Factors Controlling the Lower Radioactivity and Its Relation with Higher Organic Matter Content for Middle Jurassic Oil Shale in Yuqia Depression, Northern Qaidam Basin, China: Evidence from Organic and Inorganic Geochemistry

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ABSTRACT: Organic-rich oil shale with unusual lower radioactivity (expressed by GR) was found in Member 7 of Dameigou Formation, middle Jurassic (J₂d₇) in Yuqia depression of northern Qaidam Basin, China. In order to systematically and contrastively investigate the factors controlling the lower GR and its relation with higher organic matter (OM) content (expressed by total organic carbon, abbr. TOC), organic and inorganic geochemical analyses were performed on samples consisting of oil shale and the underlying conformable contact dark shale from Well YQ-1Y. Our study shows that GR of J₂d₇ oil shale is mainly derived from uranium and thorium. Compared with dark shale, oil shale is characterized by higher OY and TOC, lower GR, and clay mineral content. During oil shale deposition, the paleoclimate was relatively arid, indicated by a decreased C value and siderite content as well as an increased carbonate content and Classopollis. Under such paleoclimate conditions, sedimentary water became more anoxic, suggested by higher V/(V + Ni), pyrite content and lower pristane/phytane (Pr/Ph). From oil shale to dark shale deposition, according to analyses of Al₂O₃/TiO₂, TiO₂ versus Zr, La/Sc versus Th/Co, La/Th versus Hf, and La−Th−Sc, the felsic igneous rock could always be deduced as the parent rock of provenance; however, the increasing arid paleoclimate resulted in weakened chemical weathering of provenance, inferred by relatively low chemical index of alteration, chemical index of weathering, and plagioclase index of alteration corresponding to the input degree of radioactive materials and other terrigenous detrital materials (TDMs), evidenced by Ti and Al contents and terrigenous (%). Meanwhile, the relatively high P/Ti and Ba/Al both indicated increased primary paleoproductivity. Together with the maximum flooding stage of oil shale deposition, the relatively low radioactivity tends to be associated with the inhibited input of clay minerals and radioactive materials, largely caused by increasing arid paleoclimate. The accompanying decreased TDM benefited primary paleoproductivity and anoxic conditions; their combined influence could induce sapropelic OM accumulation.

1. INTRODUCTION

Oil shale has been well-studied as a type of unconventional resource with a great potential of oil and gas, which is always characterized by abundant organic matter (OM) (expressed by total organic carbon, abbr. TOC) and high radioactivity (expressed by gamma ray, abbr. GR). However, oil shale of J₂d₇ (Member 7 of Dameigou Formation, middle Jurassic, corresponding to the Upper Member of Shimengou Formation in the coal industry), in Yuqia depression of northern Qaidam Basin in China, is mainly characterized by higher TOC and unusual relatively low GR. Similar lower radioactive shales were also found in Hirka Formation in Ankara area of Turkey, Sanjianfang Formation of middle Jurassic in Tuha Basin of China, Phosphoria Formation of southwestern Montana Area of America, and so forth. Higher GR is generally regarded as one of the most susceptible indicators for identifying organic- and hydrocarbon-rich shale. Therefore, it is necessary to analyze the factors controlling the unusual lower GR and its relation with higher TOC for oil shale in the study area.

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GR of shale originates almost entirely from potassium (K)-40 and elements in the uranium (U) and thorium (Th) decay chains, in which K and Th are preferentially related to clay minerals, while the occurrence of U is controversial. Due to the anoxic conditions required for their deposition and preservation, U and OM are intimately linked; most studies support that U preferentially bonds to OM. In contrast, by the means of a sequential chemical extraction procedure, some studies propose that U and Th preferentially bond to clay minerals, phosphate, and other inorganic mineral compositions.

Furthermore, due to limited geographic size, the lacustrine environment and deposits are more easily influenced by paleoclimate change than the marine environment. Although the paleoclimates between J2d7 oil shale and dark shale in the study area have been well-researched before, the influence of the related geological process on the development of radioactive elements and OM in lacustrine shale was not clearly understood, including the water properties, provenance chemical weathering, terrigenous materials input, primary paleoproductivity, and so forth. Yang (2017) also emphasized that instead of OM, the uranium content in alum shale was controlled by physicochemical conditions of the depositional environment.

The major objectives of this paper are to (1) determine the prior rock constituent controlling the variation of radioactivity; (2) reveal the factors controlling the lower GR and its relation with higher OM content; and (3) discuss the influence of geological process evolution induced by paleoclimatic and other geological conditions on the development of radioactivity and OM content for J2d7 oil shale in Yuqia Depression of northern Qaidam Basin. This study aims to provide a comprehensive understanding of radioactivity and OM for shale and reference for shale resource evaluation and exploration.

2. GEOLOGICAL BACKGROUND

Located at the northeast margin of the Tibet Plateau, the Qaidam Basin is a Mesozoic and Cenozoic intracontinental basin that developed on a Precambrian crystalline basement. It is surrounded by the south Qilian Mountains to the northeast, the east Kunlun Mountains to the south, and the Altyn mountains to the northwest. Influenced by Indosinian orogeny, the northern fault block zone (Northern Qaidam) mainly developed a northern fault block belt in the west and Delingha depression in the east (Figure 1).

