Controls on the Organic Matter Accumulation of the Marine–Continental Transitional Shanxi Formation Shale in the Southeastern Ordos Basin

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ABSTRACT: The marine−continental transitional shale with favorable geological conditions for shale gas accumulation and broad resource prospects is widely distributed in China, which is also well developed in the Ordos Basin. The reservoir characteristic and gas-bearing properties of the transitional Shanxi Formation shale have been studied in previous studies. However, the factors influencing the organic matter (OM) accumulation have not been well studied, which restricts shale gas exploration and development of the Shanxi Formation in the Ordos Basin. According to analyses of organic geochemistry, mineral compositions, and major and trace elements, this paper has studied the paleoenvironment characteristic and its influence on the OM accumulation of the Shanxi Formation shale. The results indicate that the OM is characterized by the high mature stage and type III kerogen while the total organic content (TOC) of Member 1 is higher than that of Member 2. From Member 1 to Member 2, the paleowater depth gradually decreases, along with a gradually relative cold and dry climate, decreasing the terrestrial influx intensity and paleoproductivity and increasing the oxygen content in the water column. For Member 1, the OM accumulation is mainly controlled by the terrestrial influx intensity and paleowater depth, and other paleoenvironment factors have an unobvious contribution to the OM accumulation. For Member 2, the OM accumulation is commonly controlled by the weak terrestrial influx, low paleoproductivity, and oxic water column, resulting in the low TOC of Member 2. This study reveals the paleoenvironment characteristic and controls on the OM accumulation of the Shanxi Formation shale, which is beneficial to the reservoir selection of the Shanxi Formation in the southeastern Ordos Basin and the understanding of the OM accumulation in other transitional shales.

1. INTRODUCTION

Shale gas, which is one of the most important unconventional natural gas resources, has obtained more attention in recent years and made a great breakthrough around the world.1−7 Meanwhile, the exploration and development of shale gas have developed rapidly in China. Based on efforts made in previous years, Chinese shale gas production has reached 200 × 10^8 m^3 in 2020, ranking among the top three in the world and effectively relieving the pressure of Chinese natural gas demand. Shale gas in China is controlled by the complex tectonic geological background, and there are many types of shale gas reservoirs, which are widely distributed in marine, continental, and marine−continental transitional shales.5,6,8−10

Marine shale gas is the main research direction in China and has made a series of important breakthroughs in recent years. With regard to the accumulation mechanism, controlling factors on enrichment, geological model, and resource prospect of shale gas, previous studies have established the accumulation model and the relatively systematic geological theory of marine shale gas in southern China.4,11−14 However, compared with the development of marine shale gas, the transitional shale with a large distribution area and great resource potential lacks systematic research and has not yet made a breakthrough.11,15

The transitional shale is mainly distributed in the Carboniferous−Permian period in China, including the Northern China platform (the Ordos Basin, the Southern North China Basin, the Qinshui Basin, and the Bohaiwan Basin) and the Yangtze platform.15,16−18 The Ordos Basin, located in the central area of sedimentary basins in China, is one of the most important petroliferous basins. Meanwhile, the transitional shale in the Ordos Basin mainly distributed in the Benxi,
Taiyuan, and Shanxi Formation have been the focus of shale gas exploration in recent years. Several studies indicate that the thick Shanxi Formation characterized by humic OM, high TOC, and high organic maturity is widely distributed in the Ordos Basin and has good hydrocarbon generation conditions and reservoir forming potential. Meanwhile, some gas well data reveal that the Shanxi Formation in the southeastern Ordos Basin has a relatively good gas-bearing property, for example, the shale gas content in the Yunyeping-1 well ranges from 0.6 to 4.1 m³/t, with the daily gas production of 2.0 × 10⁴ m³, while the daily gas production in the Yunyeping-3 well and Yunyeping-6 well is 5.3 × 10⁴ and 3.0 × 10⁴ m³, respectively.

However, studies on the transitional shales in the Ordos Basin regarding the Benxi, Taiyuan, and Shanxi Formation as a whole are mainly concentrated on characteristics of the reservoir physical property and gas-bearing property, which are lack of understanding about the differences of the OM accumulation in each transitional formation. Due to rapid changes in the paleoenvironment and complex sedimentary facies in the Shanxi Formation, the lithology is complicated and the distribution of OM is uneven in the formation. OM is the material basis of shale gas accumulation, which is influenced by many factors such as sedimentary environment and material source in geological history.

Figure 1. (a) Tectonic units of the Ordos Basin and location of the SX-1 well. (b) Sedimentary facies distribution of the Permian Shanxi Formation in the Ordos Basin and its periphery (modified with permission from Li, Zhang, Li, Chen, Guo, Ma, Feng, and Zhang). (c) Stratigraphic section of Paleozoic in the southeastern Ordos Basin (modified with permission from Xiao, Liu, Zhang, Lin, and Zhang). (d) Lithology and sampling information of the SX-1 well.
ductivity, paleowater depth, terrestrial influx, and paleoredox conditions of the Shanxi Formation shale. Furthermore, based on the research of the paleoenvironment, this study establishes accumulation mechanisms of OM in different layers of the Shanxi Formation. The conclusions are significant to the understanding of OM accumulation and reservoir selection of the transitional Shanxi Formation shale in the southeastern Ordos Basin, China.

2. GEOLOGICAL SETTING

The Ordos Basin is a craton basin developed in the western area of the Sino-Korean plate, which is the second-largest sedimentary basin in China.33–35 The Ordos Basin is composed of 6 secondary tectonic units (Western edge thrust belt, Tianhuan depression, Yishan slope, Jinxi flexure belt, Yimeng uplift, and Weibei uplift), which is abundant in coal, petroleum, and natural gas36–38 (Figure 1a).

