Enrichment and Occurrence of Mn in 5−2 Coal from Qinglongsi Coal Mine, Northern Ordos Basin, China

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ABSTRACT: High concentrations of Mn were observed in 5−2 coal (Jurassic age) from Qinglongsi coal mine in the Northern Ordos Basin. To study the occurrence characteristics and sedimentary environment of the 5−2 coal (3.9 m), 22 samples were collected from a mining face. The test result indicates that the 5−2 coal is in low-ash, high-volatile, very low-sulfur, and bituminous rank, with high inertinite content. The minerals in Jurassic 5−2 coal are composed primarily of kaolinite, siderite, calcite, quartz, pyrite, K-feldspar, and fluorapatite. The Mn element is enriched in the upper part of the 5−2 coal seam with an average of 1243.01 μg/g, which is about 17.5 times higher than the average of world hard coal. The concentration level of Mn has a positive correlation with that of Fe2O3 and carbonate minerals. A weak reduction environment of the coal-accumulating swamp may induce the enrichment of Mn, which is mainly carried by siderite in the 5−2 coal.

INTRODUCTION

Coal is still a major energy source in many countries around the world.1,2 With the wide use of coal in power generation, metallurgy, chemical fertilizer, cement, and other industries, the use and research value of many trace elements and rare earth elements in coal have been gradually recognized.3−7 Some elements in coal will cause environmental pollution,8,9 while others may be enriched and mineralized after coal combustion or other treatment. Among them, Ga, Ge, U, V, Au, Ag, and rare earth elements have attracted more and more global attention due to their applications in new materials and high-tech fields. To realize the clean combustion of coal or other new uses, it is necessary to study the composition and enrichment characteristics of the elements in coal, especially the trace metal elements, which could provide a microscopic perspective of the traditional coal chemical characteristics.

Ordos Basin is one of the biggest coal mining areas in China, which is famous for its Jurassic coal with low ash yield and sulfur content.10,11 Besides that, Jurassic coal in Ordos Basin is also known for the richness in inertinite and low content of trace elements. Some scholars found that the content of some trace elements in the coal of Ordos Basin was abnormal in recent years.12,13 The content and occurrence of these trace elements in coal contain important information about the coal genetic, basin evolution, climatic variation, and tectonic events.14−19

Manganese is a transition metal element that is sensitive to oxidation–reduction. Previous reports on Mn enrichment in coal mainly focus on Carboniferous-Permian coal in north China and late Permian and late Triassic coal in south China, while a few reports on Mn enrichment focus on early and middle Jurassic coal in Ordos Basin.20−23 In the study of Jurassic coal in the Dongsheng coalfield of Ordos Basin, Zhao et al. believed that the combination of Mn and organic matter in coal was rare, less than 10%, which means that most Mn was combined with inorganic material.24 However, the authors found that the content of Mn in 5−2 coal seam of Qinglongsi coal mine was enriched in the study of clean utilization of coal in Ordos Basin, so it was necessary to retest and evaluate the geochemical characteristics of trace elements in this coal seam.

GEOLOGICAL SETTING

Qinglongsi Mine is located in the Shanbei Jurassic coalfield, Northern Ordos Basin (Figure 1), a large continental depression...
basin in the Mesozoic. Middle Jurassic is one of the two evolution peaks of the basin when it reached its maximum sedimentary range and peak of coal accumulation. The Guyinshan mountains, located at the north of the basin, were the dominant sediment source. The coal-bearing stratum in the Shanbei Jurassic coalfield is Yanan Formation (J2y), which was deposited in lacustrine, river, and delta sedimentary environments in Middle Jurassic. The thickness of the stratum varies from 118 to 311 m, and the rock is mainly composed of sandstone, siltstone, mudstone, and coal. Four sedimentary cycles can be divided according to the vertical lithologic features. The 52 coal seam is one of the five major minable seams, which locates at the lowest cycle of Yanan Formation (Figure 1).