Fluvial, deltaic, and lacustrine deposits dominate the Dameigou Formation of Jurassic. According to sedimentary environments and lithological assemblages, it can be divided into seven sections from early Jurassic (J1d1−J1d3) to middle Jurassic (J2d4−J2d7). At the late J2d7 period, the most extensive lake transgression occurred and then successively deposited dark shale and conformable overlaying oil shale.

The Yuqia depression is located in the center of the northern fault block belt and trends about 500 km². J2d7 oil shale is well-developed with a thickness ranging from 15 to 20 m and is alternated with thin marl and siltstone. The color is gray-brown and black, and the lithology is dense and delicate.
fluorescence displays can be seen under ultraviolet light, indicating favorable oil content.

3. RESULTS

3.1. Logging Data, OY, and Organic Geochemistry. It is defined neither in geology nor in chemistry that any fine-grained rock yielding an economic amount of oil higher than 3.5% at present in China can be considered as oil shale.26,27 Oil shale is mainly concentrated in the upper section of J2d7 (Figure 2). For Well YQ-1Y, OY of samples varies from 2.3 to 11.6% with an average of 6.7% in the depth of 220.22–239.00 m, which can be classified as the oil shale interval; OY of samples mainly varies from 1.3 to 5.3% with an average of 2.62% in the depth of 239.00–275.00 m, which can be classified as the dark shale interval. Meanwhile, the TOC of the oil shale interval varies from 4.93 to 17.17% with an average of 7.83% in the depth of 239.00–275.00 m, which can be classified as the dark shale interval. In the depth of 220.22–239.00 m, OY of samples varies from 2.3 to 5.3% with an average of 3.34% in the black shale interval.

3.2. Inorganic Mineral Composition. X-ray diffraction (XRD) is one of the most general techniques to characterize the inorganic mineral composition of shale shown in Table 2. The inorganic mineral compositions strongly differ from oil shale to dark shale. Except for anomalous samples, oil shale mainly develops a lower quartz content of 7.9–34.6% with an average of 22.0%, lower clay mineral content of 17.7–62.3% with an average of 37.2%, lower siderite content of 0.0–9.2% with an average of 3.5%, higher pyrite content of 0.0–6.0% with an average of 2.9%, and higher carbonate content of 3.1–58.0% with an average of 32.9%. In addition, it is obvious that the inorganic mineral compositions intensely vary vertically for oil shale but slightly change for dark shale, which indicates that the sedimentary environment evolves from stable to frequently varied ones.

3.3. Element Geochemistry. The major element data are listed in Table 3. Generally, similar to an average shale,2 the majority of samples are enriched in SiO2 and Al2O3, which is lower in oil shale (33.0 to 35.6%) (Figure 3c,e) and 44.40%–49.08%; 20.1–22.0%, lower clay mineral content of 17.7–23.8%, average 21.80%) (Figure 4). Combined with the carbonate variation of XRD results, higher and fluctuated CaO content in oil shale may indicate progressive arid and unstable climate.5,16,28,29

The trace element data are given in Table 3. To quantitatively evaluate the content of these elements, the upper continental crust (UCC)-normalized plot for all elements are shown in Figure 5. Generally, all analyzed samples show similar UCC-normalized trace elemental patterns, except for Mo depletion in dark shale, probably caused by the lower TOC.

4. DISCUSSION

4.1. Description of GR Using Radioactive Elements. Previous studies hold the view that the increase of GR for organic-rich shale is mainly contributed by enrichment of uranium—radium series.8,30,31 However, as shown in Table 3, despite lower GR in oil shale, the higher content of U (3.0–6.7 ppm) and Th (14.5–25.8 ppm) seems to be inconsistent with the radioactive characteristics of oil shale, while lower content of C24 (10.3 to 21.0%). In contrast, dark shale is enriched in C29, ranging from 45.4 to 48.8%, slightly larger than the content of C27 (33.0 to 35.6%) (Figure 3c,e).

Figure 2. Comprehensive histogram of J2d7 interest interval for Well YQ-1Y.
K (1.0–1.9\%) may dominate the GR variation. Wu and Wang\textsuperscript{5} also attributed the lower GR of Sanjianfang Formation to the decreased K and Th content. Furthermore, it should be noteworthy that although the laboratory test can reflect the geochemical characteristics of samples from J\textsubscript{2}d\textsuperscript{7} interest interval of Well YQ-1Y. (a) Plot of HI vs $T_{\text{max}}$, showing the OM type; (b) plot of Ph/nC\textsubscript{18} vs Ph/nC\textsubscript{17}, showing the OM type, source, and sedimentary condition; (c) ternary diagram of C\textsubscript{27}, C\textsubscript{28}, and C\textsubscript{29} regular steranes, showing the OM type and source; (d) $m/z$ 85 mass fragmentograms of saturated hydrocarbon fractions, in which Pr/Ph shows the redox condition of sedimentary environment; (e) $m/z$ 217 mass fragmentograms of saturated hydrocarbon fractions, in which the relative proportion of C\textsubscript{27}−C\textsubscript{28}−C\textsubscript{29} regular sterane shows the OM source.