The study area is located in the southeastern margin of the Yishan slope, and its tectonic evolution is controlled by the Ordos Basin. During the Archean-Early Proterozoic period, the basin experienced four tectonic movements, namely, the Qianxi, Fuping, Wutai, and Lviang movements.39 In the late Paleozoic, the basin began the overall tectonic divergent evolution and was affected by the Hercynian movement, which transformed from marine to continental facies, and the climate gradually became dry.40,41 In the Mesozoic period, the basin entered the evolution stage of an inland lake basin, in which the basic pattern of the basin was established.42 In the Middle Triassic, affected by the Indosinian movement, many faults, such as high-quality source rocks, petroleum, and gas resources, were developed in the basin.43 In the late Cretaceous, the basin was at the end of the Yanshan Movement, and its southeastern strata experienced a continuous tectonic uplift, which resulted in the basin pattern as a large monoclinic dip to the west.44

In the Shanxi period, due to the Hercynian movement, the basin formed a unified subsidence depression. Meanwhile, the seawater rapidly withdrew from the southeast of the basin, which led to the expansion of land area, the subsidence center area of the basin was large, and the material source was abundant.45 The basin developed alluvial plains, delta plains, delta fronts, and shallow lakes from north to south. The late and early Shanxi Formation sedimentary patterns are similar (Figure 1b). The main difference was the northward shift of the overall sedimentary facies belt, the scale of the delta plain facies decreased, and the scale of the delta front facies expanded.45,47 The Shanxi Formation shale is one of the effective source rocks in the Ordos Basin. From the information of the SX-1 well, the lithology is composed of sandstone, coal, and dark shale, while the sandy content decreases from top to bottom (Figure 1c). The organic matters of the Shanxi Formation shales are mainly type II and III kerogen, the TOC is relatively high, and the thermal evolution is in the mature stage.45,46,49

3. SAMPLES AND METHODS

The study well is located in the southeastern Ordos Basin, near Yanan City, Shanxi Province (Figure 1a). The coring information of the SX-1 well indicates that the buried depth of the Shanxi Formation exceeds 3500 m, in which the stratigraphy is dominated by fine sandstone, shale, coal, and carbonaceous shale (Figure 1c). Member 1 and Member 2 each have a set of coal seams, and the upper Member 2 has a higher sand content, while Member 1 has a higher carbon content. To study the differences of OM abundance in the Shanxi Formation, seven samples of Member 2 (SX1-1–SX1-7) and seven samples of Member 1 (SX1-8–SX1-14) are collected for relevant experiments, in which the lithology of samples is composed of fine sandstone (SX1-4), argillaceous shale (SX1-1 and SX1-3), silt shale (SX1-5 and SX1-7), shale (SX1-6 and SX1-12), carbonaceous shale (SX1-2, SX1-8, SX1-10, SX1-11, SX1-13, and SX1-14), and coal (SX1-9). In the Research Institute of Exploration and Development of Daqing Oilfield Company Ltd and the Key Laboratory of Strategy Evaluation for Shale Gas, Ministry of Natural Resources, China University of Geosciences, Beijing, ten samples are taken for mineral composition analysis, and all samples are analyzed for organic geochemistry and major and trace elements.

3.1. Organic Petrographic and Organic Geochemistry Analysis. The vitrinite reflectance (Ro) is tested by an oil-immersed reflection optical microscope, and the kerogen type dominated by maceral compositions is observed through a light microscope. Samples tested for the TOC value are ground into a powder <80 mesh and treated with hydrochloric acid (HCl) to reduce the influence of carbonates. Then, samples treated with acid are washed with distilled water and analyzed for TOC through a LEICA DM 6000 M microscope photometry system, in which the kerogen type is determined with normal white light.

Pretreatments of samples, which include chloroform extraction, methanol–acetone–benzene extraction (MAB extraction), and kerogen preparation, are required prior to analysis of kerogen carbon isotope (Corg). First, 100 g of sample powder (<80 mesh) and 500 mL of pure chloroform are prepared for chloroform extraction. The extraction process is set at 85 °C for 17 h, and the extraction is completed when the fluorescence of the extraction solution is below grade 3. Then, the MAB extraction reagent is prepared in the proportion of 70% benzene, 15% acetone, and 15% methanol, and the temperature is set at 120 °C for more than 17 h. When the extraction solution is colorless, the MAB extraction is completely followed by the reagent evaporated to dryness. Finally, kerogen is prepared with the rock residue after chloroform extraction and MAB extraction. The procedures are as follows: (1) Per gram of the sample is added 6–8 mL of HCl with a concentration of 6 mol/L, which is stirred for 1–2 h at 60–70 °C, washed with distilled water to neutral, and removed the clear liquid. (2) Per gram of the sample is added to 2.4 mL of HCl with a concentration of 6 mol/L and 3.6 mL of hydrofluoric acid (HF) with a concentration of 40%, which is stirred for 2 h at 60–70 °C, and washed with 1 mol/L HCl for three times to remove the clear liquid. (3) The kerogen obtained from the acid treatment is put in a centrifuge tube, added heavy liquid of 2.0–2.1 g/mL, dispersed by an oscillator, and centrifuged for 20 min at a speed of 2000–3000 r/min in a centrifuge. After a period of precipitation, the upper kerogen is taken out, which should be repeated three times. The separated kerogen should be frozen for 6 h at −5 °C, taken out for drying at 60 °C in an oven, ground to 100 mesh, and put into penicillin bottles for later use. Finally, an appropriate amount of prepared kerogen is oxidized into carbon dioxide and water in an oxidation furnace, and by helium flow, the separated carbon dioxide is brought into an ISOPRIME
isotope mass spectrometer, which is produced by Germany VG Company to determine Corg.

