Mixed CH4-CO2 fluid inclusions in quartz from the south wales coalfield as suitable natural calibration standards for microthermometry and Raman spectroscopy. *Chem. Geol.* 2005, 223, 3–15.

(19) Hurai, V.; Marko, F.; Tokarski, A. K.; Świerzewska, A.; Kotulová, J.; Biročet, A. Fluid inclusion evidence for deep burial of the tertiary accretionary wedge of the Carpathians. *Terra Nova* 2006, 18, 440–446.

(20) Chen, Y.; Zhou, Y. Q.; Zhang, L. P.; Wu, M. H. I.; Yan, S. Y. Discovery of CH4-rich high-pressure fluid inclusions hosted in ancalime from Dongying depression, China. *J. Petrol. Sci. Eng.* 2007, 56, 311–314.

(21) Liu, D. H.; Dai, J. X.; Xiao, X. M.; Tian, H.; Yang, C.; Hu, A. P.; Mi, J. K.; Song, Z. G. High Density Methane Inclusions in Puguang Gasfield: Discovery and a T-P Genetic Study. *Chin. Sci. Bull.* 2010, 55, 359–366.

(22) Wang, G. Z.; Liu, S. G.; Liu, W.; Fan, L.; Yuan, H. F. Process of hydrocarbon accumulation of Sinian Dengying Formation in Gaoshiti Structure, Central Sichuan, China. *J. Chengdu Univ. Tech. (Sci. Tech. Ed.)* 2014, 41, 684–693.

(23) Huang, H. Y.; He, D. F.; Li, Y. Q.; Fan, H. D. Determination and formation mechanism of the Luzhou paleo-uplift in the southeastern Sichuan Basin. *Earth Sci. Frorn.* 2019, 26, 102–120.

(24) Liu, S. G.; Deng, B.; Zhong, Y.; Ran, B.; Yong, Z. Q.; Sun, W.; Yang, D.; Jiang, L.; Ye, Y. H. Unique geological features of burial and superimposition of the Lower Paleozoic shale gas across the Sichuan Basin and its periphery. *Earth Sci. Frorn.* 2016, 23, 11–28.

(25) Mccrea, J. M. On the Isotopic Chemistry of Carbanates and a Paleotemperature Scale. *J. Chem. Phys.* 1950, 18, 849–857.

(26) Liu, B. The thermodynamic simulation of Hydrocarbon inclusions. Science Press: Beijing, China, 2005; (in Chinese).

(27) Liu, D. H.; Xiao, X. M.; Tian, H.; et al. Sample Maturation Calculated Using Raman Spectroscopic Parameters and Reflectance of Solid Bitumen. *Int. J. Coal Geol.* 2014, 121, 19–25.

(28) Hunt, J.M. Petroleum geochemistry and geology. W.J. Freeman: New York, America, 1996.

(29) Wang, M. L.; Xiao, X. M.; Wei, Q.; Zhou, Q. Thermal maturation of solid bitumen in shale as revealed by Raman spectroscopy. *Nat. Gas Geosci.* 2015, 26, 1712–1718.

(30) Liu, B.; Shen, K. The thermodynamic simulation of fluid inclusions. Science Press: Beijing, China, 1999: 27–83 (in Chinese).

(31) Kerkhof, A. Isochronic phase diagrams in the system CO2-CH4 and CO2-N2: Application to fluid inclusions. *Geochim. Cosmochim. Acta* 1990, 54, 621–629.
(34) Kerkhof, A.; Thiéry, R. Carbonic inclusions. *Lithos* 2001, 55, 49−68.

(35) Andersen, T.; Burke, E. A. Methane inclusions in shocked quartz from the Gardnos impact breccia, South Norway. *Eur. J. Mineral.* 1996, 8, 927−936.

(36) Seitz, J. C.; Pasteris, J. D.; Chou, I. M. Raman spectroscopic characterization of gas mixtures; II, Quantitative composition and pressure determination of the CO₂−CH₄ system. *Am. J. Sci.* 1996, 296, 577−600.

(37) Lin, F.; Bodnar, R.; Becker, S. Experimental determination of the Raman CH₄ symmetric stretching (ν₁) band position from 1-650bar and 0.3-22°C: Application to fluid inclusion studies. *Geochim. Cosmochim. Ac.* 2007, 71, 3746−3756.

