Trace Elemental Geochemistry and Depositional Environment of Shale Oil Reservoir Rocks within the Permian Lucaogou Formation, Jimusaer Sag

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Abstract. By analyzing the geochemical indicators of trace elements and rare earth elements in shale oil cores, this paper clarifies the depositional environment of the Lucaogou Formation, and it provides some guidance for the exploration and deployment of shale oil in the Jimsar Sag. The average value of Th/U in the Lucaogou Formation is 1.89, which of V/(V+Ni) is 0.74, which of V/Cr is 3.05, which of V/Sc is 8.31, and w(Ni) are less than 40×10⁻⁶, indicating the terrestrial reduced environment. The Sr/Ba ratio changes frequently, ranging from 0.55 to 25.62, averaging 4.42, reflecting a higher paleo-salinity. ⁸⁷Sr/⁸⁶Sr ratio ranges from 0.705286 to 0.705784, averaging 0.705486, and it is substantially lower than the average value of the strontium isotope of the crinoiduous silicon-aluminum rock. Besides, ¹⁴³Nd/¹⁴⁴Nd ratio ranges from 0.512419 to 0.512722, and sediments have the characteristics of the origin of the mantle, reflecting the intracontinental rift formation environment. The analysis of rare earth elements indicates that the sediments has the characteristics of LREE relative enrichment, Ce weak positive anomaly and Eu negative anomaly, and furtherly excluded the possibility of marine sedimentary environment. Comprehensive analysis shows the sedimentary period of the Lucaogou Formation is a reduced and salty intracontinental rift lacustrine environment.

1. Introduction

The shale oil of Lucaogou Formation in the Jimsar Sag, Junggar Basin, has shown rich prospects for oil and gas resources and huge exploration potential, causing a research boom for explorers. The researches on the tectonic setting and sedimentary environment are abundant, and the controversy is quite extensive. The viewpoint can be roughly divided into three types. Yijie Zhang et al. (2007), Chengzao Jia et al. (2012) carried out identification of salinized sedimentary markers, and they all believed that the Jimsar sag in the Early Permian belonged to the terrigenous offshore lake basin [1,2]; Jingjing Li (2009), based on trace elements and biomarker parameters, it is considered to be a rift-type continental lake basin [3]; However, Lichun Kuang et al. (2012), using outcrops, cores and geochemical parameters to analyze the sedimentary environment, which was considered to be a saline basin after the residual sea closed [4]. In this study, 30 shale oil core samples were selected from the Permian Lucaogou Formation (P2l) in the Jimsar Sag for trace element and isotope analysis, focusing on the analysis of the strontium-strontium isotope and rare earth elements in order to clarify the deposition
and tectonic environment in this area for guiding further deepening exploration. The trace element analysis was performed on an ELAN6100DRC plasma mass spectrometer with high analytical accuracy, and the isotope analysis was performed by using a Nu Plasma multi-receiving plasma mass spectrometer.

2. Redox sensitive elements and their ratio

Generally speaking, The ratio of Th/U is less than 2, which of V/(V+Ni) is more than 0.6, which of V/Cr is more than 2, and high V/Sc, and these values reflect the reduction environment\(^{[5,6]}\). Sedimentary rock samples from the Lucaogou Formation showed lower Th/U value (0.37-5.31) with an average of 1.96, the V/(V+Ni) value is between 0.57 and 0.89 with an average of 0.75, and the V/Cr ratio ranges from 1.20 to 6.38 with an average of 3.11. The V/Sc ratio of the dolomitic rock sample in the study area varies between 1.12 and 16.19, with an average of 8.62, which overall reflects the sedimentary environment is more oxygen-deficient. Shi Kean et al. (2013) considered when the V/Ni ratio is greater than 1 it’s the continental phase and conversely ti’s the marine phase\(^{[7]}\). However,The V/Ni ratio of the study area ranges from 0.13 to 8.08 with an average of 2.87. Only 3 w(Ni) values of the 30 samples are greater than 40×10\(^{-6}\), and the values are very close to the limit value 40×10\(^{-6}\), the remaining samples w (Ni) values are less than 40×10\(^{-6}\), indicating that the sedimentary environment of the study area is a terrestrial environment.

