Minerals Filling in Anhydrite Dissolution Pores and Their Origins in the Ordovician Majiagou Formation of the Southeastern Ordos Basin, China

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Mold pore cementation is the key factor constraining the reservoir property in the study area. The anhydrite dissolution pores in the Ordovician Majiagou Formation of southeastern Ordos Basin are commonly filled by minerals such as dolomite, calcite, pyrite, and quartz accounting for more than 90% of the total molds resulting in significant porosity volume reduction. The anhydrite dissolution pores in the Jingbian Gas Field in the middle east of the basin, however, are rarely filled by minerals with more than 30% molds, remaining open to become good reservoir space. Studies reveal that the calcite filling in anhydrite dissolution pores has a relatively negative $\delta^{18}O$ value (-15.58‰~8.96‰ VPDB) and negative $\delta^{13}C$ value (-7.56‰~0.26‰ VPDB), which is interpreted to be caused by thermochemical sulfate reduction (TSR). The higher homogenization temperatures (140-234°C) and high salinity (19.13-23.18 wt.% NaCl equivalent) of the primary inclusions in calcite confirm the above interpretation. Dolomite is the second most abundant carbonate formed as by-product of TSR, which is promoted by the precipitation of calcite and resulted enriched in Mg$^{2+}$/Ca$^{2+}$ ratio in the pore water. Pyrite forms by the reaction of H$_2$S released from TSR with the Fe$^{2+}$ in the horizon, which is supported by its cubic habit and relatively high $\delta^{34}S$ value (10.50‰~24.00‰ VCDT). Quartz with relatively high homogenization temperature (113-154°C) is considered to precipitate in low-pH solution from calcite and pyrite precipitation after TSR. The southeastern Ordos Basin is much lower than the Jingbian Gas Field in paleogeographic location, which is submerged in the sea water of marine phreatic environments for a long time when sea water flooded from the southeastern direction. TSR occurs due to calcium sulfate enriched in pore water resulting in the minerals of dolomite, calcite, pyrite, and quartz filling in the molds leading to the low porosity and permeability of the study area.

1. Introduction

The anhydrite nodule-bearing dolomite is widely distributed in the Ordovician Majiagou Formation of southeastern Ordos Basin. The anhydrite nodule normally occurs in settings interpreted to be sabkhas [1, 2], intertidal to shallow subtidal [3], and even deeper subtidal settings [4]. The anhydrite nodules in the present case are formed in evaporative tidal flat facies but mostly leached by fresh water [5]. The nodular morphology suggests precursor gypsum or anhydrite. The gypsum is commonly dehydrated to anhydrite in the shallow burial condition; therefore, the nodules are normally filled by anhydrite when deep buried. Nevertheless, the anhydrite has been dissolved by fresh water during an episode of subaerial exposure during the Caledonian orogeny [6] forming the major reservoir space of the basin in the Ordos Basin. However, the anhydrite dissolution pores are commonly filled by minerals, such as dolomite, calcite, pyrite, and quartz, resulting in significant porosity and volume reduction. The minerals filling in molds are...
conventionally interpreted to be formed in near surface conditions. However, the cementation of molds can occur at any time in the burial cycle from eogenesis through mesogenesis and into telogenesis.

The filling of anhydrite dissolution pores by calcite and dolomite can be interpreted as the replacement of sulfate by carbonate driven by various hydrological processes, such as bacterial sulfate reduction \[7\]. Pierre and Rouchy \[7\] interpreted the low $\delta^{13}$C value from organic origin and the low $\delta^{18}$O value caused by the large quantities of energy released during the bacterial sulfate reduction. It can also be the result of an active volcanogenic system \[2\] or even associated with cycling of seawater through hydrothermal anhydrite in mid-ocean ridges \[10\]. Late stage calcite replacement of evaporite nodules has also been reported to be associated with thermo-chemical sulfate reduction (TSR) \[11, 12\]. However, the most widely documented process is related to the meteoric water in the active phreatic zone but not in the deep subsurface \[13–15\]. The dissolution of sulfate and precipitation of minerals can significantly change the porosity and permeability of the horizon. To study the fabric and the formation process of replacement of evaporite is of economic and of scientific significance. Based on the outcrops and well cores in the southeastern Ordos Basin, thin section observation, stable isotopic analyses, scanning electron microscope (SEM), and fluid inclusion analyses are undertaken to study the time, process, and conditions of evaporite replacement to provide valuable information on the pore fluid properties and predict the reservoir quality.

2. Geological Background

The Ordos Basin, located in the middle-west of China, is the second largest basin in China with an area of 2.5 $\times$ 10$^5$ km$^2$ \[16\]. In the Ordovician Majiagou Formation, affected by the Helan Rift valley tension in the west of the basin, the rift shoulder rises forming the Central Uplift (also known as “L” shaped paleo-uplift group) \[17–19\]. Under the action of crustal equalization compensation, the compensating Shanbei Depression forms in the Middle East of the basin, which deposits anhydrite halite in drought-hot climate. The Jingbian Gas Field is located in the transitional zone between the Central Uplift and the Shanbei Depression (Figure 1). A set of dolomitecrite to fine crystalline dolomite is developed in restricted to semirestricted platforms in the Jingbian Gas Field. The study area is located in the southeast of the basin far from the central uplift depositing anhydrite nodule-bearing dolomite in evaporite platform facies.