![Figure 1. Location, generalized stratigraphic section of Yanan Formation, and the sampling section in the 52 coal of Qinglongsi Mine.](https://dx.doi.org/10.1021/acsomega.0c01863)

| sample no. | Mad (%) | Ad (%) | Vdaf (%) | Sd (%) | Spd (%) | St.d (%) | So.d (%) | Ro,ran (%) |
|------------|---------|--------|----------|--------|---------|----------|----------|------------|
| QL-01      | 6.55    | 8.86   | 32.51    | 0.30   | 0.15    | 0.00     | 0.15     | 0.52       |
| QL-02      | 7.08    | 5.28   | 37.89    | 0.23   | 0.06    | 0.01     | 0.16     | 0.54       |
| QL-03      | 5.32    | 24.67  | 49.27    | 0.19   | 0.12    | 0.02     | 0.05     | 0.53       |
| QL-04      | 6.12    | 11.94  | 37.72    | 0.21   | 0.14    | 0.01     | 0.06     | 0.53       |
| QL-05      | 6.78    | 18.67  | 39.45    | 0.17   | 0.09    | 0.02     | 0.06     | 0.52       |
| QL-06      | 6.52    | 22.14  | 47.03    | 0.17   | 0.15    | 0.00     | 0.02     | 0.51       |
| QL-07      | 5.63    | 23.44  | 48.93    | 0.18   | 0.15    | 0.00     | 0.03     | 0.54       |
| QL-08      | 6.58    | 18.73  | 44.18    | 0.18   | 0.14    | 0.00     | 0.04     | 0.53       |
| QL-09      | 6.18    | 9.98   | 35.25    | 0.17   | 0.09    | 0.01     | 0.07     | 0.53       |
| QL-10      | 6.36    | 7.80   | 35.49    | 0.24   | 0.06    | 0.01     | 0.17     | 0.53       |
| QL-12      | 6.64    | 13.49  | 33.34    | 0.22   | 0.11    | 0.00     | 0.11     | 0.53       |
| QL-13      | 6.11    | 17.34  | 35.33    | 0.17   | 0.09    | 0.01     | 0.07     | 0.53       |
| QL-14      | 6.39    | 8.23   | 39.94    | 0.19   | 0.10    | 0.00     | 0.09     | 0.52       |
| QL-15      | 6.08    | 6.71   | 38.80    | 0.24   | 0.09    | 0.02     | 0.13     | 0.54       |
| QL-16      | 6.41    | 21.69  | 33.96    | 0.16   | 0.06    | 0.01     | 0.09     | 0.52       |
| QL-17      | 6.43    | 9.19   | 34.67    | 0.20   | 0.09    | 0.01     | 0.10     | 0.53       |
| QL-18      | 5.26    | 7.66   | 39.44    | 0.21   | 0.14    | 0.00     | 0.07     | 0.53       |
| QL-19      | 5.43    | 10.37  | 40.86    | 0.21   | 0.08    | 0.00     | 0.13     | 0.54       |
| QL-20      | 5.40    | 9.41   | 39.95    | 0.22   | 0.11    | 0.01     | 0.10     | 0.53       |
| QL-21      | 4.25    | 19.53  | 41.41    | 0.21   | 0.17    | 0.01     | 0.03     | 0.54       |
| QL-22      | 5.30    | 11.87  | 35.17    | 0.20   | 0.14    | 0.01     | 0.05     | 0.56       |
| ave        | 6.04    | 13.70  | 39.07    | 0.20   | 0.11    | 0.01     | 0.08     | 0.53       |

*Note: Mad, moisture (air dry basis); Ad, ash (dry basis); Vdaf, volatile matter (dry and ash-free basis); Sd, total sulfur; Spd, pyritic sulfur; Ssd, sulfate sulfur; Sox, organic sulfur; Ro,ran, average random reflectance.*
Table 2. Maceral Composition of the Samples in the S-2 Coal of Qinglongsi Mine