| Sample | Depth (m) | Sc    | V     | WB/10\(^{6}\) | Th/U | V/(V+Ni) | V/Cr | V/Sc |
|--------|----------|-------|-------|---------------|------|----------|------|------|
| J174-5 | 3112.1   | 6.09  | 89.2  | 36.4          | 44.2 | 0.50     | 2.55 | 2.00 |
| J174-14 | 3143.7   | 14.9  | 54.3  | 29.5          | 18.5 | 3.27     | 2.42 | 1.35 |
| J174-21 | 3158.1   | 6.83  | 58.1  | 22.6          | 11.2 | 0.97     | 0.50 | 1.93 |
| J174-28 | 3174.4   | 6.00  | 77.2  | 56.6          | 51.2 | 4.34     | 2.47 | 1.76 |
| J174-33 | 3197.0   | 7.56  | 70.4  | 21.6          | 29.4 | 7.01     | 3.94 | 1.78 |
| J174-35 | 3200.0   | 7.97  | 111   | 88.8          | 66.4 | 2.94     | 2.35 | 1.26 |
| J174-69 | 3272.2   | 14.4  | 83.1  | 22.9          | 10.3 | 2.34     | 1.88 | 1.24 |
| J174-99 | 3316.2   | 8.98  | 61.1  | 9.57          | 33.6 | 2.13     | 2.14 | 1.00 |
| J174-106 | 3322.3  | 7.61  | 123   | 24.0          | 32.6 | 6.88     | 4.88 | 1.41 |
| J174-110 | 3330.1  | 3.81  | 56.9  | 14.4          | 19.9 | 2.10     | 1.85 | 1.14 |
| J251-17 | 3741.8   | 12.4  | 81.7  | 34.0          | 17.8 | 4.19     | 3.28 | 1.82 |
| J251-35 | 3756.2   | 8.74  | 65.4  | 19.4          | 32.3 | 15.8     | 3.77 | 4.20 |
| J23-1   | 2296.2   | 3.17  | 29.5  | 13.8          | 7.55 | 1.75     | 0.77 | 2.28 |
| J23-3   | 2320.7   | 1.84  | 5.04  | 2.43          | 3.81 | 3.63     | 0.68 | 5.31 |
| J24-1   | 1691.8   | 7.09  | 75.9  | 20.1          | 10.4 | 3.88     | 10.5 | 0.37 |
| J27-1   | 2297.0   | 12.0  | 110   | 43.5          | 27.9 | 5.86     | 2.00 | 2.93 |
| J28-1   | 3167.9   | 6.49  | 29.5  | 24.7          | 18.8 | 3.49     | 1.23 | 2.84 |
| J30-14  | 4146.7   | 38.6  | 43.2  | 12.2          | 5.98 | 10.7     | 4.84 | 2.21 |
| J30-16  | 4150.4   | 7.20  | 83.8  | 20.4          | 41.8 | 48.7     | 28.2 | 1.73 |
| J31-7   | 2721.5   | 19.7  | 63.5  | 11.4          | 8.74 | 2.45     | 1.45 | 1.69 |
| J32-10  | 3578.9   | 8.99  | 68.0  | 21.1          | 17.0 | 2.49     | 1.72 | 1.45 |
| J36-2   | 4138.9   | 8.91  | 80.0  | 29.3          | 24.3 | 3.61     | 1.95 | 1.85 |
| average value | 3192.5 | 9.97 | 69.1 | 26.3 | 24.3 | 6.5 | 3.88 | 1.96 | 0.75 |

3. Salinity sensitive elements and their ratio

Table 1. Redox-sensitive metal elements in the Lucaogou Formation, Jimsar Sag.