### Table 1. Organic Geochemical Results of Typical Samples from J\textsubscript{2}d\textsuperscript{7} Interest Interval of Well YQ-1Y

| Lithology  | Samples ID | Depth (m) | TOC (wt %) | $T_{\text{max}}$ (°C) | $S_1$ (mg/g) | $S_2$ (mg/g) | $S_1 + S_2$ (mg/g) | HI (mg/g) | R\textsubscript{o} (%) | Pr/Ph | Ph/nC\textsubscript{18} | Ph/nC\textsubscript{17} | C\textsubscript{27} (%) | C\textsubscript{28} (%) | C\textsubscript{29} (%) |
|------------|------------|-----------|-------------|------------------------|--------------|--------------|----------------------|-----------|-----------------|--------|-----------------|-----------------|----------------|----------------|----------------|
| Oil shale  | S2         | 220.50    | 13.51       | 431                    | 1.15         | 31.97        | 33.12                | 522.47    | 0.40            | 4.5    | 100.43          | 74.7            | 10.3          | 15.0            |                |
|            | S20        | 225.30    | 17.17       | 437                    | 0.80         | 100.43       | 101.23               | 715.92    | 0.41            | 1.5    | 94.33           | 58.0            | 21.0          | 21.1            |                |
|            | S36        | 226.84    | 9.89        | 441                    | 0.15         | 26.40        | 26.55                | 362.46    | 0.41            | 1.5    | 94.33           | 58.0            | 21.0          | 21.1            |                |
|            | S43        | 233.3     | 8.6         | 436                    | 0.41         | 24.13        | 24.54                | 441.07    | 0.41            | 1.5    | 94.33           | 58.0            | 21.0          | 21.1            |                |
| Dark shale | S62        | 248.30    | 6.07        | 439                    | 0.21         | 9.22         | 9.43                 | 193.18    | 0.41            | 1.5    | 94.33           | 58.0            | 21.0          | 21.1            |                |
|            | S78        | 260.45    | 6.01        | 440                    | 0.10         | 9.93         | 10.03                | 226.69    | 0.43            | 1.5    | 94.33           | 58.0            | 21.0          | 21.1            |                |
|            | S86        | 264.60    | 5.53        | 441                    | 0.18         | 3.58         | 3.76                 | 133.38    | 0.44            | 1.5    | 94.33           | 58.0            | 21.0          | 21.1            |                |
|            | S94        | 272.10    | 6.98        | 443                    | 0.05         | 6.31         | 6.36                 | 155.58    | 0.44            | 1.5    | 94.33           | 58.0            | 21.0          | 21.1            |                |
chemical element of shale more real, a limited number of samples can hardly represent the whole interval, especially for oil shale with intensive variation in vertical composition. Natural gamma ray spectroscopy (NGS) logs can continuously record the changes of radioactive element content. Due to lacking NGS in Well YQ-1Y, the Well CY-1, with integrated logging series and well developed interest interval, can be selected as the supplement well. As shown in Figure 6, for oil shale ranging from 1920.25 to 1929.65 m in Well CY-1, U and Th contents from NGS are strongly and positively correlated with GR, while K exhibits little correlation with GR, implying that radioactivity in J2d7 oil shale is mainly derived from U and Th.

4.2. Correlation between Rock Constituent and Radioactivity. The effect of OM depends on its amount, maturity, and type. Compared with dark shale, higher TOC and similar Tmax and Ro for oil shale indicate that OM content and maturity are hardly associated with the lower radioactivity of oil shale in the area (Figure 2, Table 1). The influence of OM type on radioactivity is still discussed controversially. In the plot of Pr/nC17 versus Ph/nC18 (Figure 3b), the terrestrial oxidizing environments lead to Pr formation, and the lacustrine/marine reducing environments lead to Ph formation. As shown in Figure 3b and Table 1, relatively low Pr/nC17 in oil shale implies the lacustrine and mixed OM source, while relatively moderate Pr/nC17 in dark shale implies a mixed OM source. In the ternary plot of C27−C28−C29 regular steranes (Figure 3c) and m/z 217 mass fragmentograms of saturated hydrocarbon fractions (Figure 3e), C27 and C28 regular steranes are mainly derived from aquatic organisms and C29 regular sterane is typically derived from terrestrial higher plants. As shown in Figure 3c and Table 1, the dominance of C27 regular sterane in oil shale implies the aquatic organism source; the similar abundance of C27 and C29 regular steranes in dark shale implies a mixed source of lacustrine and terrestrial OM. Accordingly, both biomarker parameters and pyrolysis results (Figure 3a) show type I−II1 OM for oil shale, indicating the greater contribution of sapropelic OM and increasing distance from the shore. In theory, this location always develops in anoxic and semi- to deep lacustrine, which is favorable for the concentrations of radioactive elements and the developments of adsorbents, such as clay minerals, OM, and so forth. However, the input of terrestrial radioactive materials and other terrestrial materials is also easily inhibited, which will be discussed later combined with more evidence.

The correlation of GR with clay mineral content is relatively good and more positive than that with OM (Figure 2, Table 2). Except for sample S15 and S46, the clay mineral content is relatively low for most oil shale (17.7−45.8%, average 30.9%) but relatively high in dark shale (44.9−58.0%, average 51.4%), which is consistent with the lower GR of oil shale and supports the suggestion that radioactive elements are more likely to develop in clay minerals than OM. Furthermore, adsorption ability of radioactive elements of different clay minerals intensively varies from strong to weak; they are montmorillonite, illite/montmorillonite, illite, kaolinite, and chlorite, in which the latter two have little contribution to the radioactivity of rocks and can be largely dismissed. The content of montmorillonite in oil shale is relatively higher than that of dark shale but illite/montmorillonite, with secondary adsorption capacity, shows clearly lower content in oil shale, which is in accordance with lower GR in oil shale.