| Sample No. | T (%) | C1 (%) | C2 (%) | C3 (%) | V (%) | I (%) | L (%) | M (%) |
|------------|-------|--------|--------|--------|-------|-------|-------|-------|
| QL-01      | 0.0   | 34.6   | 1.4    | 0.0    | 36.0  | 0.0   | 2.8   | 61.5  |
| QL-02      | 0.6   | 45.7   | 0.0    | 0.0    | 46.2  | 0.0   | 1.2   | 50.9  |
| QL-03      | 0.9   | 52.8   | 0.5    | 0.0    | 54.2  | 0.0   | 0.9   | 37.6  |
| QL-04      | 1.3   | 41.5   | 0.0    | 0.0    | 43.6  | 0.0   | 0.8   | 48.0  |
| QL-05      | 2.4   | 43.8   | 0.0    | 0.0    | 46.2  | 0.0   | 1.0   | 41.9  |
| QL-06      | 1.8   | 46.8   | 0.0    | 0.0    | 49.1  | 0.5   | 1.8   | 46.4  |
| QL-07      | 0.0   | 48.0   | 1.3    | 0.0    | 49.3  | 0.0   | 1.8   | 39.6  |
| QL-08      | 0.0   | 45.9   | 0.5    | 0.0    | 46.4  | 1.1   | 1.5   | 55.1  |
| QL-09      | 0.0   | 36.1   | 0.0    | 0.0    | 36.1  | 0.0   | 1.0   | 50.9  |
| QL-10      | 0.0   | 36.9   | 0.5    | 0.0    | 37.4  | 0.0   | 1.4   | 59.0  |
| QL-12      | 1.8   | 38.5   | 0.9    | 0.0    | 41.2  | 0.0   | 2.7   | 54.3  |
| QL-13      | 2.2   | 39.0   | 0.0    | 0.4    | 41.7  | 0.0   | 2.7   | 54.3  |
| QL-14      | 0.9   | 64.2   | 0.5    | 0.0    | 65.6  | 0.0   | 1.4   | 33.5  |
| QL-15      | 0.5   | 49.7   | 0.0    | 0.0    | 50.3  | 0.0   | 1.0   | 44.6  |
| QL-16      | 1.7   | 40.0   | 0.0    | 0.0    | 41.7  | 0.0   | 1.3   | 54.3  |
| QL-17      | 1.3   | 46.8   | 0.0    | 0.0    | 48.1  | 0.0   | 0.4   | 49.8  |
| QL-18      | 0.9   | 62.9   | 0.0    | 0.0    | 63.8  | 0.0   | 0.9   | 32.1  |
| QL-19      | 0.4   | 48.0   | 0.0    | 0.0    | 48.1  | 0.0   | 0.4   | 49.8  |
| QL-20      | 0.4   | 53.0   | 0.0    | 0.0    | 53.4  | 0.0   | 0.9   | 44.0  |
| QL-21      | 0.0   | 63.0   | 0.5    | 0.0    | 64.7  | 0.0   | 0.5   | 28.8  |
| QL-22      | 2.3   | 41.3   | 0.0    | 0.0    | 43.7  | 0.0   | 1.9   | 53.1  |

Note: V, vitrinite; T, telinite; C1, collotelinite; C2, collodetrinite; C3, corpogelinite; VD, vitrodetrinite; TV, total vitrinite; I, inertinite; FI, pyrofusinite; F, fusinite; SF, semi fusinite; Ma, macrinite; ID, inertodetrinite; TI, total inertinite; L, liptinite; Sp, sporinite; Cu, cutinite; Re, resinite; Sub, suberinite; Ba, barkinite; LD, liptodetrinite; TL, total liptinite; M, minerals; CM, clay minerals; SM, sulfide minerals; CaM, carbonate minerals; TM, total minerals; V/I, total vitrinite/total inertinite.
RESULTS

Coal Chemistry and Vitrinite Reflectance. The S−2 coal is classified as highly volatile bituminous coal in rank according to the ASTM D388-2017, with the average random vitrinite reflectance and volatile matter yields of the sample being 0.53% and 39.07%, respectively (Table 1). The average value of moisture and ash are 6.04% and 13.70%, respectively, so the S−2 coal is classified as low-ash coal according to the Chinese Standard GB/T 15224.1-2018. Total sulfur values of all the samples are less than 0.50%, which belongs to ultralow-sulfur coal. Organic sulfur and pyritic sulfur account for the largest proportion of the total sulfur, with average contents of 0.08% and 0.11%, respectively.