- J174-5, J174-14, J174-21, J174-28, J174-33, J174-35, J174-69, J174-99, J174-106, J174-110, J251-17, J251-35, J23-1, J23-3, J24-1, J27-1, J28-1, J30-14, J30-16, J31-7, J32-10, J36-2, average value
Both strontium (Sr) and barium (Ba) belong to the alkaline earth metal (Group IIA) element, and barium (Ba) has a lower solubility than strontium (Sr). In the water environment with low salinity and low sulfate ion content, strontium (Sr) and barium (Ba) ions are stored in the form of bicarbonate. With the increasing salinity and sulfate ion concentration the barium (Ba) element is first precipitated in the form of barium sulfate. But only when the water body (lake water or seawater) is concentrated to a certain extent, barium sulfate precipitation can be produced [8]. It is generally considered that the Sr/Ba ratio of the continental sediment is less than 1, and the Sr/Ba ratio of the marine sediment is greater than 1, and the ratio is more accurate than the paleo-salt.

The Sr/Ba ratio of 30 samples from the Lucaogou Formation in the study area ranges from 0.55 to 25.62 with an average of 4.42, reflecting a higher paleo-salinity. The carbon and oxygen isotope conversion of the carbonate rock has an ancient salinity (Z value) between 119 and 140. The Sr/Ba ratio changes frequently, and the difference is as high as 46 times, which indicates that the lake salinity of the Lucaogou Formation in the study area has frequent changing features.

**Figure 1.** Standardized spider map of the original mantle of the Lucaogou Formation. (Original cellar data from Sun and McDonough, 1989)

The radioactive elements Th, uranium (U) and lead (Pb) in the rocks of the Lucaogou Formation are much higher than the original mantle, and some titanium (Ti) elements compared to the original mantle are relatively lossy, while the content of phosphorus (P) elements varies widely, which may be caused by the difference in the degree of bioaccumulation in unequal depositional periods.

4. **Geochemical characteristics of strontium and strontium isotopes**

The 9 samples selected in this study were collected from the drilling core of the Lucaogou Formation in the study area, and 3 samples of them were whole rock samples, and the remaining 6 ones were selected from the calcite micro-region (Note: subscript w represents micro-sampling samples, Conversely, the whole rock sample). The samples are fresh and surface-removed, and the sputum (Sr) and strontium (Nd) isotope tests are performed.

**Table 2.** Results of strontium and strontium isotope analysis of jet sedimentary rocks.

| Sample number | Depth (m) | Sr (ppm) | 87Sr/86Sr | Nd (ppm) | 143Nd/144N |
|---------------|-----------|----------|-----------|----------|-------------|
| J174-35       | 3200.00   | 973      | 0.705737  | 14.7     | 0.512597    |
| J174-99       | 3316.20   | 1742     | 0.705293  | 13.5     | 0.512588    |
| J174-99W      | 3316.20   | 2041     | 0.705355  | 17.2     | 0.512420    |
| J174-106      | 3322.30   | 968      | 0.705784  | 28.1     | 0.512599    |
| J174-106W     | 3322.30   | 1680     | 0.705448  | 18.3     | 0.512711    |
| J174-109W     | 3328.30   | 2951     | 0.705286  | 8.3      | 0.512722    |
| J251-35W      | 3756.23   | 1875     | 0.705613  | 15.1     | 0.512419    |
The experimental results show that the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the nine dolomite samples in the Lucaogou Formation in the study area are between 0.705286 and 0.705784, with an average of 0.705486 (Table 2). The values are much lower than those of the crust source of the crustaceous silicalite. The average value is $0.720\pm0.005$, which is close to the global isotope mean isotope average of 0.70350\cite{9}. The range of strontium and strontium isotope ratios is small, and the range of $^{143}\text{Nd}/^{144}\text{Nd}$ varies between 0.512419 and 0.512722. It can be seen from Figure. 2 that most of the rocks in the Lucaogou Formation in the study area fall within and near the normal mantle evolution trend line. The strontium and thorium isotopes of the Lucaogou Formation in the study area are very stable and have the characteristics of mantle source, reflecting its inland rift formation environment.

![Figure 2. the correlation diagram of the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotope](according to Zindler and Hart, 1986)

5. Geochemical characteristics of rare earth elements

(1) Total amount of rare earth elements and distribution mode

Due to the "lanthanum shrinkage" effect of rare earth elements, the atomic structure and crystal chemical properties of the elements are similar, generally produced collectively. And the atoms are most likely to lose the outermost electrons, presenting a $+3$ valence form with some alkaline characteristics. The REE of sedimentary rocks in the Lucaogou Formation in the study area varies widely, ranging from $38.00\times10^{-6}$ to $161.93\times10^{-6}$, with an average of $91.00\times10^{-6}$, which is much lower than the total amount of rare earth elements in the upper crust ($146.37\times10^{-6}$) and North American shale ($160.12\times10^{-6}$). Focused on the lithology, the REE value of the tuff rock is larger, while the $\sum$ REE value of the dolomitic rock is relatively smaller.