In the late Ordovician, the basin was uplifted and subjected to exposure for more than 140 My during Caledonian orogeny, forming a significant regional unconformity above the Majiagou Formation \[6\]. The Ordovician Majiagou Formation can be divided into six members. Member 6 is eroded in most regions and only found in the southern part of the basin with a thickness of 10 to 20 m. Members Ma$_1$, to Ma$_5$ are developed all over the basin and can be laterally traced for several kilometers. Owing to the periodic sea-level changes, a set of transgression-regressive cycles are deposited in the Majiagou Formation, in which Ma$_1$, Ma$_3$, and Ma$_5$ members are mainly composed of dolomite and anhydrite in evaporite platform facies, whereas the Ma$_2$, Ma$_4$, and Ma$_6$ members are dominated by limestone and dolomite in open platform facies (Figure 1) \[16, 20\]. Up to 10 sub-members (Ma$_1$, Ma$_2$, ..., Ma$_{10}$) have been identified in member 5 with cyclic carbonate-evaporite intervals related to the short term sea-level variations (Figure 1) \[5\]. The Ma$_1$, to Ma$_5$ submembers are mainly composed of fine microcrystalline dolomite, anhydrite, karst breccia, and anhydrite nodule-bearing dolomite. Because of the dissolution of anhydrite nodules in meteoric water, a favorable reservoir developed in the upper four submembers of the Ma$_5$ member, which became the major gas producing strata. Yican 1 well, drilled in 2014, produces 3.5 $\times$ 10$^4$ m$^3$ gas daily in Ma$_2$ and Ma$_3$ submembers where the anhydrite nodules, dolomite, and fractures are developed.

The anhydrite dissolution pores account for more than 90% of pore types both in the Jingbian Gas Field and the southeastern Ordos Basin. Mold pore cementation is the key factor constraining the reservoir property in the study area. The anhydrite dissolution pores in the Jingbian Gas Field are mostly filled by dolomite accounting for less than 70% of the total porosity with abundant pores remaining open, whereas the anhydrite dissolution pores of Yican 1 well are mainly filled by minerals accounting for more than 90% of the overall porosity in southeastern Ordos Basin, leading to the significant reduction of porosity (Figure 2) \[21, 22\]. Therefore, the porosity differences between the Jingbian Gas Field and the southeastern Ordos Basin are mainly caused by the filling degree of the anhydrite dissolution pores. Accurate analysis of the genesis of minerals filling in the pores is beneficial to understand the fluid activity process and predict effective reservoirs.

3. Samples and Methods

More than 60 samples from the Ordovician Majiagou Formation of Yican 1 well in the southeastern Ordos Basin over a depth of 2631 to 3132 m are examined by an optical microscope. Data from other wells of the Jingbian Gas Field were used for comparison.

Hand specimens of carbonates have been sampled selectively with a small drill to obtain samples from a very limited area. Samples used for carbon and oxygen analysis are mainly obtained from the gypsum molds and dolomite matrix. Powder samples (~30–50 mg per single sample) of limestone, dolostone, and anhydrite were extracted for carbon and oxygen isotope measurements. The powdered samples were heated to remove organic materials and then reacted with anhydrous phosphoric acid under vacuum to release CO$_2$ at 25°C for 24 h. The CO$_2$ was then analyzed for carbon and oxygen isotopes on a Finnigan MAT251 mass spectrometer. All carbon and oxygen data are reported in %o units relative to the Vienna Pee Dee Belemnite (VPDB) standard (Hoefs, 2009). The precision for both $\delta^{13}$C and $\delta^{18}$O measurements is better than ±0.1‰. Ultrafabrics were studied using a Melin-type scanning electron microscope (SEM) (Carl Zeiss AG) operated at 15–20 kV with a 10 nA beam cut and a working distance of 10 mm. The mineral composition was
observed by back scattered electron image (BSE), and the elemental concentrations and spatial variation of micron-sized spots were determined using energy-dispersive spectrometry (EDS) at the China University of Petroleum (College of Geosciences), which could generate high-resolution, high-magnification images revealing carbonate textures.

A total of 14 pyrite samples were analyzed for their sulfur isotope ratios. 30 mg of pyrite was mixed with Cu₂O at 1100 °C under vacuum to produce SO₂. SO₂ was then analyzed on a Delta v plus Isotope Ratio Mass Spectrometer. The δ³⁴S values are reported relative to the Vienna-Canyon Diablo Troilite (V-CDT) standard [23]. The precision is better than 0.1‰.

Fluid inclusion heating-freezing analyses were conducted via a ZEISS Axioskop 40 A Pol with a Linkam THMS600 heating and cooling stages. An ultraviolet fluorescence system was used to discern hydrocarbon inclusions. The final melting temperature $T_m$ and the homogenization temperature $T_h$ were measured in all samples. Accuracy for measurements for homogenization temperature and melting temperature is ±1°C and ±0.1°C, respectively. The melting temperatures were converted to salinity values (equivalent wt.% NaCl) according to standard equations [23]. The bulk melting was close to the NaCl eutectic in most samples.