Coal Macerals. Vitrinite and inertinite are the main coal maceral components, while the liptinite and inorganic mineral contents are very low (Table 2). The relatively high content of inertinite is one of the significant features of the Jurassic coal in Ordos Basin. Minerals in samples mainly consist of clay minerals, sulfide minerals, and carbonate minerals. The V/I value of S−2 coal is between 0.6 and 2.8, with an average of 1.2. Collodetrinite is the dominant component in the vitrinite group; telinite, collinite, and corpocollinite contribute with relatively low content in the S−2 coal. The inertinite group is composed of fusinite, semifusinite, inertodetrinite, macrinite, and funginite; among them, semifusinite is the predominant component. The liptinite group includes resinite, cutinite, suberinite, barkinite, and liptodetrinite in the S−2 coal seam, and sporinite is the most widely distributed.

The content of each maceral composition varies dramatically in the vertical direction, and the variation trends are different. Telinite contents can be divided into three cycles of increasing first and then decreasing vertically. The content of collodetrinite has similar cycle regularity, but the regularity of each cycle is different. Fusinite contents vary frequently with unobvious regularity. The change in semifusinite content is basically similar, which can be vertically divided into four cycles, while the change in sporinite content is basically the opposite (Figure 2).

Minerals in Coal. XRD analysis shows that the main minerals in the sample are quartz, illite, siderite, K-feldspar, and muscovite (Figure 3), and the weight percentage of siderite is 0.5%. Optical microscopic observation and SEM-EDS examination of samples show that siderite (Figure 4a) and calcite (Figure 4b) are the major carbonate minerals, with calcite always filled in cracks. The clay mineral is mainly kaolinite (Figure 4c), which is usually filled in the cavity of plant cells or distributed in strips. Sulfite minerals and silicate minerals are less observed in the sample, but pyrite filling in cracks and quartz (Figure 4d)
is found. In addition, fluorapatite (Figure 4e) and K-feldspar (Figure 4f) are found in the coal samples, although their contents are very low.

**Geochemical Composition.** The major element oxides in coal (high-temperature ash oxides of coal) are mainly composed of SiO₂ and Fe₂O₃, followed by CaO and Al₂O₃. As a whole, SiO₂, Fe₂O₃, and CaO are of the same order of magnitude, Al₂O₃, SO₃, MgO, and P₂O₅ are of a lower order of magnitude, and Na₂O, K₂O, and TiO₂ are of the lowest order of magnitude. Compared with the general characteristic of the Jurassic coal ash composition in Ordos Basin, the S⁻² coal ash composition of Qinglongsi Mine is characterized by higher Fe₂O₃ content and lower Al₂O₃ content. Vertical distribution characteristics of Fe₂O₃ and CaO contents are quite different (Figure 5). Fe₂O₃ contents in the upper coal seam are significantly higher than that in the lower coal seam; CaO contents in the upper coal seam and lower coal seam are 20.92% and 8.59% on average, respectively. Variation tracks of SiO₂ and Al₂O₃ contents in the vertical direction are similar; in addition, the variation tracks of MgO, Na₂O, K₂O, and TiO₂ show certain similarities with them.
Table 3: Concentration of Trace Elements in the 5° Coal of Qinglongsi Mine (Whole Coal Basis, μg/g)

| Element | QL-01 | QL-02 | QL-03 | QL-04 | QL-05 | QL-06 | QL-07 | QL-08 | QL-09 | QL-10 | QL-11 | QL-12 | QL-13 | QL-14 | QL-15 | QL-16 | QL-17 | QL-18 | QL-19 | QL-20 | QL-21 | QL-22 | Average |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|
| Li      | 3.81  | 3.37  | 3.36  | 3.07  | 3.07  | 2.86  | 2.75  | 2.75  | 2.75  | 3.07  | 3.07  | 3.07  | 3.07  | 3.07  | 3.07  | 3.07  | 3.07  | 3.07  | 3.07  | 3.07  | 3.07  | 3.07  |
| Be      | 0.75  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  |
| B       | 0.90  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  | 0.87  |
| Mg      | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  | 2.57  |
| Ca      | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  | 5.11  |
| Sr      | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  | 5.63  |
| Yb      | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  | 0.93  |
| Zr      | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  | 3.87  |
| Nb      | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  |
| Mo      | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  |
| Zn      | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  | 1.24  |
| Cu      | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  | 0.75  |
| Pb      | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  | 0.64  |
| Sn      | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  | 0.83  |