A strong positive relationship between U−Th and phosphate for shale has been found in some basins. However, phosphate...
Table 3. Some Element Contents for Samples from Jd7 Interest Interval of Well YQ-1Y

| Lithology   | Samples ID | Depth (m) | Al2O3 (%) | K2O (%) | CaO (%) | MgO (%) | TiO2 (%) | P2O5 (%) | Th (%) | La (%) | C value | V/(V + Ni) | Al2O3/TiO2 | Th/Co | La/Th | Al/Si | CIA  | CIW  | PIA  | ICV  | Ti (%) | Al (%) | Terrigenous (%) | P/Ti | Ba/Al |
|-------------|------------|-----------|-----------|---------|---------|---------|----------|----------|--------|-------|---------|------------|------------|--------|--------|-------|------|------|------|------|-------|------|---------------|------|-------|
| Oil Shale   | S4         | 221.05    | 15.7      | 23.9    | 0.25    | 0.72    | 28.74    | 2.84     | 1.15   | 1.52  | 0.46    | 81.12      | 91.38      | 90.13  | 4.45   | 0.20  | 5.17 | 33.99 | 0.26  | 89.16 |
|             | S15        | 224.05    | 25.8      | 29.3    | 0.88    | 0.7     | 32.3     | 2.90     | 1.14   | 1.14  | 0.45    | 83.98      | 93.97      | 93.16  | 1.11   | 0.32  | 9.23 | 53.99 | 0.28  | 42.04 |
|             | S22        | 225.85    | 14.5      | 21      | 0.18    | 0.73    | 30.52    | 2.80     | 1.2    | 1.45  | 0.33    | 77.52      | 88.6       | 86.7   | 4.12   | 0.19  | 5.01 | 30.99 | 1.06  | 96.47 |
|             | S32        | 228.17    | 23.8      | 29.8    | 0.68    | 0.73    | 28.96    | 2.90     | 1.14   | 1.35  | 0.39    | 81.56      | 91.53      | 90.35  | 1.24   | 0.32  | 8.28 | 53.99 | 0.59  | 54.97 |
|             | S42        | 232.42    | 17.4      | 30.2    | 0.21    | 0.7     | 26.55    | 2.91     | 1.02   | 1.74  | 0.33    | 77.74      | 87.94      | 86.12  | 2.93   | 0.28  | 6.60 | 46.99 | 0.40  | 94.48 |
|             | S46        | 234.40    | 22.1      | 42.2    | 0.68    | 0.66    | 26.32    | 3.01     | 0.83   | 1.91  | 0.40    | 82.14      | 92.83      | 91.76  | 0.76   | 0.41  | 9.47 | 67.98 | 0.31  | 59.43 |
|             | Average    |           | 19.88     | 29.40   | 0.48    | 0.71    | 28.90    | 2.89     | 1.08   | 1.50  | 0.39    | 80.68      | 91.04      | 89.70  | 2.43   | 0.29  | 7.29 | 47.99 | 0.48  | 72.76 |
| Dark Shale  | S59        | 246.15    | 21.39     | 2.76    | 0.58    | 0.43    | 0.11     | 0.78     | 1.87   | 0.11  | 4.82    | 54.72      | 51.30      | 134    | 10.10  | 23.4  | 43.8 | 112   | 164   | 78.5  |
|             | S76        | 258.95    | 20.12     | 2.15    | 0.9     | 0.25    | 0.37     | 0.68     | 1.69   | 0.63  | 12.13   | 44.4       | 589.0      | 109    | 6.83   | 23.5  | 3.73 | 152   | 173   | 71.1  |
|             | S90        | 269.20    | 23.82     | 2.45    | 1.11    | 0.25    | 0.18     | 0.78     | 1.2    | 0.12  | 6.36    | 48.11      | 261.0      | 132    | 5.20   | 20.8  | 4.31 | 40.2  | 150   | 53.9  |
|             | Average    |           | 21.78     | 2.45    | 0.86    | 0.31    | 0.22     | 0.75     | 1.59   | 0.29  | 7.77    | 49.08      | 454.3      | 125.00 | 7.38   | 22.57 | 41.4 | 101.4 | 162.3 | 67.83 |

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minerals are not tested in samples of the study area (Tables 2 and 3), which infers that the effect of phosphate may be ignored in the study area.

4.3. Paleoclimate Reconstruction. Influenced by the breakdown of monsoonal circulation, a hot-arid event was widely developed in Qaidam Basin from middle to upper Jurassic (J2−J3). However, the key paleoclimate transformation of J2d7 shale deposition has not been significantly researched in detail with drilling cores.13,29

The chemical index of alteration (CIA = \(100 \times \frac{\text{Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}}\)) has been widely used to evaluate the climate changes and degree of chemical weathering, in which all oxides are in molar proportions, and CaO* represents the amount of CaO incorporated in silicate fraction, which is difficult to accurately estimate in the absence of data on the carbonate content of the sediments.29,36 For this study, CaO was corrected for phosphate using P2O5. If the remaining number is less than that of Na2O, this value of CaO was accepted. Otherwise, it is assumed that the value of Na2O as that of CaO*.37 Generally, higher CIA values indicate enhanced chemical weathering in humid climate, and lower values indicate less chemical weathering occurring in arid climate.