4. Results

4.1. Petrography. Anhydrite nodules primarily occur in thinly laminated dolomicrite, which also occur interlayered with anhydrite. The thinly laminated dolostones contain increasing amounts of anhydrite nodules from downward to upward of the unit. The nodules are spherical, ovoid, or, in some cases, elongate, ranging from 1 to 2 mm across (Figures 3(a)–3(d) and 4(a)–4(k)). Synsedimentary and early diagenetic nodular and contorted anhydrite structures are common diagnostic features of modern tidal environments [10]. The anhydrite nodules are partially or totally dissolved, where the carbonates display a vuggy internal...
Figure 2: The distribution map of minerals filling in anhydrite dissolution pores in the Ordovician Majiagou Formation of Ordos Basin (modified from [21, 22]).
microstructure, leaving molds to increase the overall reservoir properties. The anhydrite dissolution pores are more developed in the Jingbian Gas Field, which are rarely or partially filled by minerals (Figures 3(a)–3(d)). However, in the southeastern Ordos Basin, the molds are normally cemented by calcite, dolomite, quartz, etc. which resulted in the significant reduction of primary porosity in some core intervals.

4.1.1. Dolomite. Two types of dolomites are identified in the anhydrite dissolution pores. The first type is the fine crystalline dolomite at the bottom of the nodules (Figures 3(a)–3(d) and 4(c)–4(j)). The dolomite crystals at the bottom of the nodule are larger than the matrix dolomite with sizes ranging from 0.01 to 0.04 mm. The crystal density decreases, and the size increases from the bottom of the nodule towards the center of the mold. The fine crystalline dolomites are always at the bottom of the nodule as “seepage silts” forming the geo-petal structures indicating the top of the horizon. The fine crystalline dolomite accounts for 60%-70% of the total nodule with the remaining pores open (Figures 3(a)–3(d)) or filled with other minerals (Figures 4(a)–4(k)). The pores are mainly filled with this type of dolomite in the Jingbian Gas Field with the remaining pores open (Figure 2). The remained pores account for 20%-30% of the nodule forming the major reservoir space of the unit.

The other type of dolomite occurs as euhedral dolomite crystals in the upper part of the nodules with crystal sizes in the range of 50-500 μm (Figures 4(c)–4(e)). The crystals are in rhombic morphology with cloudy surface. Fluorescent light images show that the hydrocarbon inclusions are abundant in the pores of seepage silt at the bottom of the nodule, and some are observed in the lattice defect of dolomite crystals (Figure 4(f)). Some dolomite crystals have slightly curved crystals with undulose extinction as saddle dolomites (Figure 4(g)).

4.1.2. Calcite. Different from the concentric structure defined by a succession of different types of quartz and carbonate phases documented in many literatures [10, 24], the nodules in this study are commonly composed of “seepage silt” at the bottom and carbonate phases and quartz at the top. The molds are formed by the dissolution of anhydrite and filled with blocky calcite spar (Figures 4(h)–4(j)). The calcite crystal morphology is outlined by the outer envelopes of the pore space. Individual crystal is normally coarse to very coarse crystalline of about 500-1000 μm in diameter. Some crystals are clear with crossed twinning apparently free of evaporite inclusions (Figure 4(h)). Many of the calcites contain primary hydrocarbon inclusions as shown in fluorescent light images (Figure 4(k)).

4.1.3. Quartz. The quartz is observed to fill the same pore or vug with calcite in direct contact with the long axes commonly perpendicular to the surface in which they lie as a single euhedral crystal (Figures 4(d) and 4(h)). The crystals are clear with few inclusions, which display unit or undulose extinction. The single euhedral crystal is mainly hexagonal, bipyramidal, and up to 0.5 mm long. SEM photos show the
Figure 4: Continued.
4.3. Homogenization Temperature of Fluid Inclusions. The fluid inclusions in calcite have a varied size of 1-10 μm but are mostly smaller than 5 μm as single or groups (Figures 7(a)–7(c)). Some fluid inclusions are two-phase liquid-gas inclusions, which can be classified as primary and secondary inclusions. The primary inclusions occur as a single inclusion in the crystal or isolated away from other primary inclusions (Figure 7(c)). The fluid inclusion assemblage (FIA) concept has also been used in the study as they are cooccurrence of different types of inclusions of the same origin in the same host minerals [25]. An ultraviolet fluorescence system was used to discern hydrocarbon inclusions. Under the optical microscope, liquid hydrocarbon inclusions show light brown or straw yellow in transmission light, and the gas hydrocarbon inclusions are commonly brown colors (Figure 7(d)). Some gas hydrocarbon inclusions show brownish black color in transmission light (Figures 7(e) and 7(f)), whereas under ultraviolet fluorescence light, the hydrocarbon always shows fluorescence color from green (Figure 7(g)), strong yellow (Figures 7(h) and 7(i)), to weak blue and orange color with increasing thermal evolution degree.

The homogenization temperatures of the primary inclusions in calcite and dolomite are in between 140 and 234°C ($T_h = 6$) and 190 and 193°C ($T_h = 2$), respectively (Table 1). The NaCl-equivalent salinities range from about 19.13 to 23.18 weight % approaching halite saturation. The quartz filling in the anhydrite dissolution pores had similar fluid inclusion homogenization temperatures as the associated calcite cements in a range of 113-154°C with an average 131°C ($n = 4$).

4.4. The Total Salinity of Formation Water. The total salinity of formation water has been analyzed as listed in Table 2. The total salinity of the formation water of the Ordovician Majia-gou Formation in the southeastern Ordos Basin is very high, which can be up to 295.04 g/L, an average 150.31 g/L. The water type is mainly CaCl$_2$. The high salinity of the formation water shows that the CaSO$_4$ concentration is very high as shown in Table 2.