3.2. Mineral Composition Analysis. Ten samples of the Shanxi Formation, which are ground to less than 80 mesh to completely disperse minerals before the experiment, are selected to analyze the mineral composition. The compositions are measured by X-ray diffraction (XRD) using a Rigaku Ultima IV rotating anode X-ray diffractometer with 40 kV and 40 mA.

3.3. Major and Trace Element Composition Analysis. The samples are smashed to powder to eliminate the influence of minerals and particle size before the element experiment. The composition is analyzed by an Axios Max X-ray fluorescence (XRF) spectrometer with 60 kV and 160 mA.

Trace-element concentrations are measured by an ICP-RQ inductively coupled plasma-mass spectrometer (ICP-MS). Samples are ground to less than 200 mesh and dried for 3 h at 105 °C in an oven. Then, 0.1 g of the sample is selected and dissolved with 2 mL of HF, 2 mL of HCl, and 6 mL of nitric acid in a closed container. The acid is cleared by an acid removal at 160 °C for 90 min and then tested by ICP-MS directly.

Trace elements consist of terrestrial detritus and authigenic fraction, of which the authigenic fraction can record the paleoenvironmental characteristics and changes in the water column. However, biogenic carbonates and opal minerals in the sediments can dilute the trace-element concentrations of authigenic components, leading to deviations in studying the paleoenvironment directly from the measured results. Therefore, when using trace elements as indexes, the stable Al element is used to standardize trace-element concentrations, and element contents of post-Archean Australian shale (PAAS) are used to calculate the enrichment factor. The calculation formula is as follows

$$X_{\text{EF}} = \frac{(X/\text{Al})_{\text{sample}}}{(X/\text{Al})_{\text{PAAS}}}$$

where X represents the concentration of element X in samples, which is standardized with reference to the concentration of element X in PAAS. If EF < 1, the element is deficient; if EF > 1, the element is enriched.

The concentration of elements can be influenced by the paleoclimate change in the sedimentary geological history. The contents of Fe, Mn, Cr, V, Ni, and Co are relatively high in a warm and humid climate, while the contents of Ca, Mg, K, Na, Sr, and Ba are relatively high in a cold and dry climate because these elements are precipitated in large quantities to form various salts and deposited on the water bottom due to the enhanced alkalinity of water medium along with the evaporation of water. Therefore, these elements can be used as a proxy for paleoclimate in the form of C-value, which is calculated as follows

$$C - \text{value} = \frac{\Sigma(\text{Fe} + \text{Mn} + \text{Cr} + \text{Ni} + \text{V} + \text{Co})}{\Sigma(\text{Ca} + \text{Mg} + \text{Sr} + \text{Ba} + \text{K} + \text{Na})}$$

Paleoclimate can also influence the weathering effect, resulting in that the chemical index of alteration (CIA) is applied to evaluate the weathering intensity and indicate the paleoclimate change. Previous studies have shown that high CIA values represent the substantial removal of mobile cations (e.g., Ca$^{2+}$, Na$^{+}$, K$^+$) relative to stable residual constituents (Al$^{3+}$, Ti$^{4+}$) through intensive chemical weathering, likely under warm and humid conditions. Low CIA values, however, indicate the near absence of chemical weathering, thereby reflecting cool and/or arid conditions. The formula of CIA is as follows

$$\text{CIA} = \frac{[\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO*} + \text{Na}_2\text{O} + \text{K}_2\text{O})]100}{(100/C_{\text{Al}})}$$

where the major elements are all in molar units and CaO* only refers to CaO in the silicate fraction. Because of the low content of carbonate in the Shanxi Formation samples (Table 4), CaO is corrected by the P$_2$O$_5$ data (CaO* = CaO − 10/3 × P$_2$O$_5$). If the mole proportion of CaO* is more than that of Na$_2$O, the CaO* value is equaled to the Na$_2$O value. Otherwise, the CaO* value is equaled to the CaO value. Meanwhile, the calculation of CIA should consider the diagenetic addition of K because of postdepositional K alteration in many pre-Paleozoic siliciclastic sediments, nevertheless, the influence of K$_2$O correction on CIA is not significant in post-Paleozoic samples. Therefore, this study has not corrected the diagenetic addition of K.

4. RESULTS

4.1. Organic Petrographic and Organic Geochemistry Characteristics. TOC values and thermal maturity of samples from Member 2 and Member 1 are listed in Table 1. TOC of Member 2 ranges from 0.33 to 2.19% with an average value of 0.89%, while TOC of Member 1 shale samples is in the range of 0.75–7.49% (averaging 3.82%), and the coal sample (SX1-9) has a high TOC value of 42.74%. Ro of five samples varies from 2.60 to 3.08% (averaging 2.90%), which indicates that the Shanxi Formation samples are in the high mature stage.