The CIA value is always influenced by sediment recycling, determined by the index of compositional variability (ICV = \(\frac{\text{Fe}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{MnO} + \text{TiO}_2}{\text{Al}_2\text{O}_3}\)) in molecular proportions.38,39 Samples with high ICV values > 1 belong to the first-cycle deposits in tectonically active settings. In contrast, samples with lower ICV values < 1 ought to form in cratons or quiescent environments, where sediment recycling is active but may also be produced by intense chemical weathering of first-cycle materials.39 It generally accepted that the sediment recycling can cause higher CIA values, which cannot really reflect the paleoclimate and chemical weathering.38 In the study area, oil shale samples have higher ICV values > 1 (1.11−4.45, average 2.77), with an exception of ICV value < 1 for one sample (0.76). All dark shale samples have lower ICV values < 1 (0.56−0.90, average 0.7) (Table 3). However, for two sets of continuously shale deposition, it is not appropriate to infer the influence of sediment recycling. For the ICV formula, the loss of unstable Na and K in the process of transporting and depositing also leads to the decrease of ICV in shale. Besides, ICV formula was initially applied to sediment recycling in a single continental crustal block, which differs from the background of the study area. Therefore, due to imperfect explanation of influence of sediment recycling, the CIA of dark shale can still be recommended as the proxy.

In the study area, the CIA values were 77.52−83.98 (average 80.68) for oil shale and 82.93−87.27 (average 85.55) for dark shale, suggesting that a less humid climate led to weakened chemical weathering during oil shale deposition (Figure 2, Table 3). Moreover, based on the classified criteria of humid climate (CIA > 65),18 all samples deposit under humid climate. However, it is noted that as a climate indicator, CIA should be used in low carbonate (<30%) sediments.40 The carbonate values are 3.1−58.0% (average 33.3%) for oil shale and 0.0−6.4% (1.3%) for dark shale (Table 2), which infers that the humid climate of oil shale, interpreted by CIA, may be improper. Even so, the arid or semiarid climate always facilitates the formation of carbonate minerals;41 therefore, the relatively high content of carbonate minerals for oil shale mainly implies relatively arid climate.

The C value, equaling to the ratio of \(\Sigma(\text{Fe} + \text{Mn} + \text{Cr} + \text{Ni} + \text{V} + \text{Co})/\Sigma(\text{Ca} + \text{Mg} + \text{Sr} + \text{Ba} + \text{K} + \text{Na})\), can evaluate the paleoclimate more rationally, in which Fe, Mn, Cr, Ni, V, and Co
tend to enrich under humid climate, while Ca, Mg, Sr, Ba, K, and Na are a preferable concentrate under arid climate. Generally, the C values > 0.8, 0.6−0.8, 0.4−0.6, 0.2−0.4, and <0.2 respectively indicate a humid, semihumid, semiarid−semi­humid, semiarid, and arid paleoclimate.15,42 As shown in Figure 2 and Table 3, the C values of oil shale were 0.18−0.88 (average 0.48), suggesting fluctuated and semiarid to semihumid climate. In addition, from dark shale to oil shale, a decreased siderite content (Table 2) and increased *Classopollis* in palynological assemblages both support more arid climate of J2d7 oil shale at the late middle Jurassic.24

4.4. Redox Condition. The effects of redox conditions on U to Th are different. U is easily oxidized as a soluble hexavalent U (+6) state and travels with water. Once it changes from the anoxic to tetravalent U (+4) state from solution in an anoxic environment, it can form uranium-organic or clay colloids and/or compounds based on their high ion-exchange capacity. In contrast, though Th is attributed to stable chemistry and insoluble or less soluble in water, its occurrence in sedimentary rocks is also mainly controlled by the adsorption of clay minerals,10,31,43 which is more likely to develop in anoxic and stable conditions. Hence, the anoxic water condition is beneficial for the enrichment of both U and Th in sedimentary rocks.

Due to the redox attributes of Pr and Ph shown above (Section 4.2), the ratio of Pr to Ph can be served as an indicator of redox conditions for the sedimentary environment.32,44,45 In general, ratios of <1.0, 1.0−3.0, and >3.0 can be interpreted as anoxic, suboxic, and oxic conditions, respectively.35 Compared with dark shale samples, Pr/Ph of oil shale samples is relatively low (Figure 2, Table 1), showing more anoxic conditions.

In addition, U, Th, V, Ni, Cr, and Co elements are some indicator trace elements that reflect the redox condition of the sedimentary environment. The ratio of these elements, for example, U/Th, V/(V + Ni), V/Cr, and Ni/Co, is always used to determine the redox condition. U/Th of >1.25, V/Cr of >2, Ni/Co of >7, and V/(V + Ni) of >0.5 indicate anoxic conditions.1,4,46,47 For oil shale samples in the study area, these proxies are approximately equal to that of dark shale samples, which infers similar redox conditions (Table 3). However, due to the multi-interpretation of element parameters, not all indexes are close to or even opposite to each other. The lower U/Th, V/Cr, and Ni/Co indicate suboxic−oxic conditions, which is inconsistent with the anoxic condition inferred by higher V/(V + Ni). Comprehensively, considering the higher content of pyrite (Table 2), a typical anoxic mineral48 and lower Pr/Ph of oil shale, it is rational to propose increased anoxic conditions from dark shale to oil shale.

4.5. Radioactive Materials Supply. The radioactive minerals in sedimentary rock can originate from weathering of granitic rocks, hydrothermal fluids, and products of volcanism.9 In the middle Jurassic of Qaidam, there was no evidence of large scale volcanic activity and hydrothermal fluids activity.18,23 suggesting radioactive elements mainly derived from the
weathering of parent rock. Therefore, the radioactivity material supply can be studied as the following three aspects.