Figure 4: Minerals filling in anhydrite dissolution pores of the Ordovician carbonate in Yichan 1 well in the southeastern Ordos Basin. (a) Anhydrite nodule-bearing dolomite in Yichan 1 well, 2298.6 m, Ma$_5$. (b) Anhydrite dissolution pores filled with dolomite, calcite, and pyrite in Yichan 1 well, 2642.5 m, Ma$_5$, sample 96. (c) Anhydrite dissolution pores filled with dolomite, calcite, and quartz, 2641.4 m, Ma$_5$, sample 92. (d) Anhydrite dissolution pores filled with dolomite, calcite, and pyrite, 2642.5 m, Ma$_5$, sample 96. (e) Ultraviolet fluorescence photo shows hydrocarbon inclusions enriched in dolomite at the bottom of the nodule and lattice defect of calcite at the top of nodule, 2642.5 m, Ma$_5$, sample 96. (f) Saddle dolomite showing undulose extinction in the anhydrite dissolution pores, 2951.5 m, Ma$_5$, sample 242. (g) Calcite with crossed twinning and euhedral quartz filling in calcite and dolomite, 2640.9 m, Ma$_5$, sample 90. (h) Calcite with crossed twinning and euhedral quartz filling in the anhydrite dissolution pores, 2641.4 m, Ma$_5$, sample 92. (i) Anhydrite dissolution pores filled with calcite and quartz, 2642.5 m, Ma$_5$, sample 96. (j) Anhydrite dissolution pores filled with dolomite and calcite, 2640.9 m, Ma$_5$, sample 90. (k) Ultraviolet fluorescence photo shows hydrocarbon inclusions enriched in dolomite at the bottom of the nodule and lattice defect of calcite at the top of nodule, 2640.9 m, Ma$_5$, sample 90. (i) SEM photo of calcite, pyrite, and quartz filling in the anhydrite dissolution pores, 2641.4 m, Ma$_5$, sample 92.
5. Discussions

Anhydrite nodule-bearing dolomite was interpreted to be formed by the penecontemporaneous dolomitization mode of the sabkha evaporative tidal flat [26]. The anhydrite and dolomite cyclical intervals are typical for shallow subtidal to supratidal evaporative settings. The dissolution molds are permeated by meteoric water during an episode of subaerial exposure during the Caledonian orogeny as they are restricted to the upmost 10 m below unconformity [6]. However, the cementation of the molds probably occurs in late burial settings.

5.1. Origin of Minerals Filling in Anhydrite Dissolution Pores

5.1.1. Calcite. The clean calcites containing no anhydrite inclusions suggest that they grow slowly in an open space where the anhydrite has been removed, which is confirmed by the existence of seepage silt at the bottom of the mold. The hydrocarbon inclusions in the calcite and in the residual pores at the bottom seepage silt indicate that the calcite probably precipitates when the hydrocarbon migrates to react with the dissolved sulfate in the pores. The original pore water in the Majiagou Formation would have been normal seawater to evaporative brines as the host rock consists of shallow marine platform limestone in the lower part of the formation and extensive evaporative facies in the upper part of the formation [27–29]. The initial pore fluid could have been diluted by meteoric water in much of the basin during the extended period of subaerial exposure [29]. The aqueous fluid inclusions in calcite filling in the molds, however, have
Figure 7: Continued.
Figure 7: Characteristics of fluid inclusions in minerals filling in anhydrite dissolution pores in Yican 1. (a) Two-phase liquid-vaporous inclusions (WL+V) in calcite filling in anhydrite dissolution pores corresponding to Figures 4(j) and 4(k), 2640.9 m, Ma51, sample 90. (b) Two-phase liquid-vaporous inclusions (WL+V) in calcite filling in anhydrite dissolution pores corresponding to Figure 4(i), 2642.5 m, sample 96. (c) Two-phase liquid-vaporous inclusions (WL+V) in calcite filling in anhydrite dissolution pores, 2641.8 m, sample 94. (d) Two-phase hydrocarbon inclusions of calcite filled in fracture showing light brown (OL) and black color (OV) in transmission light, 2642.5 m, sample 96. (e, f) Vaporous hydrocarbon inclusions (OV) of calcite showing black color in transmission light, 2635 m, sample 73. (g) Two-phase hydrocarbon inclusions of calcite filled in fracture showing light yellow (OV) and no fluorescence light (OV) in ultraviolet fluorescence light (the same thin section of (d)), 2642.5 m, sample 96. (h) Liquid hydrocarbon (OL) in the dolomite at the bottom of mold showing light green color in ultraviolet fluorescence light, 2641.8 m, sample 94. (i) Vaporous hydrocarbon inclusions (OV) of calcite showing yellow color in ultraviolet fluorescence light (the same thin section of (f)), 2635 m.

Table 1: Homogenization temperature of fluid inclusions in minerals filling in anhydrite dissolution pores in Yican 1 of the southeastern Ordos Basin.