| Table 1. TOC Value and Thermal Maturity of the Shanxi Formation Samples |
|-----------------------------|-----------------------------|-----------------------------|
| formation                  | member | sample | TOC (%) | Ro (%) |
| Shanxi Formation           | Member 2 | SX1-1    | 0.44    |       |
|                            |        | SX1-2    | 0.33    |       |
|                            |        | SX1-3    | 1.04    |       |
|                            |        | SX1-4    | 0.37    |       |
|                            |        | SX1-5    | 2.19    | 2.60  |
|                            |        | SX1-6    | 0.68    |       |
|                            |        | SX1-7    | 1.21    |       |
|                            | Member 1 | SX1-8    | 2.24    | 2.99  |
|                            |        | SX1-9    | 42.74   |       |
|                            |        | SX1-10   | 2.62    | 2.90  |
|                            |        | SX1-11   | 4.92    |       |
|                            |        | SX1-12   | 7.49    | 2.93  |
|                            |        | SX1-13   | 0.75    |       |
|                            |        | SX1-14   | 4.91    | 3.08  |

Maceral compositions of samples, which are applied to identify kerogen types, reveal that the kerogen of these samples is dominated by sapropelinite, followed by inertinite, with a certain amount of vitrinite and a low content of exinite (Table 2, Figure 2). TI index is usually used to estimate the kerogen type, which is as follows

$$\text{TI} = \frac{(\text{sapropelinite} \times 100 + \text{exinite} \times 75 - \text{vitrinite} \times 50 - \text{inertinite} \times 100)}{100}$$

The calculation results show that the TI index ranges from −89.92 to 39.92, indicating that the Shanxi Formation kerogen is mainly composed of type II with a little type III.
Table 2. Maceral Compositions, TI Index, and Kerogen Type of the Shanxi Formation Samples

| sample | sapropelite (%) | exinite (%) | vitrinite (%) | inertinite (%) | TI index | Type | $\delta^{13}C_{org}$ (%) | type |
|--------|----------------|-------------|---------------|---------------|----------|------|----------------|------|
| SX1-5  | 0.00           | 0.00        | 40.33         | 59.67         | -89.92   | III  | -23.73         | III  |
| SX1-8  | 68.33          | 0.67        | 6.67          | 24.33         | 39.33    | II 2 | -23.78         | III  |
| SX1-10 | 67.67          | 0.33        | 5.33          | 26.67         | 37.17    | II 1 | -23.96         | III  |
| SX1-12 | 69.00          | 0.33        | 5.67          | 25.00         | 39.92    | II 1 | -25.00         | III  |
| SX1-14 | 68.00          | 0.67        | 7.00          | 24.33         | 38.75    | II 1 | -24.36         | III  |

Figure 2. Transmission polarized micrograph of kerogen.

Table 3. Mineral Compositions and Clay Compositions of the Shanxi Formation Samples

| member | sample | quartz | feldspar | siderite | pyrite | clay content (%) | illite | I/S | kaolinite | chlorite | content (%) |
|--------|--------|--------|----------|----------|--------|------------------|--------|-----|-----------|----------|-------------|
| Member 2 | SX1-4 | 39.2   | 1.6      | 3.0      | 0.0    | 56.2             | 50.52  | 17.87| 21.90     | 9.71    |
| SX1-5  | 31.0   | 0.7    | 8.6      | 0.0      | 59.7   | 41.31            | 32.52  | 23.47| 7.00      | 1.20    |
| SX1-6  | 34.4   | 1.5    | 2.4      | 0.0      | 61.7   | 47.83            | 19.13  | 27.15| 5.89      | 4.10    |
| SX1-7  | 41.7   | 2.4    | 0.6      | 0.0      | 55.3   | 42.14            | 7.73   | 42.72| 7.41      | 4.10    |
| SX1-8  | 32.5   | 2.4    | 0.7      | 0.0      | 64.4   | 15.34            | 2.98   | 62.51| 19.17     | 4.10    |
| SX1-10 | 40.6   | 2.2    | 1.0      | 0.0      | 56.1   | 56.07            | 0.00   | 33.97| 9.97      | 4.10    |
| SX1-11 | 40.4   | 0.9    | 0.0      | 7.1      | 51.6   | 26.97            | 6.15   | 61.73| 5.14      | 4.10    |
| SX1-12 | 30.3   | 1.1    | 7.1      | 0.0      | 61.5   | 28.40            | 0.00   | 67.54| 4.05      | 4.10    |
| SX1-13 | 8.0    | 0.0    | 3.1      | 3.2      | 85.7   | 4.93             | 0.00   | 91.70| 3.36      | 4.10    |
| SX1-14 | 9.8    | 0.0    | 1.2      | 0.0      | 89.1   | 8.35             | 6.18   | 82.45| 3.02      | 4.10    |

Note: I/S means illite–smectite mixed clay.

Figure 3. Mineral composition and clay composition of the Shanxi Formation samples.

Maceral composition experiment can be influenced by thermal maturity and area of observation, which can result in errors in judging the kerogen type. Therefore, this study uses kerogen carbon isotope to further determine the kerogen type, which has been proved in previous studies. According to values of $\delta^{13}C_{org}$, the kerogen type is divided into four categories: type I (−35 to −30‰), type II (−30 to to −27.5‰), type II (−27.5‰ to −25‰), and type III (≥−25‰). Meanwhile, thermal maturity is an important factor when considering kerogen carbon isotope. When organic matter is in the high-over mature stage, thermal alteration of primary $\delta^{13}C_{org}$ should be minimal as metamorphism up to lower greenschist facies results in <3‰ $^{13}C$-enrichment. Furthermore, thermal degradation resulting from the burial of sedimentary rocks would not be likely to change the secular pattern of $\delta^{13}C_{org}$ values within a narrow
samples should not be in experiment, values of the Shanxi Formation samples are all according to the results of the kerogen carbon isotope compositions and $\delta^{13}$C values of the Shanxi Formation is type III. Combined with maceral compositions and $\delta^{13}$Corg values, the Shanxi Formation kerogen is type III, which is beneficial to gas generation.