4.5.1. Parent Rock Types of Provenance. Nearly all felsic rocks (granite and syenite) are more radioactive than maﬁc (gabbro and basalt) and ultramaﬁc (peridotite) rocks.49, therefore, it is necessary to distinguish the parent rock types of provenance for oil shale from dark shale. Due to the least chemical mobility during the process of weathering, transport, diagenesis, and metamorphism, some high ﬁeld strength elements (e.g., Th, Ti, and Zr), transition trace elements (e.g. Sc and Co), and rare earth elements are used to characterize the parent rock types of provenance.29,50–52

Hayashi et al.30 suggested that the Al2O3/TiO2 weight ratio vary from 3 to 8 and >200 for maﬁc igneous rock, 8 to 21 and 195 to 55 for intermediate igneous rock, and 21 to 70 and <55 for felsic igneous rock. In the TiO2 versus Zr diagram, both oil shale and dark shale samples fall close to the boundary between the felsic and intermediate igneous ﬁeld (Figure 7a) but belong to the distribution of felsic rock based on the Al2O3/TiO2 ratios (Table 3); such difference may be caused by the fractionation of zircon and Ti-bearing minerals during transport and deposit of sediments. Cullers31 proposed that high ratios of La or Th to Sc or Co suggest derivation from silicic sources while low ratios suggest a basic parent rock. In the La/Sc versus Th/Co diagram (Figure 7b), all samples are plotted in the ﬁelds of silicic rocks. Besides, in the La/Th versus Hf diagram (Figure 7c), the La/Th value is uniformly lower for all analyzed samples, indicating a predominant derivation from a felsic source. Considering the Permain–Triassic and Ordovician–Early Devonian source from Qilian Mountains for sediments of middle Jurassic,34 the following data can represent the geochemical characteristics of provenance rocks: ~430 Ma granite exposed in the Luliangshan area,29 ~437.4 Ma granodiorite exposed in the Tuanyunshan area,35 ~271 Ma quartzdiorite exposed in the Lulehe area,29 and eclogite (basalt as protolith, magmatic age of ~850 Ma) with a metamorphic age of ~433 Ma in the Yuka area.29 In La–Th–Sc ternary diagram (Figure 7d), all samples fall into the area between granite and granodiorite, with a high content of La and low content of Sc; this implies a predominant felsic composition since Sc is abundant in maﬁc igneous rocks. In addition, compared with dark shale, oil shale samples plot far away from granite and close to granodiorite; however, this slight difference is hard to discriminate the radioactive element content in provenance during different deposition periods.

To summarize, oil shale and dark shale were from a similar type of provenance comprising mainly felsic igneous rocks.

4.5.2. Chemical Weathering. In the process of chemical weathering for parent rock, relatively active alkali and alkaline elements (e.g. Na, K, Ca, and Mg) in provenance are ﬁrst leached out and then transported and deposited in a favorable environment, while stable elements shown above can be retained in provenance.

The aforementioned CIA for ﬁne-grained rocks is always thought to be easily affected by the diagenetic K-metasomatism and need to be corrected by the A–CN–K (Al2O3/(CaO + Na2O)–K2O) ternary diagram.36,57 However, K-metasomatism slightly changes the CIA of studied samples, especially for dark shale (Figure 8), which may be attributed to the low K abundance in formation waters.29 Therefore, it is unnecessary to correct CIA in the study area. In addition, Harnois38 argued that potassium may be leached as an active element or accumulate in the residue as a stable element during weathering and then proposed chemical index of weathering (CIW = 100 × Al2O3/(Al2O3 + CaO* + Na2O)) as an improved measure of weathering degree, which excludes K2O from CIA. However, considering that the Al associated with K-feldspar was not accounted in CIW, Fedo et al.57 advocated that CIW is inappropriate to quantify chemical weathering intensity, especially for K-feldspar-rich rock, and proposed the plagioclase index of alteration (PIA = 100 × (Al2O3–K2O)/(Al2O3–K2O + CaO* + Na2O)), modiﬁed from CIW.

The values of CIA, CIW, and PIA of samples are shown in Table 3 and Figure 2. It is obvious that the value of CIW is similar to that of PIA, suggesting low content of K-feldspar, which is supported by XRD data (Table 2). In theory, chemical weathering conditions can be classiﬁed into three degrees: incipient (CIA = 50–60, PIA = 50–69), intermediate (CIA = 60–80, PIA = 69–86), and extreme (CIA = 80–100, PIA = 86–100) degrees, respectively.29,57 The CIA for all samples ranges from 77.52 to 87.27 with an average of 82.30, and the PIA ranges from 86.12 to 96.26 with an average of 91.43, suggesting intermediate to extreme chemical weathering conditions. Furthermore, oil shale samples have CIA values ranging from 77.51 to 83.98 with an average of 80.68 and PIA values ranging from 86.12 to 93.16 with an average of 89.70, lower than that of dark shale, which means a decreased degree of chemical weathering from dark shale to oil shale.