<table>
<thead>
<tr>
<th>No.</th>
<th>Samples</th>
<th>Minerals filling in molds</th>
<th>Homogenization temperature (°C)</th>
<th>Average (°C)</th>
<th>Melting temperature (°C)</th>
<th>Calculated salinity (%)</th>
<th>Average (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>94</td>
<td>Dolomite</td>
<td>190</td>
<td>193</td>
<td>-17.3</td>
<td>20.45</td>
<td>21.81</td>
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<td>2</td>
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<td>Dolomite</td>
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<td>172</td>
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<td>23.18</td>
<td></td>
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<tr>
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<td>90</td>
<td>Calcite</td>
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<td></td>
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<td>19.13</td>
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<tr>
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<tr>
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<td>21.03</td>
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<tr>
<td>6</td>
<td>94</td>
<td>Calcite</td>
<td>170</td>
<td></td>
<td>-18.4</td>
<td>21.26</td>
<td></td>
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<tr>
<td>7</td>
<td>96</td>
<td>Calcite</td>
<td>140</td>
<td></td>
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<td>23.18</td>
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<tr>
<td>8</td>
<td>96</td>
<td>Calcite</td>
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<td>23.18</td>
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<td>94</td>
<td>Quartz</td>
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<td>-20.1</td>
<td>22.44</td>
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<td>10</td>
<td>94</td>
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<td>Quartz</td>
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<td>21.47</td>
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<td>12</td>
<td>96</td>
<td>Quartz</td>
<td>154</td>
<td></td>
<td>10</td>
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Table 2: Formation water composition of some wells of the Ordovician Majiagou Formation in the southeastern Ordos Basin.

<table>
<thead>
<tr>
<th>Well</th>
<th>Formation</th>
<th>Section (m)</th>
<th>K⁺+Na⁺ (mg/L)</th>
<th>Ca²⁺ (mg/L)</th>
<th>Mg²⁺ (mg/L)</th>
<th>Cl⁻ (mg/L)</th>
<th>HCO₃⁻ (mg/L)</th>
<th>SO₄²⁻ (mg/L)</th>
<th>Total salinity (g/L)</th>
<th>Water type</th>
</tr>
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<tbody>
<tr>
<td>Yi 5</td>
<td>Ma₅₁</td>
<td>2317.0-2326.0</td>
<td>16749</td>
<td>79320</td>
<td>7660</td>
<td>180940</td>
<td>839</td>
<td>9529</td>
<td>295.04</td>
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<tr>
<td>Yi 6</td>
<td>Ma₅₁</td>
<td>2295.0-2336.0</td>
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<td>66198</td>
<td>11951</td>
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<td>874</td>
<td>6556</td>
<td>266.54</td>
<td>CaCl₂</td>
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<td>Yi 18</td>
<td>Ma₅₃</td>
<td>2358.0-2379.0</td>
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<td>10060</td>
<td>916</td>
<td>68225</td>
<td>530</td>
<td>10850</td>
<td>126.96</td>
<td>CaCl₂</td>
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<tr>
<td>Yi 8</td>
<td>Ma₅₁</td>
<td>2247.0-2257.0</td>
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<td>20623</td>
<td>3968</td>
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<td>204</td>
<td>20494</td>
<td>121.74</td>
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<td>Yi 14</td>
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<td>2279.0-2300.0</td>
<td>9975</td>
<td>15090</td>
<td>1831</td>
<td>43619</td>
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<td>Yi 12</td>
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<td>2347</td>
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<td>8575</td>
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Table 3: Carbon and oxygen isotope results of calcite filling in mold and corresponding dolomite matrix in Yican 1 well in the southeastern Ordos Basin.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Depth (m)</th>
<th>Lithology</th>
<th>Formation</th>
<th>$\delta^{13}$C of calcite in mold (VPDB ‰)</th>
<th>$\delta^{18}$O of calcite in mold (VPDB ‰)</th>
<th>$\delta^{13}$C of dolomite matrix (VPDB ‰)</th>
<th>$\delta^{18}$O of dolomite matrix (VPDB ‰)</th>
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<tr>
<td>92</td>
<td>2641.38</td>
<td>Dolomicrite</td>
<td>Ma$_5^1$</td>
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<td>-11.12</td>
<td>-0.59</td>
<td>-8.04</td>
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<tr>
<td>152</td>
<td>2688.00</td>
<td>Dolomicrite</td>
<td>Ma$_6^4$</td>
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<td>-14.32</td>
<td>-1.01</td>
<td>-9.89</td>
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<tr>
<td>164</td>
<td>2729.92</td>
<td>Dolomicrite</td>
<td>Ma$_6^5$</td>
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<td>-11.27</td>
<td>-6.87</td>
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<td>Dolomicrite</td>
<td>Ma$_6^6$</td>
<td>-6.25</td>
<td>-12.52</td>
<td>-2.21</td>
<td>-8.36</td>
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<tr>
<td>186</td>
<td>2808.49</td>
<td></td>
<td>Ma$_4$</td>
<td>-2.70</td>
<td>-15.58</td>
<td>-1.93</td>
<td>-10.32</td>
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<tr>
<td>220</td>
<td>2821.06</td>
<td></td>
<td>Ma$_4$</td>
<td>-2.77</td>
<td>-13.49</td>
<td>-0.92</td>
<td>-6.75</td>
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<tr>
<td>228</td>
<td>2823.70</td>
<td></td>
<td>Ma$_4$</td>
<td>-7.20</td>
<td>-11.76</td>
<td>-0.14</td>
<td>-7.80</td>
</tr>
<tr>
<td>229</td>
<td>2823.80</td>
<td></td>
<td>Ma$_4$</td>
<td>-6.41</td>
<td>-10.09</td>
<td>0.18</td>
<td>-7.00</td>
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<tr>
<td>232</td>
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<td></td>
<td>Ma$_3$</td>
<td>-3.71</td>
<td>-8.96</td>
<td>-3.11</td>
<td>-7.10</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>Ma$_3$</td>
<td>-4.66</td>
<td>-12.12</td>
<td>-1.84</td>
<td>-8.47</td>
</tr>
</tbody>
</table>