4.2. Mineral Compositions. According to the XRD experiment, mineral compositions of the Shanxi Formation samples are shown in Table 3 and Figure 3. The Shanxi Formation samples are dominated by clay minerals, along with a low content of brittle minerals (quartz and feldspar). With the increase of buried depth, brittle minerals gradually decrease, and clay minerals gradually increase, in which kaolinite content gradually increases and illite content gradually decreases (Figure 3).

4.3. Major and Trace Element Composition. The results of the major elements experiment are listed in Table 4. The most abundant major element in the Shanxi Formation samples is silicon (Si), whose oxide content ranges from 25.319 to 70.608%, with an average of 53.587%, followed by aluminum (Al), with its oxide content ranging from 14.656 to 2.280%, averaging 34.248%, and then followed by iron (Fe), calcium (Ca), phosphorus (P), and manganese (Mn) in order, with their oxide contents of 0.404−1.514%, 0.232−1.529%, respectively.

The major elements of rock often have a good indicating relationship with its mineral composition. Ross and Bustin indicate that Si, Al, and Ca can reflect the relative contents of quartz, clay, and carbonate minerals, which is consistent with a high content of Si quartz and Al clay minerals and a low content of Ca carbonate minerals.

According to types of element compounds, trace elements in the crust can be divided into four categories, which are lithophile elements (Al, K, Na, Mg, Sr, Ba, Rb, etc.), siderophile elements ($V, Cr, Mn, Ti, Co, Ni, Mo, etc.$), chalcophile elements ($Cu, Zn, Cd, Sb, S, etc.$), and atmophile elements. A total of 27 trace elements have been tested in the...
Diﬀerent trace elements and element ratios are usually applied to discuss paleoproductivity, paleoclimate, and paleoredox conditions, etc. Ba, Mo, Cu, Zn, and Ni are common nutrient elements in trace elements, which can be used to represent paleoproductivity. The contents of Ba, Mo, Cu, Zn, and Ni in the Shanxi Formation in the study area are $265.51 - 1702.07$ ppm, $0.33 - 27.70$ ppm, $271.70 - 2416.25$ ppm, $264.14 - 1692.29$ ppm, and $264.14 - 1692.29$ ppm, respectively. These elements fluctuate greatly in diﬀerent layers of the Shanxi Formation, reﬂecting the erratic paleoproductivity in the Shanxi Period, which may be aﬀected by frequent regression and transgression of marine. From the perspective of the Ba element alone, the paleoproductivity of the Shanxi Formation is lower than that of the Wufeng–Longmaxi Formation shale$^{68}$ and Niutitang Formation shale,$^{69}$ which are relatively successful in exploration and development in South China.

The enrichment factors of trace elements calculated by formula (1) are shown in Table 6. The calculation results indicate that the paleoproductivity-sensitive element Ba of the Shanxi Formation is relatively deﬁcient, $Ba_{EF}$ is between $0.22$ and $1.38$, with an average of $0.70$, while other paleoproductivity indicators Cu, Zn, and Ni are relatively enriched, of which $Cu_{EF}$ is $2.10 - 62.15$ (averaging $15.97$), $Zn_{EF}$ is $1.21 - 25.05$ (averaging $6.83$), and $Ni_{EF}$ is $0.24 - 945$ (averaging $1.13$). The paleoredox-sensitive elements V, Cr, and Co are relatively

| member | sample | $V_{EF}$ | $Cr_{EF}$ | $Co_{EF}$ | $Ni_{EF}$ | $Ba_{EF}$ | $Mo_{EF}$ | $Cu_{EF}$ | $Zn_{EF}$ | $Sr_{EF}$ | $Zr_{EF}$ | $U_{EF}$ | $Rb_{EF}$ |
|--------|--------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|---------|-----------|
| Member 2 | SX1-1  | 0.38  | 0.33  | 0.21  | 0.24  | 0.76  | 0.20  | 6.38  | 2.94  | 1.43  | 0.36  | 0.76  | 0.58  |
| SX1-2  | 0.42  | 0.40  | 0.18  | 0.32  | 0.95  | 0.44  | 10.84 | 5.24  | 2.93  | 0.40  | 0.95  | 0.56  |
| SX1-3  | 0.40  | 0.37  | 0.25  | 0.30  | 0.65  | 0.22  | 9.60  | 4.57  | 0.78  | 0.34  | 0.94  | 0.60  |
| SX1-4  | 0.47  | 0.30  | 0.32  | 0.43  | 0.84  | 0.22  | 8.81  | 4.17  | 1.16  | 0.49  | 0.77  | 0.70  |
| SX1-5  | 0.55  | 0.54  | 0.70  | 0.65  | 0.91  | 0.76  | 44.31 | 18.26 | 1.20  | 0.78  | 1.03  | 0.68  |
| SX1-6  | 0.42  | 0.18  | 0.26  | 0.41  | 0.58  | 0.32  | 3.33  | 1.74  | 0.46  | 0.40  | 0.77  | 0.52  |
| SX1-7  | 0.47  | 0.31  | 0.18  | 1.49  | 0.57  | 0.18  | 23.21 | 9.38  | 0.76  | 0.43  | 0.71  | 0.55  |
| SX1-8  | 0.35  | 0.31  | 0.23  | 0.34  | 1.13  | 0.66  | 5.20  | 2.99  | 2.35  | 0.70  | 0.75  | 0.23  |
| SX1-9  | 0.29  | 0.31  | 0.20  | 1.00  | 0.41  | 3.51  | 20.36 | 8.18  | 1.03  | 1.54  | 4.35  | 0.16  |
| SX1-10 | 0.42  | 0.34  | 0.13  | 0.26  | 0.67  | 0.22  | 16.77 | 6.93  | 1.01  | 0.49  | 0.65  | 0.48  |
| SX1-11 | 1.35  | 1.37  | 1.92  | 9.45  | 1.38  | 35.73 | 62.15 | 25.05 | 3.21  | 3.09  | 27.03 | 0.80  |
| SX1-12 | 0.39  | 0.19  | 0.17  | 0.30  | 0.38  | 0.55  | 2.75  | 1.57  | 0.53  | 0.49  | 0.87  | 0.27  |
| SX1-13 | 0.37  | 0.20  | 0.18  | 0.43  | 0.22  | 1.16  | 7.78  | 3.35  | 0.42  | 0.56  | 0.71  | 0.07  |
| SX1-14 | 0.43  | 0.40  | 0.11  | 0.25  | 0.29  | 0.99  | 2.10  | 1.21  | 0.44  | 0.54  | 0.96  | 0.19  |