4.5.3. Degree of the Detrital Inﬂuence. The detrital inﬂuence can indicate the input degree of radioactive materials and other terrigenous detrital materials (TDMs) into water as the product of chemical weathering. The contents of Ti and Al can reﬂect the changes of the TDM input.29,60 Besides, the amount of terrigenous detritus [terrigenous (%)] can be calculated by the formula of (TiSample/TiShale) × 100, in which TiShale is 5995 ppm for PAAS.61

The contents of Ti and Al in oil shale samples are 0.18–0.41% (average 0.29%) and 5.01–9.47% (average 7.29%), respectively, while they are 0.41–0.47% (average 0.44%) and 10.65–12.61% (11.52%) for dark shale (Figure 2). Furthermore, terrigenous (%) of oil shale samples is 30.99–67.98% (average 47.99%), decreasing by over one-third compared with that of dark shale (67.98–77.98%, average 74.65%). These proxies mean a
decreased input of radioactive materials and other TDM from dark shale to oil shale.

4.6. Primary Paleoproductivity. Several elements, such as phosphorus (P) and barium (Ba), are widely used to evaluate the primary paleoproductivity. In order to eliminate the influence of terrigenous clastic materials, represented by the major elements of Al and Ti, the ratios of P/Al or P/Ti and Ba/Al are considered as paleoproductivity proxies.15,59

As shown in Figure 2 and Table 3, P/Ti is relatively higher but variable in oil shale (0.26−1.06, average 0.48) than that in dark shale (0.19−0.35, average 0.25). Similarly, higher Ba/Al ratios are found in oil shale (42.04−96.47, average 72.76) but are lower in dark shale (22.70−55.32, average 40.45). These results suggest increased primary paleoproductivity from dark shale to oil shale.

4.7. Controls on the Lower Radioactivity of Oil Shale. In terms of rock constituent, the relatively low clay mineral content of J2d7 oil shale may account for its lower radioactivity (Section 4.2, Figure 2). Meanwhile, under the condition of similar parent rock types of provenance, weakened chemical weathering and decreased detrital influx reduce radioactive material supply for oil shale (Section 4.5, Figure 2). In contrast, the TOC and anoxic condition are negatively correlated with GR for shale in the study area, but it is physicochemically unconvincing to propose that they are detrimental to the enrichment of radioactive elements (Sections 4.2 and 4.4, Figure 2).

Due to inorganic affinity of radioactive elements, we infer that only if a certain level of radioactive material supply is reached and first meets the combination of clay minerals and other inorganic constituents, there will be surplus radioactive materials to combine with OM, otherwise the OM content could be a minor factor. Besides, the suboxic lake condition for dark shale with relatively high radioactivity suggests that the influence of radioactive material supply on radioactivity development is more important.

Furthermore, it should be noted that the clay minerals, chemical weathering, and detrital influx do not show a strong relationship with GR, suggesting that one of these factors alone is insufficient to dominate the GR of shale (Figure 9a−c). Except for one sample of dark shale, the good linear positive correlations between the C value and clay minerals (r = 0.84) (Figure 9d), CIA (r = 0.94) (Figure 9e), and terrigenous (%) (r = 0.86) (Figure 9f) show that paleoclimate has a large impact on the above factors. At the late of J2d7 in the study area, the gradually increasing arid paleoclimate from dark shale to oil shale not only reduced the supplies of radioactive materials, clay minerals, and other TDM but also enhanced the evaporation of lake water, which might promote the concentration of radioactive materials to some degree; however, the lake water body of the maximum flooding stage during oil shale deposition would greatly dilute the limited radioactive elements at the same time.
The impact of TDM input on OM accumulation is diverse. On the one hand, the volcanism, together with the input of detrital materials in relation to the elevated continental weathering, could facilitate OM accumulation. However, on the other hand, detrital materials also have a diluting effect on OM accumulation. In the study area, from dark shale to oil shale deposition, based on the negative correlation between P/Ti and terrigenous (%) \( r = 0.81 \) (Figure 9g), the dilution effect of TDMs on OM accumulation may be dominant. The decreased TDM reflected a weakened detrital influx into the lake; this not only improved the primary paleoproductivity of aquatic organisms by weakening dilution but also facilitated reduced bottom water environments by reducing the oxygen input. The correlation coefficient between TOC and P/Ti was not strong \( r = 0.22 \) (Figure 9i); however, there were overall relatively higher P/Ti and Ba/Al values during oil shale deposition, indicating that high primary paleoproductivity was indeed beneficial to OM accumulation. Besides, TDM also affects OM accumulation by influencing the deposition rate of OM, which either provides sites for OM adsorption or dilutes OM. The negative correlations between TOC and terrigenous (%) \( r = 0.67 \) indicated increased TDM which mainly resulted in dilution of OM accumulation in the study area (Figure 9i).

Therefore, during the maximum flooding stage of oil shale deposition, the relatively low radioactivity tends to be associated with the inhibited input of clay minerals and radioactive materials, largely caused by increasing arid paleoclimate. The accompanying decreased TDM benefited primary paleoproductivity and anoxic conditions; their combined influence could induce sapropelic OM accumulation.

### 4.8. Evolution Model of Radioactivity and OM for Shale

During the deposition period of dark shale, the humid climate condition favored the chemical weathering of provenance and the growth of higher terrestrial plants, which could result in the moderate-high degree input of radioactive materials, clay minerals, humic OM, and other terrigenous matters into lake. Meanwhile, because of the limited scale of lake water at an initial stage of transgressive system tract, OM accumulation would be easily diluted by the moderate-high TDM, accompanied by relatively suboxic conditions and low primary paleoproductivity. Thus, dark shale with relatively high radioactivity and moderate OM content could be formed in this environment (Figure 10a).