high $T_h$ values (140-234°C) and high salinity (19.13-23.18 wt.% NaCl equivalent). The occurrence of fluids with salinities of higher than that of seawater (ca. 3.5 wt.%) is a direct indication of no influence of meteoric water. The exclusion of the involvement of meteoric water in spite of a substantial period of subaerial exposure suggests that the calcite filling in molds might have occurred after the subaerial exposure event and probably in the burial conditions. The homogenization temperature of calcite and dolomite is 140-174°C and 190-196°C, respectively, reflecting the deep burial diagenetic setting. The calcite filling in molds, therefore, is interpreted to have been precipitated from residual evaporative brine that had been locally preserved in the basin. Carbonate reservoirs with associated anhydrite, such as the anhydrite dissolution pores, are optimum sites for TSR, where the evaporative brines are remained in the pores.

This interpretation is further supported by the carbon and oxygen isotope composition of the calcite filling in the anhydrite dissolution pores. The presence of a possible hydrocarbons in the molds, together with its very low carbon isotope (-7.56‰ to 0.26 VPDDB) in calcite (Figure 6, Table 3) suggests that the calcite precipitation occurred in the presence of liquid hydrocarbons [30]. The oxygen isotope of calcite filling in anhydrite dissolution pores range from -15.58‰ to -8.96‰ VPDDB, significantly negative to those in matrix dolomite, ranging from -10.96‰ to -6.75‰ VPDDB (Figure 6, Table 3) indicating the effect of elevated temperatures, which drive the thermal fractionation of diagenetic carbonate [31–33]. The calcite, therefore, is most likely by-product of TSR, where the hydrocarbon reacts with sulfate in residual pore water in high temperature of deep burial condition. The porosity is lost due to the precipitation of authigenic calcite and dolomite.

The simplest TSR reaction can be written as [34]

$$nCaSO_4 + C_nH_{2n+2} \rightarrow nCaCO_3 \text{ (or } CO_2) \ + H_2S + (n-1)S + nH_2O.$$  

(1)

The reaction provides the most reasonable explanation for both occurrences of authigenic calcite and oxidization of organic matter whose carbon is incorporated into the calcite [35, 36].

Although the lowest temperature for TSR is controversial, the available data indicate that as a generalization, the minimum temperature range of TSR is about 100-140°C [37]. Hence, in most geological settings, TSR occurs as soon as the temperature reaches this range, provided the necessary “ingredients” (sulfate, reactive organics, and some sulfur in a reduced form) are present [38]. Since uplifting and erosion in Caledonian, the Ordovician stratum is buried continuously until the late Cretaceous [39] (Figure 8). Using geothermal gradients of 36°C/km and a surface temperature of 20°C, the temperature of 100°C reflects a depth of about 2200 m in early Triassic. TSR can proceed from 2200 m to the maximum depth of about 5000 m in late Cretaceous.

5.1.2. Dolomite. The fine crystalline dolomite at the bottom of the nodules is commonly interpreted to be formed by the dissolution of anhydrite and the reprecipitation of dolomite solution as “seepage silt.” The composition of this dolomite, therefore, is the same as the matrix dolomite, whereas the
crystal size is commonly larger than that of matrix. The occurrence of seepage silts is a typical characteristic of meteoric water flushing in epigenetic stage.

The milky white, medium to coarse crystalline saddle dolomites in anhydrite dissolution pores are probably TSR dolomite. The abundant hydrocarbons in the pores of seepage silt at the bottom of the mold and in the lattice defect of dolomite crystals indicate simultaneously migration of hydrocarbons with the formation of crystalline dolomite. Saddle dolomite with undulose extinction is the typical characteristic of hydrothermal effect [33, 40], which is confirmed by its high homogenization temperature up to 193°C. Dolomite is the second most abundant carbonate formed as byproduct of TSR. TSR dolomite is almost exclusively restricted to the anhydrite-bearing dolomite associated with TSR calcite. Pressure solution is considered the chief source of Mg2+ for TSR dolomite [37]. The precipitation of calcite increases the Mg2+/Ca2+ ratio in the pore water, which also promotes the dolomitization.

5.1.3. Pyrite. Pyrite is pervasively observed to occur as cubic, euhedral crystal (10-1000 μm) at the bottom of the mold or surrounding it. The cubic habit of pyrite (and the absence of frambooidal pyrite) may indicate a nonbacterial origin with a relatively slow crystal growth rate during burial diagenesis at elevated temperatures.

Pyrite can be formed by the reaction of Fe2+ with S2- as soon as in contact. S2- can be originated from deep magma in volcanism [41], desulfurization of organic matter [42], bacterial sulfate reduction (BSR) [43, 44], or TSR. Previous studies reveal that the δ34S of deep magma ranges from -5.6‰ to 5.5‰ [45]. The Ordos Basin is a stable cratonic basin, which excludes the possibility of volcanism. The pyrite formed by BSR commonly has a negative δ34S value with an average from -42.7‰ to -5‰ [46, 47]. BSR is known from a multitude of geological settings that range in temperature from 0 to about 80°C [48, 49]. The homogenization temperature of fluid inclusions in calcite is between 140 and 234°C, in which the sulfate reduction bacteria cease to metabolize. The δ34S value of TSR pyrite is commonly positive, which is reported to be from 8.9‰ to 23.4‰ of the pyrite from the Dengying Formation in Sichuan Basin [50] and 30‰ to 33‰ from the Upper Cambrian [36]. The pyrite in this study has a range of δ34S from 10.50‰ to 24.00‰ with average 17.33‰ (n = 11), which can only be obtained from TSR.

