Study on Uranium Occurrence State of Sandstone-Type Uranium Deposits in Qianjiadian Region, Songliao Basin, China

Bo Zhang 1, 2, Jianguo Li 2, 3, Peisen Miao 1, 2, Qinghong Si 1, 2

1 Tianjin Center of China Geological Survey, Tianjin, China
2 Key Laboratory of Uranium Geology, China Geological Survey, Tianjin, China
3 Institute of Exploration Techniques, CAGS, Langfang Hebei, China

Abstract. The Qianjiadian uranium deposit is located in the southwest margin of Songliao basin. In this paper, electron probe, energy spectrum, back scattering analysis, scanning electron microscopy and other experimental methods are used to study uranium occurrence form and uranium mineral type in Qiandaidian uranium deposit. The results are shown as follows. (1) The occurrence forms of uranium in Qiandaidian uranium mining area include uranium minerals, adsorption uranium. The uranium in low-grade ore is mainly in the form of dispersive adsorption, which is clay mineral and organic matter adsorption. The high-grade ore mainly exists in the form of uranium mineral, the type of uranium mineral is mainly pitchblende, followed by coffinite, a small amount of uranium mineral containing titanium. (2) Uranium minerals are often closely symbiotic with pyrite, carbonate and so on, most of them develop in the pyrite, carbonate margin and fractures in the form of colloidal, there are also granular, pellet independent distribution. (3) Uranium minerals are rich in Phosphorus, and there is an obvious positive correlation between Phosphorus and Silicon. It has been found that some samples contain phosphorus-rich uranium aggregates in microspheres, which is considered as a strong evidence that microorganisms are involved in uranium mineralization at low temperature.

1. Introduction

The sandstone-type uranium deposit has become one of the key uranium deposit types for exploration due to its shallow burial, large reserves, low cost and environmental protection [1]. The Qianjiadian uranium deposit is located in the southwest of Songliao Basin. Previous studies in Qianjiadian uranium deposit area centered on metallogenic geological characteristics [2], interlayer oxidation [3], hydrocarbon reduction [4], altered minerals [5], metallogenic model [2, 6] and other issues have carried out fruitful research. The occurrence state of uranium is one of the important contents in the study of uranium mineralization. Previous studies on the occurrence state of uranium in the Qianjiadian uranium mining area have done some work, but there are still some differences on the dominant form of uranium occurrence. According to some opinions, the main existing form of uranium is dispersive adsorption uranium [7], which is mainly organic matter and clay adsorption. Another view holds that uranium mainly exists in the form of uranium minerals, and the uranium minerals are pitchblende [8], but they are very small and can only be seen in some rich minerals.
In order to find out the occurrence of uranium in the region and the combination of the mineral association further, selected the ore bearing samples which just obtained from Qianjiadian uranium deposit, and used the experimental methods such as scanning electron microscopy, electron probe, energy spectrum analysis to discuss the occurrence state of uranium, the genesis of uranium minerals and their mineral assemblages.

2. Geological setting

The Songliao Basin, located in northeast China (Fig. 1a), is a large continental sedimentary basin formed from the late Mesozoic, rich in oil, gas, uranium and other resources. The Songliao Basin can be divided into six first-order tectonic units: the Northern Plunge, the Central Depression, the Northeastern Uplift, the Southeastern Uplift, the Western Slope, the Southwestern Uplift (Fig. 1b). The Qianjiadian uranium deposit is located in the southwest of the Songliao Basin (Fig. 1b) and is distributed in an NE-oriented band.

![Figure 1](image)

In the Qianjiadian deposit, the strata exposed by drilling include the upper cretaceous Qingshankou Formation (K$_2$qn), Yaojia Formation (K$_2$y), Nenjiang Formation (K$_2$n) and Quaternary (Fig. 1d). The Yaojia Formation is the main ore-bearing horizon in this region, which can be divided into two sections. The lower part of Yaojia Formation is mainly composed of light gray fine sandstone and light red fine sandstone, with gray mudstone and purplish red mudstone, with a thickness of 60~80m. The upper Yaojia Formation section is mainly composed of light grey fine sandstone and light grey mud-gravel fine sandstone, with purplish red and light grey argillaceous siltstone, with a thickness of 65~90m. The formation monocline is produced with a dip angle of 3°~5° and a thickness of 50~230m. From the plan view, the uranium ore body develops in a semi-ring around the denudation skylight of the Baixingtu Uplift (Fig. 1c), which is consistent with the occurrence of the sedimentary sand body in the section.
The ore body occurs in gray and light gray fine sandstone, and there is also a small amount of uranium mineralization or even rich mineralization in the gray mudstone lens or mudstone interlayer. The Yaojia Formation has a stable mud-sand-mud structure, with good permeability and thick sand body, which is a favorable position for sand body formation.

3. Samples and methods

3.1. Sampling

During the sample collection, the γ-ray responses were measured for potential host sandstones with a gamma radiometer HD-2000 to roughly distinguish the mineralized ore and barren samples. Twenty three drill core samples from six holes (Fig. 1c).

3.2. Methods

Electron probe and backscatter images were observed at the laboratory of at Tianjin Center, China Geological Survey. The electronic probe instrument model is Shimadzu EMPA-1600. The test conditions: The accelerating voltage and probe current were 15kV and 20nA, the beam spot diameter is 1μm according to the size of uranium mineral particles, the element measurement time is 20s, the test elements mainly include U, Si, Ca, Ti, Al, Fe, etc.

Both SEM and EDS were performed in the Beijing Research Institute of Uranium Geology. The instrument model of SEM was Nova Nano SEM450. The detection method was based on GB/T17361-2013 "Microbeam analysis, identification of authentic clay minerals in sedimentary rocks, sem and eds". The model of X-ray diffraction analysis instrument is Panalytical X 'pert PRO X-ray diffractometer, with a working voltage of 40 kV and a current of 40 mA. The X-ray target is a Cu target, and the measuring Angle ranges from 5° to 70°.