With the increasing arid paleoclimate from dark shale to oil shale deposition, the chemical weathering and related detrital influx gradually began to weaken; thus, the supply of radioactive materials, clay minerals, and other terrigenous matters have been restrained. Meanwhile, with the continuous tectonic subsiding of basin, the lacustrine water almost evolved to the maximum flooding stage despite intense evaporation, which provided a sufficient favorable space for the enrichment of sapropelic OM, accompanied by relatively anoxic conditions and high primary paleoproductivity; however, the limited radioactive elements also have been largely diluted. Therefore, oil shale with relatively low radioactivity and high OM content could be formed in this environment (Figure 10b).

### 5. CONCLUSIONS

Based on organic and inorganic geochemical study of samples which consist of oil shale and dark shale in Jd7 Yuqia depression of Northern Qaidam Basin, the following conclusions can be drawn.

1. The radioactivity of oil shale displays intense vertical variation. Because U and Th contents from NGS are strongly correlated with GR, it can be inferred that the variation is mainly derived from these two elements.
2. The radioactive elements are preferentially bonded to inorganic mineral compositions. In the study area, the inhibited input of clay minerals and radioactive materials control the lower radioactivity of oil shale. The OM content and anoxic lake conditions could be minor factors.
3. Combined with the influence of the maximum flooding stage, the increasing arid paleoclimate from dark shale to oil shale has played a very important role in decreasing the radioactivity by reducing the supply of clay minerals, radioactive materials, and other TDM, which also benefited primary paleoproductivity and anoxic conditions; their integrated effect could induce sapropelic OM accumulation.
4. It is important to note that there still exist many oil shales which develop in similar conditions and exhibit both high TOC and high GR; however, the summary shown above is also reasonable, at least in the study area. Therefore, the relationship between the OM content and radioactivity is very complex; rather than only assuming a positive correlation, its characteristics and formation mechanism need to be analyzed in a specific environment and then, it can effectively guide the identification and exploration of oil shale and other organic- and hydrocarbon-rich fine-grained sedimentary rocks.

### 6. METHODS

A total of 90 core samples were collected from Well YQ-1Y (Figures 1 and 2). To avoid contamination by the hydrocarbon product, all samples were collected and stored in a fabric or paper bag until they were tested. All samples were tested for OY product, all samples were collected and stored in a fabric or paper bag until they were tested. All samples were tested for GR, TOC, and U and Th contents from NGS. A total of 90 core samples were collected from Well YQ-1Y.
representatives for detailed investigations. In addition, partial published data of Well CY-1 in the study area were used to supplement our study.19,21,22

OY was determined by Gray-King low-temperature dry distillation up to 600 °C at the Key Laboratory of Coal Resources Exploration and Comprehensive Utilization, Ministry of Land and Resources at Xi’an, China.

Organic geochemistry of the sample was tested at the Key Laboratory of Exploration Technologies for Oil and Gas Resources, Ministry of Education, Yangtze University, China.

For analyses of TOC, each sample was crushed into grains less than 200 mesh and then, we treated 0.10 g with diluted hydrochloric acid to remove inorganic carbon. After being washed and oven dried, the TOC of sample was determined using the Leco CS230 carbon—sulfur analyzer. Rock pyrolysis was performed by the OGE-VI oil and gas evaluation station, which provides S1, S2, S3, and Tmax when the sample was heated from 300 to 650 °C by 25 °C/min in a helium atmosphere. Vitrinite reflectance (R0) analysis was performed using the Leitz MPV-III micro-spectrophotometer. The measurements were collected using 50X oil immersion objective under 23 ± 2 °C temperature and 70% humidity condition.

For analyses of gas chromatography—mass spectrometry (GC—MS), after being Soxhlet extracted and separated, the saturated hydrocarbon of the sample was conducted at HP6890N GC/5979I MSD. A 60 m × 0.25 mm × 0.25 μm HP-5MS fused silica capillary column was equipped with helium as the carrier gas and boosted at a constant rate of 1.0 mL/min. Biomarker ratios were calculated from the peak areas of individual compounds.

Mineralogy and element analyses were conducted at the MLR Key Laboratory of Genesis and Exploration of Magmatic Ore Deposits at the Xi’an Center of the China Geological Survey, China.

For analyses of mineralogical composition, sample powders of 200 mesh were scanned with a Rigaku D/max-2500PC X-ray diffractometer using Cu Kα radiation at 40 kV and 100 mA. Data were recorded at a scan rate of 10°/min with a step size of 0.02 for whole rock analysis and a scan rate of 4°/min with a step size of 0.02° for clay fraction analysis, respectively.

For analyses of elements, samples were first crushed into a 200 mesh carbide by a tungsten ball mill. The powdered sample was heated to 1050 °C and then dissolved in a mixture of Li2BO2 + LiBO2. The major element content was analyzed by PANAlytical Axios 4.0 kW X-ray fluorescence spectrometry and expressed with an oxidation form, including SiO2, Al2O3, Fe2O3, FeO, CaO, MgO, K2O, Na2O, TiO2, P2O5, and MnO. The relative analytical uncertainty is within 5%. For trace element analyses, sample powders were digested with a mixture of HF and HNO3 in high-pressure Teflon containers at 190 °C for 48 h. The trace element content was analyzed by Thermo X Series II inductively coupled plasma mass spectrometry. The relative analytical uncertainty is within 10% for most trace elements.

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. The contribution of G.C. and W.G. to the study is equal.

Notes

The authors declare no competing financial interest.

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