H2S is the most convincing and commonly known byproduct of TSR [51, 52]. However, the H2S concentration is very low in Yican 1 well, which is only observed at 2823.7 m with low concentration. The most important reason for the widespread of pyrite and scarcity of H2S is due to the presence of significant amount of Fe2+ in the horizon (Table 4). H2S released from TSR is initially dissolved in the formation water in H+ and S2− form (Reactions (2) and (3)). The later will react with Fe2+ within seconds to minutes to form metal sulfides (Reaction (4)). H2S effectively removed as metal sulfide precipitation almost instantaneously, as soon and as long as base metals are available [38]. The Fe2+ content can be up to 23112:5 × 10^-6 (Table 4) at the H2S produced site of Yican 1 well, which abundantly assumed the H2S released from TSR. The reaction between Fe2+ and H2S reduces the concentration of H2S and increases the pervasively occurrence of pyrite.

\[ H_2S(aq) \rightarrow H^+ + HS^-, \]  
\[ 2HS^- \rightarrow 2H^+ + S_2^2-. \]
Table 4: Geochemistry data of pyrite from Yican 1 in the southeastern Ordos Basin.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Depth (m)</th>
<th>Formation</th>
<th>Lithology</th>
<th>Pyrite $\delta^{34}$S (VCDT, ‰)</th>
<th>Matrix $\delta^{13}$C (VPDB, ‰)</th>
<th>Matrix $\delta^{18}$O (VPDB, ‰)</th>
<th>Matrix Fe $\times 10^{-6}$</th>
<th>Matrix Mn $\times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>71</td>
<td>2634.7</td>
<td>Ma$_1$</td>
<td>Dolomericite</td>
<td>11.90</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>72</td>
<td>2634.9</td>
<td>Ma$_1$</td>
<td>Dolomericite</td>
<td>18.80</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>83</td>
<td>2637.4</td>
<td>Ma$_1$</td>
<td>Micrite limestone</td>
<td>11.10</td>
<td>-10.28</td>
<td>-10.62</td>
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<tr>
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<td>2638.7</td>
<td>Ma$_1$</td>
<td>Micrite limestone</td>
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</tr>
<tr>
<td>108</td>
<td>2646.6</td>
<td>Ma$_1$</td>
<td>Micrite limestone</td>
<td>-7.6</td>
<td>-1.44</td>
<td>-9.77</td>
<td>8312.50</td>
<td>224.88</td>
</tr>
<tr>
<td>122</td>
<td>2677.5</td>
<td>Ma$_1$</td>
<td>Dolomericite</td>
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<td>-0.86</td>
<td>-8.69</td>
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<tr>
<td>249</td>
<td>2954.5</td>
<td>Ma$_2$</td>
<td>The fine crystalline dolomites</td>
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<td>-0.46</td>
<td>-8.74</td>
<td>3387.50</td>
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<tr>
<td>308</td>
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<td>Ma$_1$</td>
<td>Dolomericite</td>
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<td>-3.25</td>
<td>-7.84</td>
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<td>139.44</td>
</tr>
<tr>
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<td>Ma$_1$</td>
<td>Dolomericite</td>
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<td>19412.50</td>
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<td>Dolomericite</td>
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<td>321</td>
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<td>Dolomericite</td>
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<td>/</td>
<td>/</td>
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<tr>
<td>329</td>
<td>3128.76</td>
<td>Ma$_1$</td>
<td>Dolomericite</td>
<td>20.30</td>
<td>-0.90</td>
<td>-7.50</td>
<td>9912.50</td>
<td>410.52</td>
</tr>
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</table>
5.1.4. Quartz. The silicification of evaporite is commonly thought to occur prior to significant burial (less than 500 m) [11]. Quartz is conventionally interpreted to be precipitated from solutions with higher silica concentrations from the dissolution of clastic quartz and other silicates of the mudstones or surrounding detrital deposits. The
dissolution and replacement of anhydrite by quartz, therefore, are indicative of the circulation of groundwater super-saturated in silica [24]. In the present case, the lack of anhydrite inclusions in quartz indicates that the quartz post-dates the dissolution of anhydrite. The euhedral morphology of the quartz suggests that the quartz grows in sufficient space, where the anhydrite had probably been removed to form central hollows that later allows the euhedral crystals to grow. The relatively high homogenization temperature of fluid inclusions in quartz (113-154°C) strongly suggests that they are formed in deep burial conditions, which is probably related to TSR. Quartz is considered kinetically favorable to precipitate from low-pH solution [53-55]. H⁺ released from calcite (Reaction (1)) and pyrite precipitation (Reaction (2) and (3)) is expected to locally decrease the pH value of the formation water, which is favorable for the precipitation of authigenic quartz. This can give a good explanation for the close temporal and spatial association of calcite and quartz [55]. In the present case, the authigenic quartz filling in anhydrite mold is, therefore, formed as a burial diagenetic process instead of an early diagenetic process.

5.2. Diagenesis Evolution and Comparison with the Jingbian Gas Field. The paleogeographic location of the southeastern Ordos Basin is much lower than that of the Jingbian Gas Field [56]. The sedimentary environment of the Jingbian Gas Field is mainly dolomitic flat subfacies and anhydrite-bearing dolomite flat subfacies of the supratidal zone, whereas the southeastern Ordos Basin is mainly located in anhydrite-dolomite flat subfacies and anhydrite lake subfacies of intertidal zone (Figure 9). When the sea level decreases, the anhydrite nodules begin to form in the Jingbian Gas Field of supratidal zone. For longer evaporative time, the anhydrite nodules are more abundant, and the nodule size is larger in the Jingbian Gas Field (Figure 3, Figures 9(a) and 9(b)).