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The contents of trace elements and rare earth elements (REEs) of the coal samples and the major element of the coal ashes are given in Table 3, and the concentration coefficient (CC) ratio compared with world hard coal is used to represent the enrichment of trace element. The enrichment levels are divided as significantly enriched (10 < CC < 100), enriched (5 < CC < 10), slightly enriched (2 < CC < 5), normal (0.5 < CC < 2), and depleted (CC < 0.5). The calculation result shows that the concentration coefficient of Mn is 7.28 so that Mn is enriched in 5−2 coal of Qinglongsi Mine. The enrichment level of Sr (CC = 0.87) and Cs (CC = 0.54) is normal, and other trace elements are all depleted for their concentration coefficients are less than 0.5 (Figure 6).

According to the testing data, the concentration coefficient (CC) of Mn ranges from 0.3 to 27.8, and the average Mn content is about eight times the world average concentration (70 μg/g) in the whole coal bed. The vertical section of Mn content in coal bed varies greatly, and several parts can be divided according to the Mn contents (Figure 7). Among them, the high enrichment part from QL-03 to QL-09 is obvious, and the average content is 1243.01 μg/g, about 17.5 times higher than that for the world coal. Beyond that, QL-13 to QL-14 and QL-16 to QL-22 are two weak enrichment parts. The contents of Mn in three parts of QL-01 to QL-02, QL-10 to QL-12 and QL-15 are at a normal level. According to the variation laws of Mn contents vertically, four cycles can be divided, with each cycle representing a complete change rule of Mn content from high to low. The cycles are QL-22 to QL-15, QL-15 to QL-11, QL-11 to QL-04, and QL-03 to QL-01.

■ DISCUSSION

Sedimentary Environment of Manganese Deposition.

The organic macerals of stratified samples can be used to characterize the types of peat bogs formed by coal seams. Vitrinite represents a wet reduction environment, inertinite represents a dry oxidation environment, and the ratio of vitrinite to inertinite (V/I) can directly reflect the water cover degree of swamp and the dry and wet conditions of climate. Chinese scholars divide V/I into four categories, which, respectively, represented deep water (V/I > 4), extremely wet and water-covered (1 < V/I < 4), wet and water-covered (0.25 < V/I < 1), and dry and extremely dry (V/I < 0.25) environments. The value in the lower part of 5−2 coal seam is large and changes greatly, with an average of 1.39, while the V/I value in the upper part of 5−2 coal seam is small and changes little, with an average of 0.95. This reflects the evolution of the environment of 5−2 coal from an extremely wet and water-covered environment to a wet and water-covered environment.

The gelification index (GI) reflects the water depth of the peat swamp, while the structural preservation index (TPI) reflects the type of coal-forming plant. The GI-TPI diagram divides coal facies into low forest swamp, dry forest swamp, wet forest swamp, and water-covered forest swamp. The S−2 coal was mainly distributed in low-level peat swamp and dry forest swamp, and the water cover depth was characterized by frequent changes. Coal-forming plants belong to the mixed type of herbaceous plant and woody plant (Figure 8a). Plant index VI can reflect the relationship between woody plants and herbaceous plants. Groundwater impact index (GWI) reflects the degree of peat swamp water cover, and the value of GWI represents the groundwater level. It can also be seen from the GWI-VI diagram that the coal-forming plants of S−2 coal were...
between the herbaceous plants and woody plants and generally belong to the eutrophic environment with slightly strong hydrodynamic conditions (Figure 8b). According to the vertical change in Mn content in the control coal (Figure 7), it is reasonable to speculate that the enrichment of Mn in 5−2 coal occurs in the dry environment to the humid environment, and the evolution environment of woody plants to herbaceous plants. Moreover, in the relatively stable humid environment (QL-03 to QL-07), it is more beneficial to the enrichment of Mn.