The LREE/$\sum$HREE values of the sedimentary rocks of the Lucaogou Formation in the study area are 3.37-8.81, with an average of 5.83, which generally reflects the characteristics of the LEE relative enrichment pattern (Figure. 3). Heavy rare earth elements are more likely to precipitate from sediments because of their smaller atomic radius, stronger penetrability, and greater alkalinity. However, light rare earths are more easily adsorbed by fine particles such as clay\cite{10}. In addition, La/Sm is 3.51-6.04 with an average of 4.39. La/Sm reflects the degree of fractionation among LREE, and the larger the ratio is, the stronger the fractionation among LREE is.

![Figure 3. Normalized distribution pattern of rare earth element chondrite](image)
Environmental sensitive rare earth elements

Ce and Eu are variable-value rare earth elements that are very sensitive to environmental changes. They often form Ce and Eu anomalies by separation of valence states and separation of adjacent rare earth elements during environmental changes. The Lucaogou Formation in the study area is characterized by weak positive anomalies and negative Eu anomalies, which are completely different from the negative anomalies and Eu positive anomalies commonly found in marine environments.

Morad and Felitsyn (2001) found that when the La/Sm of the sample was greater than 0.35 and there was no correlation between La/Sm and δCe, the enthalpy (Ce) anomaly of the sediment can reflect the physicochemical conditions of the formation environment. In this study, the sample J174-33 with La/Sm of less than 0.35 in the sedimentary rocks of the Lucaogou Formation in the study area was excluded. The La/Sm of the remaining 10 samples is 3.51-6.04, with an average of 4.39, and the correlation coefficient between La/Sm and δCe (R2) is 0.4962, and the correlation is poor (Figure 4). Among the 10 samples, the δCe of 6 samples were more than 1.00 and 4 samples were less than 1.00, but they are close to 1.00, and the average value is 1.01. The overall characteristics of weak Ce positive anomaly indicated that the Lucaogou group had the enrichment of Ce4+. The δEu ranges from 0.55 to 0.77, with an average of 0.62 and a significant Eu negative anomalies. Combined with the analysis of trace elements, isotopes and rare earth elements, the Jimusaer Permian Lucaogou Formation is a reduced and salinized intracontinental rift lake sedimentary environment.