When uplifted in Caledonian orogeny in late Ordovician, the horizon experienced the leaching of meteoric water resulting in the anhydrite nodules dissolved, leaving the molds enriched in anhydrite dissolution water (Figures 9(c) and 9(d)). With the sea level increasing in Carboniferous-Permian, the southeastern Ordos Basin is flooded by the ocean from the south and east direction subsequently [22]. The formation is submerged in sea water of marine phreatic environments for a long time, leading to the pore water enriched in marine water. Owing to the periodic sea-level changes, the connate marine pore water is altered locally by minor amounts of evaporative water during shallow burial resulted in the pore water enriched in calcium sulfate (Table 2). Most minerals are preferentially hydrophilic so that a film of residual water lines the grain framework even in hydrocarbon gas-bearing reservoirs [57]. The amount of this residual water is generally ~10% of the pore volume of the rock. Reactions occurring in solution are generally many orders of magnitude faster than reactions between gases and solids [58]. Therefore, the hydrocarbons reacted with the dissolved anhydrite in solution in the residual water film rather than as a solid-gas reaction [34]. Since being uplifted in the Caledonian orogeny in the late Ordovician of the lower Paleozoic, the Ordos Basin experienced continuous burial until the deepest burial in the early Cretaceous, as shown in previous studies (Figure 8) [39]. The burial temperature has been above the minimum temperature of about 100°C in 2200 m of the early Triassic (using 36°C/km as a geothermal gradient and 20°C as surface temperature) necessary for TSR, the calcium sulfate enriched in pore water will react with hydrocarbons to form H2S and CO2. TSR will continue to the maximum burial of about 5000 m, equivalent to the temperature of 200°C. Calcite and dolomite are interpreted to be formed in late-diagenetic stage based on the petrographic and geochemical evidence investigated in this study (Figures 9(e) and 9(f)). The spatial distribution of calcite, along with that of secondary dolomite, authigenic quartz, and pyrite, in combination with carbon and oxygen data further indicates that the calcite in anhydrite dissolution pores is genetically related to thermochemical sulfate reduction.

In contrast to the southeastern Ordos Basin, the Jingbian Gas Field is located in the tectonic high in paleogeography, and the anhydrite dissolution water after leaching by meteoric water is taken away from its open system, leaving the molds open (Figure 9(e)). The sea water flooded in the southeastern direction has not emerged within the Jingbian region. The TSR reaction rarely occurs for the lack of dissolved sulfate in the pore water. Although some molds are also filled with minerals in the Jingbian Gas Field, the filling degree is much lower than that in the southeastern Ordos Basin (Figure 2). Therefore, the resultant porosity in the mold is preserved resulting in the high porosity and permeability of the Jingbian Gas Field (Figures 2 and 3).

6. Conclusions

The anhydrite nodule-bearing dolomite is widely distributed in the upper Majiagou Formation of the southeastern Ordos Basin. Nevertheless, the anhydrite dissolution pores are commonly filled by minerals such as dolomite, calcite, pyrite, and quartz, which resulted in significant porosity and volume reduction. The calcite filling in anhydrite dissolution pores is interpreted to be precipitated as TSR by-product, which is supported by its relatively negative δ18O value (-15.58‰ ~ -8.96‰ VPDB) and negative δ13C value (-7.56‰~0.26‰ VPDB). The higher homogenization temperatures (140-234°C) and high salinity (19.13-23.18 wt.% NaCl equivalent) of the primary inclusions in calcite confirm the above interpretation. Dolomite is the second most abundant carbonate formed as a by-product of TSR, which is promoted by the precipitation of calcite and resulted enriched in Mg²⁺/Ca²⁺ ratio in the pore water. Pyrite forms by the reaction of H2S released from TSR with the Fe²⁺ in the horizon, which is supported by its cubic habit and relatively high δ34S value (10.50‰~24.00‰). Quartz with relatively high homogenization temperature (113-154°C) is considered to precipitate in low-pH solution from calcite and pyrite precipitation after TSR.

The paleogeographic location of the southeastern Ordos Basin is much lower than that of the Jingbian Gas Field, which is submerged in the sea water of marine phreatic environments for a long time when sea water flooded from the
southeastern direction. Owing to the periodic sea-level changes, the connate marine pore water is altered locally by minor amounts of evaporative water during shallow burial resulted in the pore water enriched in calcium sulfate. The Jingbian Gas Field, however, is located in the tectonic high in paleogeography which has not been emerged by sea water. TSR rarely occurs for the lack of enriched pore water. Therefore, the resultant porosity in the nodule is preserved and rarely filled by other minerals resulting in the high porosity and permeability of the Jingbian Gas Field.

Data Availability
The data presented in this study are available on request from the corresponding author.

Conflicts of Interest
The authors declare no conflict of interest.

Authors’ Contributions
Conceptualization, methodology, and writing of original draft were done by Lihong Liu. Investigation and writing (review and editing) were done by Chunlian Wang. Resources and funding were done by Zhili Du. Validation, visualization, and project administration were done by Jianghua Gong. All authors have read and agreed to the published version of the manuscript.

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