Mn contents in 5−2 coal vary significantly in the vertical scale, indicating zonation in layers. This information is important for judging its correlation with primary deposits. Rare earth element content in sedimentary rock is often used to extract the environment evolution information, and Zn, Ni, Ga, U, Th, V, and Cr are indicator elements in the redox condition of sedimentary environments. U and Th have similar geochemical properties. While Th is insoluble in supergene conditions, U will be oxidized and dissolved in water in oxidation conditions. As a result, the ratio of Th and U can be used to indicate the redox conditions, with a large Th/U ratio representing a relative oxidation environment. Based on the same principle, (Zn + Ni)/Ga, (V + Ni)/V, and Cr/V are also used for the recognition of paleo-sedimentary redox conditions, with a higher value of each ratio representing relative oxidation conditions and lower values representing relative reducing conditions.

There is a remarkable resemblance between the variation trends of vertical ratio and that of the Mn content in the 5−2 coal of Qinglongsi Mine. The trend is more obvious in (Zn + Ni)/Ga, (V + Ni)/V, and Cr/V (Figure 9), where the lower part of the coal column is characterized by relatively low Mn content and the ratios are also in low level. In the upper section, where Mn is enriched, the ratios are extremely high. In addition, their changing rules correspond to the Mn contents, which suggest that the enrichment of Mn in coal is highly correlated with the relative oxidation conditions. Mn would be oxygenated in oxidation conditions, then deposited, and enriched in sediments; however, it would be reduced and mobilized in reducing conditions. It is obvious that Mn contents in the coal are significantly influenced by the paleoredox condition of sedimentary environments, and the enrichment of Mn is the result of relative oxidation of peat swamp.

REEs have strong stability during weathering, transportation, sedimentation, and diagenesis, so the geochemical characteristics of REEs in coal can be used to identify the source and sedimentary environment of inorganic minerals in coal, and the sedimentary environment of Mn formation in coal can be further studied. The average value of LREE/YREE is 7.21, indicating the enrichment of LREE (light rare earth elements) and deficiency of HREE (heavy rare earth elements). The differentiation type of LREE and HREE is a typical character of general sedimentary rocks. Distribution patterns of REEs standardized by upper crust background value show an obvious negative anomaly of Ce and Eu (Figure 10). The anomaly of Ce is closely related to the sedimentary environment, Ce will be oxidized into Ce in the oxidizing condition, causing the loss of Ce in the sediment. The negative anomaly of Ce is closely related to the redox condition of the sedimentary environment. The vertical change in δCe is in high consistency with the four cycles of Mn content, although in a reverse trend (Figure 9). The anomaly characteristic of Ce has verified the assumption that the enrichment of Mn in 5−2 coal is mainly caused by a relative oxidation environment.
Mode of Manganese Occurrence. Mn content in coals mainly existed in the carbonate minerals, especially in siderite and ankerite. Clay minerals and siderite concretions were the major source of Mn in coal mine drainage. Mn could combine with an organic-functional group, so it also existed in pyritic and organic materials.

The relations between trace element concentrations and ash yield or other indexes may provide information about their affinity relationship and the modes of occurrence of specific element. Pearson correlation coefficients (r) were calculated between Mn content and ash yield, volatile matter yield, total sulfur, pyritic sulfur, sulfate sulfur, organic sulfur, major element oxides, and trace elements; some of the results are presented in Figure 11. Results show that Mn is strongly correlated (r > 0.5) with ash, which suggests that Mn has an inorganic affinity. Relations between Mn and sulfur forms are varied. The content of Mn has a weak positive correlation with the content of pyritic sulfur and a negative correlation with the content of organic sulfur and sulfate sulfur.