(38) Lu, W. J.; Chou, I. M.; Burruss, R. C.; Song, Y. C. A unified equation for calculating methane vapor pressures in the CH₄−H₂O system with measured Raman shifts. *Geochim. Cosmochim. Ac.* 2007, 71, 3969−3978.

(39) Hansen, S. B.; Berg, R. W. Raman spectroscopic studies of methane gas hydrates. *Appl. Spectrosc. Rev.* 2009, 44, 168−179.

(40) Liu, D. H.; Xiao, X. M.; Tian, H.; Yang, C.; Hu, A. P.; Song, Z. G. Identification of Natural Gas Origin Using the Characteristics of Bitumen and Fluid Inclusions. *Pet. Explor. Dev.* 2009, 36, 375−382.

(41) Bodnar, R. Revised equation and table for determining the freezing point depression of H₂O−NaCl solutions. *Geochim. Cosmochim. Ac.* 1993, 57, 683−684.

(42) Veizer, J.; Ala, D.; Azmy, K.; Bruckschen, P.; Buhl, D.; Bruhn, F.; Carden, G. A. F.; Diener, A.; Ebneth, S.; Godderis, Y.; et al. ⁸⁸Sr/⁸⁶Sr, δ¹³C and δ¹⁸O evolution of Phanerozoic seawater. *Chem. Geol.* 1999, 161, 59−88.

(43) Taylor, K.; Gawthorpe, R.; Curties, C.; Marshall, J. D.; Awwiller, D. N. Carbonate Cementation in a Sequence-Stratigraphic Framework: Upper Cretaceous Sandstones, Book Cliffs, Utah-Colorado. *J. Sediment. Res.* 2009, 70, 360−372.

(44) Emery, D.; Robinson, A. *Inorganic Geochemistry: Applications to Petroleum Geology.* Blackwell Scientific Publications: London, England, 1993.

(45) Wu, A. B.; Zhang, J. K.; Wang, J. L.; Luo, J. G.; Luo, Q.; Jiang, Z. X. Genisis, diagenetic model and geological significance of calcite veins in organic-rich shale: a case study of the Longmaxi Formation, southern Sichuan Basin, China. *Geol. Rev.* 2020, 66, 88−100.

(46) Tissot, B. P.; Welte, D. H. *Petroleum formation and occurrence—a new approach to oil exploration.* Elsevier Applied Science Publishers Ltd: London, England, 1978.

(47) Goldstein, R. H.; Reynolds, T. J. Systematics of fluid inclusions in diagenetic minerals: SEPM Short Course. *Soc. Sediment. Geol.* 1994.

(48) Gao, J. *Paleo-temperature and pressure and origin of paleo-fluid of fracture veins in the Wufeng-Longmaxi shales of Yudong area.* China University of Geosciences: Wuhan, China, 2018.

(49) Becker, S. P.; Eichhubl, P.; Laubach, S. E.; Reed, B. M.; Lander, R. H.; Bodnar, R. J. A 48 my history of fracture opening, temperature, and fluid pressure: cretaceous Travis Peak Formation, East Texas Basin. *Geol. Soc. Am. Bull.* 2010, 122, 1081−1093.

(50) Gasparri, M.; Sassi, W.; Gale, J. F. W. Natural sealed fractures in mudrocks: a case study tied to burial history from the Barnett Shale, Fort Worth Basin, Texas. *USA. Mar. Petrol. Geol.* 2014, 55, 122−141.

(51) Gao, J.; He, S.; Zhao, J. X.; Yi, J. Z. Geothermometry and geobarometry of overpressured lower Paleozoic gas shales in the Jiaoshiba field, Central China: Insight from fluid inclusions in fracture cements. *Mar. Petrol. Geol.* 2017, 83, 124−139.

(52) Nie, H. K.; He, Z. L.; Wang, R. Y.; Zhang, G. R.; Chen, Q.; Li, D. H.; Lu, Z. Y.; Sun, C. X. Temperature and origin of fluid inclusions in shale veins of Wufeng-Longmaxi Formations, Sichuan Basin, south China: Implications for shale gas preservation and enrichment. *J. Petrol. Sci. Eng.* 2020, 193, 107329.

(53) Duan, Z.; Møller, N.; Weare, J. H. An equation of state for the CH₄−CO₂−H₂O system: I. Pure systems from 0 to 1000°C and 0 to 8000 bar. *Geochim. Cosmochim. Ac.* 1992, 2605−2617.