| Sample serial | La/Sm | δCe | δEu |
|---------------|-------|-----|-----|
| J174-5        | 33.23 | 62.95 | 8.25 | 32.59 | 6.34 | 1.17 | 5.47 | 0.81 | 4.65 | 0.90 | 2.53 | 0.38 | 2.32 | 0.34 | 161.93 | 0.89 | 0.59 |
| J174-14       | 11.39 | 27.21 | 3.19 | 13.37 | 3.09 | 0.64 | 3.13 | 0.53 | 3.46 | 0.74 | 2.30 | 0.37 | 2.56 | 0.40 | 72.38 | 1.07 | 0.63 |
| J174-17       | 7.31  | 17.18 | 2.33 | 10.13 | 2.08 | 0.39 | 1.89 | 0.30 | 2.03 | 0.51 | 1.85 | 0.34 | 2.41 | 0.39 | 49.14 | 1.00 | 0.59 |
| J174-21       | 7.84  | 15.89 | 1.82 | 6.73  | 1.30 | 0.25 | 1.17 | 0.18 | 1.08 | 0.22 | 0.65 | 0.10 | 0.67 | 0.10 | 38.00 | 0.98 | 0.62 |
| J174-28       | 16.90 | 37.87 | 4.55 | 18.60 | 3.93 | 0.77 | 3.74 | 0.62 | 3.93 | 0.81 | 2.39 | 0.37 | 2.34 | 0.35 | 97.18 | 1.02 | 0.61 |
| J174-33       | 20.76 | 51.94 | 6.59 | 31.53 | 8.20 | 1.56 | 8.46 | 1.47 | 9.77 | 2.12 | 6.35 | 0.93 | 5.83 | 0.88 | 156.39 | 1.05 | 0.57 |
| J174-35       | 14.08 | 29.76 | 3.52 | 14.68 | 2.96 | 0.72 | 2.66 | 0.40 | 2.38 | 0.48 | 1.39 | 0.21 | 1.36 | 0.20 | 74.80 | 0.99 | 0.77 |
| J174-69       | 14.23 | 35.46 | 4.20 | 17.48 | 4.04 | 0.75 | 4.14 | 0.67 | 4.10 | 0.82 | 2.43 | 0.37 | 2.35 | 0.35 | 91.38 | 1.06 | 0.59 |
| J174-99       | 12.71 | 28.42 | 3.13 | 13.46 | 3.04 | 0.60 | 2.96 | 0.48 | 2.97 | 0.60 | 1.82 | 0.32 | 2.35 | 0.38 | 73.23 | 1.06 | 0.60 |
| J174-106      | 26.70 | 58.73 | 6.64 | 28.06 | 6.25 | 1.10 | 5.88 | 0.92 | 5.16 | 0.95 | 2.63 | 0.41 | 2.77 | 0.43 | 146.63 | 1.03 | 0.55 |
| J174-110      | 7.36  | 15.24 | 1.84 | 7.74  | 1.66 | 0.37 | 1.58 | 0.24 | 1.45 | 0.29 | 0.85 | 0.13 | 0.83 | 0.13 | 39.72 | 0.97 | 0.69 |

CI Chondrite: 0.31 0.808 0.122 0.6 0.195 0.0735 0.269 0.0474 0.332 0.0718 0.21 0.0324 0.0290 0.0332 3.30 1.00 1.00
Original cellar: 0.71 1.83 0.28 1.37 0.44 0.17 0.60 0.11 0.74 0.16 0.48 0.07 0.48 0.07 7.51 0.99 1.01
Upper crust: 30.00 64.00 7.10 26.00 4.50 0.88 3.80 0.64 3.50 0.80 2.30 0.33 2.20 0.32 146.37 1.02 0.63
Americanshale: 31.50 66.50 7.90 27.00 5.90 1.18 5.20 0.79 5.80 1.04 3.40 0.50 2.97 0.44 160.12 1.00 1.00
Note: Rare earth element data for chondrite is quoted from (Boynton W V, 1983); The original mantle REE data are derived from (McDonough W F, 1991); Rare earth element data for North American shale is derived from (Haskin et al, 1984). The lithology of the rare earth element test samples (J174-5 to J174-110) of the Lucaogou Formation in the study area are as follows: Cloud-containing ash tuff; tuffaceous mud crystal dolomite; tuffaceous mud crystal dolomite; calcite-bearing carbonated tuff dolomite; mud-crystal dolomite spheroidal limestone; tuffaceous muddy crystalline dolomite; algae cloud rock Thin layer calcite carbonate rock; algae cloud rock with thin layer calcite carbonate rock; Calculation formula: $\delta Ce = \frac{2(Ce_{sample} / Ce_{chondrite})}{(La_{sample} / La_{chondrite} + Pr_{sample} / Pr_{chondrite})}$; $\delta Eu = \frac{2(Eu_{sample} / Eu_{chondrite})}{(Sm_{sample} / Sm_{chondrite} + Gd_{sample} / Gd_{chondrite})}$.

6. Conclusion

(1) The redox sensitive elements of the Lucaogou Formation in the study area and their ratios indicate that the sedimentary environment is a terrestrial reduced environment. Salinity sensitive elements and their ratios indicate that paleo-salty is high and it varies frequently. The results of Sr and Nd isotope analysis indicate that the sediment has the characteristics of mantle source formation and the environment of intracontinental rift formation.

(2) The rare earth elements exhibit the characteristics of relative enrichment of LREE, weak positive anomaly of Ce and negative anomaly of Eu. Based on the comprehensive analysis, the Permian Lucaogou Formation in the Jimsar Sag is a reduced and salinized intracontinental rift lake sedimentary environment.

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