The Pearson correlation coefficients between Mn and Fe₂O₃ in coal ash are high (Figure 10). It can be inferred that Mn...
occurs in an Fe-bearing mineral rather than quartz, calcite, or clay minerals. Relations between Mn and minerals strengthen the speculation. The correlation coefficient between Mn and carbonate minerals is 0.74, and the value is only 0.18 between Mn and clay minerals. Based on the above data analysis, an Fe-rich carbonate mineral is the most likely Mn-bearing mineral. Based on the knowledge, dispersive X-ray (SEM-EDX) analysis, which focuses on Fe-rich carbonate minerals, was carried out. Siderite is the only mineral with a high content of Mn (Figure 12), and it has a high content in the S−2 coal. Siderite is an indicator of a weak reduction environment in the sedimentary environment analysis. Therefore, the weak reduction environment that developed in the Mn-rich coal seam is consistent with the generation environment of siderite.

**CONCLUSIONS**

1. Manganese is enriched in S−2 coal of Qinglongsi Mine, Northern Ordos Basin, and the average and maximum contents of manganese in the whole seam are 541.34 and 1943.10 μg/g. The upper part of the coal seam is rich in Mn, with an average content of 1243.01 μg/g, which is about 17 times higher than the average content in world hard coal.

2. Inertinite is enriched in the S−2 coal of Qinglongsi Mine, and semifusinite is the major component. Minerals in coal mainly consist of kaolinite, siderite, calcite, quartz, pyrite, K-feldspar, and fluorapatite. Based on the analysis of organic macerals and inorganic geochemistry, it is shown that the S−2 coal with rich Mn in Qinglongsi Mine was formed in a weak reducing sedimentary environment, and siderite is the major occurrence mineral.

**SAMPLING AND ANALYTICAL METHODS**

**Sampling.** The thickness of S−2 coal in Qinglongsi Mine varies from 2.3 to 5.0 m. Coal samples were collected from the S−2 coal mining face in Qinglongsi Mine. The thickness of sampled coal seam was 3.9 m. Twenty-two samples, with 21 coal samples and one sandstone sample (sample QL-11), were collected from the top to the bottom using a channeling sampling strategy. Coal samples were collected at a nearly equal interval, and each sample’s range is about 0.2 m vertically.

**Proximate Analyses.** The basic test of coal quality including the analysis of moisture content, ash yield, and volatile content was carried out according to the Chinese standard GB/T30732-2014. Sulfur forms and total sulfur content were measured according to the Chinese standard GB/T215-2003.

**Maceral Analyses.** Maceral analyses were performed by reflected-light, oil-immersion microscopy using a Leica-BMRXP photometer microscope with the magnification of 200× according to the standard ICCP System. The samples were polished and dried at 30−40 °C, and then the vitrinite reflectance of coal was measured by a microscope photometer.

**Geochemical Analysis.** Samples were crushed and ground to 200 mesh and divided into two parts for geochemical analysis. One part of each sample was used to analyze the composition of the main inorganic elements (the major elements of the minerals in the coal). Another part was digested by hydrofluoric acid and nitric acid, and then the content of trace elements and rare earth elements was detected using a Thermo Fisher ICP-Qc-type inductively coupled plasma mass spectrometer.

**Mineral Analyses.** Minerals of cross sections were measured using a German Zeiss SIGMA-type high-resolution
field emission scanning electron microscope. Electronic probe analysis was performed in conjunction with the British Oxford X-Max spectrometer to determine the mineral carrier of the corresponding element in the sample. In addition, the coal samples were added for XRD test. The organic matter was removed by a plasma ashing instrument at 200 °C, and the mineral composition of the samples was quantitatively analyzed by a Panaco X’Pert3 Powder X-ray powder diffractometer, Netherlands, according to Chinese standards for oil and gas industry SY/T 5163-2018.70

Figure 11. Relations between (a) Mn and coal ash, (b) Mn and clay minerals and carbonate minerals, (c) Mn and SiO₂, Al₂O₃, Fe₂O₃, CaO, and MgO, and (d) Mn and K₂O, Na₂O, SO₃, TiO₂, and P₂O₅.

Figure 12. SEM and EDX images of the siderite Mn occurrence in the 5−2 coal of Qinglongsi Mine.

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