Figure 4. Proxies for paleoredox conditions of the Shanxi Formation in the southeastern Ordos Basin.
deficient, with VEF of 0.29−1.35 (averaging 0.48), CrEF of 0.20−1.37 (averaging 0.39), and CoEF of 0.11−1.92 (averaging 0.36), while MoEF and UEF vary in a wide range with averaging values of 3.23 and 2.98, respectively.

5. DISCUSSION

5.1. Paleoredox Conditions. The redox condition-sensitive trace elements have different characteristics in disparate sedimentary environments, in which some elements are stable in an anoxic environment and dissolved gradually along with the increase of oxygen content in the water column. Therefore, trace-element enrichment factors and their relevant ratios can be used as indicators for the paleoredox conditions of the sedimentary environment.

Redox-sensitive trace elements (V, Mo, U) are widely used proxies for paleoredox conditions. V, Mo, and U exist as soluble V⁵⁺, Mo⁶⁺, and U⁴⁺ in the oxic environment, while these elements are transformed into insoluble V⁢³⁺, Mo⁴⁺, and U⁴⁺ under anoxic conditions and preserved in the sediments. Meanwhile, the concentration of Mo is usually used to classify paleoredox conditions, in which noneuxinic, intermittently/seasonally euxinic, and permanently euxinic environments are distinguished by ≤25 ppm and ≥100 ppm. High Mo concentration tends to occur in the euxinic waters, where H₂S is high, whereas U is enriched in anoxic water without the requirement for free H₂S. Therefore, high MoEF/UEF ratios tend to indicate euxinic water column conditions.

The concentration of Mo in the Shanxi Formation samples is lower than 25 ppm, indicating the oxic environment. The enrichment factors of V, Mo, and U in Member 2 are relatively lower than those in Member 1 (Figure 4), which have reached a peak around the depth of 3580−3595 m, and the variation characteristics indicate that the oxygen content of Member 2 paleowater is higher than that of Member 1. Mo concentration and MoEF/UEF have similar change characteristics, indicating that the Shanxi Formation deposits under oxic water and the
In geological history, which in carried out many nutrients into sedimentary water in slightly decrease from Member 1 to Member 2 and reach a similar longitudinal variation characteristic that the values gradually decrease from Member 1 to Member 2, which indicates that the terrestrial influx intensity of the Shanxi Formation weakens tardily during the geological history. This kind of change may be caused by the frequent transgression and regression, and the change identifies with the change of TOC in the Shanxi Formation (Figure 5). Therefore, the relatively strong terrestrial influx carries more nutrient substances into the water column, which results in the higher oxygen consumption and suboxic environment in Member 1, while Member 2 belongs to the oxic environment because of the relatively weak terrestrial influx and lower oxygen consumption.

5.2. Paleoproduction Conditions. The paleoproduction influences the material basis of OM, which is one of the important factors of shale gas accumulation. TOC is the intuitive indicator of paleoproduction in sediments, which mainly comes from the sinking OM in the surface ocean. The concentrations of nutrient elements (e.g., Cu, Zn, and Ni) in the water column significantly control the marine primary productivity, which can be preserved in sediments along with OM and used as proxies for paleoproduction. Meanwhile, the productivity of phytoplankton and bacteria is correlated with Mo and U contents, which can be applied as indicators (Mo/Al and U/Al) for paleoproduction.

In Figure 5, TOC, Mo/Al, U/Al, CuEpp, ZnEpp, and NiEpp have the similar longitudinal variation characteristic that the values slightly decrease from Member 1 to Member 2 and reach a peak in the depth of 3580–3595 m, representing the little change of paleoproduction in the Shanxi Formation samples, which indicates that the accumulation is not controlled by the paleoproduction in the Shanxi Formation.

5.3. Terrestrial Influx Intensity. The terrestrial influx has carried out many nutrients into sedimentary water in geological history, which influences the accumulation of OM through the intensity change. The distribution of elements in different types of source rocks is different, in which mafic igneous rock contains more nutrient element P compared with felsic igneous rock, which influences the accumulation of OM. The distribution of TiO₂ and Zr is commonly used as proxies to distinguish the source rock types. The data of TiO₂-Zr in the Shanxi Formation sediments from the SX-1, CY1, and CY2 well (data of CY1 and CY2 well is from Zhao, Li, Wang, Wu, Wang, Qin, Cheng, and Li) indicate that the source rock type of the Shanxi Formation is mainly felsic igneous rock (Figure 6), which rarely influence the difference of OM accumulation.

Elements Ti, Zr, and Al are relatively stable and rarely influenced by the weathering effect and diagenetic processes, resulting in that these elements are good indicators for the terrestrial influx intensity. Al is mainly derived from aluminosilicate in clay minerals, whereas Ti and Zr are effectively preserved in clay minerals and heavy minerals such as quartz, zircon, and pyroxene. Therefore, ratios of Ti/Al and Zr/Al are chosen as good indicators for the terrestrial influx intensity. As shown in Figure 5, Al concentration and Ti/Al and Zr/Al ratios have the same change characteristic, and the values gradually decrease from Member 1 to Member 2, which indicates that the terrestrial influx intensity of the Shanxi Formation weakens tardily during the geological history. This kind of change may be caused by the frequent transgression and regression, and the change identifies with the change of TOC in the Shanxi Formation (Figure 5). Therefore, the relatively strong terrestrial influx carries more nutrient substances into the water column, which results in the higher oxygen consumption and suboxic environment in Member 1, while Member 2 belongs to the oxic environment because of the relatively weak terrestrial influx and lower oxygen consumption.

5.4. Paleowater Depth. The depth of the water column can influence the accumulation of OM, in which deep water with weak hydrodynamic force is conducive to the accumulation and shallow water has the opposite effect. Rb and K are commonly used as the proxy for paleowater depth because of the adsorption difference on the surface of clay minerals. Compared with K, Rb has stronger adsorption ability on clay minerals. Therefore, with the migration of clay minerals in water, the concentration of Rb increases, resulting in the positive relationship between paleowater depth and the Rb/K ratio.

The Rb/K ratio of the Shanxi Formation sediments from the SX-1 well ranges from 44.74 to 159.00 (Table 7), in which the ratio gradually decreases from Member 1 to Member 2 (Figure 7). Rb/K ratios of Member 1 and Member 2 in the CY2 well are in the range of 67.72–79.18 and 55.66–64.56, respectively, suggesting the analogous variation trend that the ratio decreases from lower to upper of the Shanxi Formation. Lithologic assemblage can also reflect the change of paleowater depth, in which sandstone and carbonate are deposited in shallow water environment and mudstone is deposited in deep water environment. As shown in Figure 1, the sandy content increases from Member 1 to Member 2, which indicates that the paleowater depth decreases from Member to Member 2. Based on the analyses of the Rb/K ratio and lithologic assemblage, the paleowater depth of the Shanxi Formation has been shoaled from Member 1 to Member 2, resulting in the increase of hydrodynamic force, which is unfavorable for the accumulation of OM. Meanwhile, Member 1 with a deeper paleowater depth is close to the provenance, which is more convenient for the migration of terrestrial nutrient to sedimentary water than Member 2, leading to the relatively strong terrestrial influx in Member 1 of the Shanxi Formation.

5.5. Paleoclimate Changes. Changes in temperature and humidity influence the stratification of water and the preservation of sediments, thereby affecting the enrichment and preservation of OM in sediments. Therefore, the paleoclimate analysis of reservoirs is helpful to explain the distribution and variation characteristics of OM.

Clay minerals are particularly sensitive to changes in the geological environment because of the crystal structure and small particle size, in which kaolinite develops in the acidulous, warm and humid environment due to the loss of alkali metal in
relatively strong leaching of weathering, and illite develops in the alkalescent, cold and dry environment resulting from the relatively weak leaching in weathering. From Member 1 to Member 2, the decrease of kaolinite content and the increase of illite indicate that the paleoenvironment of the Shanxi Formation sediments changes from warm and humid climatic conditions to relatively cold and dry climatic conditions (Figure 3).

In addition to clay minerals, the concentration of climate-sensitive trace elements Sr and Cu can also be used as a proxy for paleoclimate changes. Cu is more stable than Sr in the leaching effect of weathering, resulting in a high Sr/Cu ratio in the cold-dry climate with strong weathering and a low Sr/Cu ratio in the warm-humid climate with weak weathering. Previous studies have indicated that Sr/Cu is lower than 10 referring to the warm and humid climate, while Sr/Cu is higher than 10 representing cold and dry climate. The ratio of the Shanxi Formation sediments in the SX-1 well ranges from 0.11 to 1.81 with an average value of 0.57, which indicates that the sedimentary environment of the Shanxi Formation is a warm and humid climate (Table 7 and Figure 7). The ratio of the Shanxi Formation samples in the CY2 well is between 1.48 and 7.43 with an average value of 3.97, which also reflects the warm and humid paleoclimate in the Shanxi period.

Previous studies have indicated that the C-value increases from 0 to 1, reflecting the climate changes from cold-dry to warm-humid. According to formula (2), the value of the Shanxi Formation sediments in the study area varies from 0.09 to 0.60 (averaging 0.27) (Table 7). Noteworthily, the C-value of Member 2 is between 0.11 and 0.36 (averaging 0.21), while the C-value of Member 1 ranges from 0.09 to 0.60 (averaging 0.34), which reveals the paleoclimate of Member 2 is colder and drier than that of Member 1 consistent with the variation of the C-value in Figure 7.

The high CIA value represents the strong weathering intensity in a warm and humid climate, while the low CIA indicates the cold and dry climate. Previous analyses of clay mineral composition, Sr/Cu, C-value, and CIA, this study suggests that Member 1 is in a relatively warm and humid climate conducive to the OM accumulation while Member 2 with a relatively cold-dry climate has low TOC (Figure 7).

5.6. Accumulation Mechanisms of OM in the Shanxi Formation Shale. The accumulation of OM is a complicated geological process, which is greatly influenced by the paleoenvironment (paleoredox, paleoproductivity, terrestrial influx, and paleoclimate), and is mainly divided into productivity mode and preservation mode. According to the above discussions, the paleoclimate indexes indicate that the relatively warm-humid climate of Member 1 is conducive to the OM accumulation while Member 2 with a relatively cold-dry climate has low TOC (Figure 7).
Figure 8. continued
The paleoredox change mainly influences the OM preservation condition, therefore controlling the OM accumulation. As shown in Figure 8a,b, the indexes \((V_{EF}, Mo_{EF}, \text{and} \ U_{EF})\) have positive relationships between TOC of Member 2 while there is no relationship in Member 1. Therefore, the contribution of the paleoredox condition is different in the two members, in which TOC increases with the decrease of oxygen content in Member 2 and the paleoredox condition has an unobvious contribution to the OM accumulation of Member 1.

Additionally, relationships between paleoproductivity and TOC demonstrate the different contributions of paleoproductivity in Member 2 and Member 1 (Figure 8c–f). In Member 2, the paleoproductivity indexes \((Cu_{EF}, Zn_{EF}, Ni_{EF}, U/Al, \text{and} \ Mo/Al)\) are positively correlated with TOC in different degrees, which is conducive to the OM accumulation. However, there is no linear relationship between paleoproductivity indexes and TOC in Member 1, which indicates that
the paleoproductivity has no contribution to the OM accumulation.

As shown in Figure 8g,h, the terrestrial influx intensity is positively correlated with TOC in Member 2 and Member 1, therefore, the terrestrial influx is the main controlling factor of the OM accumulation in the Shanxi Formation, which may have resulted from the provenance uplift, frequent transgression, and regression. The above analysis show that the paleoenvironment characteristics are quite different in Member 2 and Member 1 due to the evolution of the transitional facies, which results in the differences of the OM accumulation in the Shanxi Formation. In the sedimentary stage of Member 1, the relatively warm and humid climate is beneficial to the growth of higher plants and other organisms, which can produce a large amount of OM. Meanwhile, the water depth is relatively deep, which indicates that the paleowater is close to the terrestrial provenance, resulting in the relatively strong terrestrial OM input. The strong terrestrial influx leads to a high depositional rate, which can dilute the autogenetic paleoproductivity in the paleowater, therefore the paleoproductivity has no contribution to the OM in Member 1. Moreover, the suboxic water has no influence on the OM accumulation, which results from the strong terrestrial influx. Summarily, the OM accumulation of Member 1 is mainly controlled by the terrestrial influx intensity and paleowater depth, where the strong terrestrial influx weakens the influence of other paleoenvironment factors (Figure 9a).

In the sedimentary stage of Member 2, the relatively cold and dry climate is not favorable for the growth of higher plants. Along with the regression from the southeastern Ordos Basin, the paleowater depth is lower than that of Member 1, and the sand content of the upper Member 2 gradually increases. Meanwhile, because of the low water depth, the sedimentary water is far away from the terrestrial provenance, resulting in a relatively weak terrestrial influx with less OM. The positive relationships between paleoproductivity, paleoredox conditions, and TOC indicate that the oxygen content and the paleoproductivity jointly enhance the OM accumulation. In general, the OM accumulation of Member 2 is comprehensively controlled by the paleowater depth, terrestrial influx, paleoproductivity, and paleoredox conditions, however, the weak terrestrial influx, low paleoproductivity, andoxic water conjointly result in the low TOC (Figure 9b).

6. CONCLUSIONS

The Shanxi Formation shale is deposited in the marine—continental transitional facies with frequent transgression and regression, in which the southeastern Ordos Basin mainly develops the delta front and shallow lake facies. The OM is characterized by the high mature stage and type III kerogen, indicating a high potential for shale gas generation. However, the TOC shows an interlayer difference, in which the TOC of Member 1 ranging from 0.75 to 7.49% (averaging 3.82) is higher than that of Member 2 (0.33−2.19%, averaging 0.89%). The paleoenvironment of the Shanxi Formation has great differences along with the gradual withdraw of seawater from the southeastern Ordos Basin. From Member 1 to Member 2, the paleoclimate changes from relatively warm and humid to relatively cold and dry, which is gradually in conducive to the growth of higher plants and other organisms. The paleowater depth of Member 2 is shallower than that of Member 1, resulting in that the water of Member 2 is farther from the provenance than that of Member 1, therefore reducing the terrestrial influx intensity. Moreover, from Member 1 to Member 2, the paleoproductivity has gradually decreased and reached a peak in Member 1, while the oxygen content has gradually increased and the paleowater column changes from suboxic to oxic environments.

Considering the differences of the paleoenvironment in the Shanxi Formation, the accumulation mechanisms of OM have been studied. The OM accumulation of Member 1 with higher TOC is mainly controlled by the terrestrial influx intensity and paleowater depth, where the strong terrestrial influx weakens the influence of other paleoenvironment factors. The OM accumulation of Member 2 is comprehensively controlled by the paleowater depth, terrestrial influx, paleoproductivity, and paleoredox conditions, however, the weak terrestrial influx, low paleoproductivity, and oxic water conjointly result in the low OM abundance. The paleoenvironment characteristic and its influence on the OM accumulation of the transitional Shanxi Formation shale have been studied in this paper, which can improve the understanding of the OM accumulation in other transitional shales and provide a theoretical basis for the reservoir selection of the Shanxi Formation shale gas exploration and development in the southeastern Ordos Basin.

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Notes

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