4. Result

4.1. Petrological characteristics of uranium bearing sandstone

The uranium bearing strata in the study area are the lower part of Yaojia Formation of upper cretaceous. The lithology is mainly light grey, off-white medium to fine grained sandstone, and the local ones are variegated sandstone, grey siltstone, grey coarse sandstone, etc., which usually contain carbonaceous clastic and pyrite, with multiple layers of red and grey mudstone lenses, and the vertical rock particle size changes frequently, which is the sedimentary product of braids.

The sandstone types are mainly feldspathic litharenite and litharenite, rarely coarse sandstone. Most of the ore-bearing sandstone is dense in cementation degree, and the clastic particles are mainly in point contact and line contact. The clastic particles are of moderate sorting, and the grinding is mostly of sub-angular - angular shape, with medium roundness deviation. On the whole, the sandstone in the lower part of Yaojia Formation belongs to the low maturity litharenite and feldspar sandstone according to the classification of mineral composition and chemical composition, which conforms to the general characteristics of braided channel subfacies deposition and is very beneficial to uranium mineralization.

4.2. Main composition of uranium minerals

The results of electron probe experiments are shown as follows (Table 1), the main uranium minerals in the Qiandaidian uranium mine area are pitchblende and coffinite. The element composition of pitchblende and coffinite has regular differences. The content of U element in pitchblende is high, while the content of Si and P element is low. Its UO₂ is 67.75-89.19% (average 77.07%), SiO₂ is 0.37-7.52% (average 3.61%), and P₂O₅ is 2.13-8.46% (average 4.86%). The content of U in coffinite is relatively low, while that of Si and P is relatively high. The contents of UO₂, SiO₂ and P₂O₅ are respectively 66.38-72.40% (average 70.13%), 9.12-10.35% (average 9.49%) and 6.54-7.52% (average 7.02%). In addition, a small number of titanium-uranium minerals were found (Fig. 3f).the titanium-bearing minerals are
distributed among the quartz particles in the form of debris particles, and the distribution of uranium and titanium elements is not uniform.

4.3. The existing forms of uranium minerals

4.3.1. Individual uranium minerals. Uranium minerals were enriched in lithic particles in irregular granular form, and the fracture and fracture surfaces of elastic particles such as feldspar and quartz were used as the occurrence space. The particle size is generally about 5μm, or even smaller.

4.3.2. Symbiotic with pyrite. Uranium minerals are closely associated with pyrite, it mostly distributed in sandstone elastic particle pores, fractures, or elastic internal dissolution cavities. It can be divided into four conditions. ① Uranium minerals are distributed in colloidal pyrite particles (Fig. 2a). ② Distribution of uranium minerals in the margins of massive pyrite or in gaps between particles (Fig. 2b). ③ The uranium mineral is filled in the cracks formed by the dissolution of the quartz edge and grows around the edge of the veined pyrite (Fig. 2c). ④ The symbiosis of uranium minerals with strawberry pyrite (Fig. 2d).

![Figure 2. BSE image of uranium minerals in Qianjiadian mining area.](image)

Cal- calcite; Kln-Kaolinite; Kfs- K-feldspar; Qtz- Quartz; Br- Titanium-uranium mineral; Urn- Uranium mineral

4.3.3. Adsorbed by clay minerals, organic matters. It is found for the first time that uranium minerals are closely related to clay minerals in microcosmic. The uranium minerals adhere to the surface of kaolinite, and maintain the mineral form of kaolinite locally, indicating that uranium minerals and kaolinite formed at the same time or later than kaolinite (Fig. 2e). At the same time, it can also be observed that uranium minerals coexist with vermicular kaolinite aggregates. It was found that the main clay minerals enriched in ore bearing section of uranium industrial pore are kaolinite, which has a significant positive correlation with uranium content. In addition, organic matter such as plant carbon chips and carbon fragment fossils are common materials in ore bearing strata of the study area, which provide physical barrier and geochemical reducing material basis for uranium mineralization.
adsorption or fluid remains to be further studied. Whether the specific cause of the close symbiosis between uranium minerals and kaolinite in space is greater than that of kaolinite, which is in contradiction with the observed phenomenon. Therefore, the positively charged uranyl ions in the epigenic zone are easy to be adsorbed by clay minerals, organic matter and other highly absorbent particles due to their weak hydrolysis ability and poor migration ability. The study area is mainly composed of kaolinite adsorbed uranium minerals (Fig. 2e). No other clay minerals are directly related to uranium minerals. In clay minerals, the adsorption capacity of montmorillonite and illite is greater than that of kaolinite, which is in contradiction with the observed phenomenon. Therefore, whether the specific cause of the close symbiosis between uranium minerals and kaolinite in space is adsorption or fluid remains to be further studied.

| Number | MgO | Al₂O₃ | SiO₂ | P₂O₅ | PbO₂ | ThO₂ | UO₂ | K₂O | CaO | FeO | SO₄ | Na₂O | TiO₂ | MnO | Total | Type               |
|--------|-----|-------|------|------|------|------|-----|-----|-----|-----|-----|-----|-----|-----|-------|-------------------|
| Q4.37-01 0.12 0.04 0.78 2.13 0.00 0.05 78.12 0.17 3.94 0.79 / | 1.52 1.25 0.12 90.54 | Pitchblende |
| Q4.37-02 0.14 0.06 5.63 7.30 0.00 0.00 67.75 0.13 4.35 0.70 / | 0.02 3.44 0.06 89.58 | Pitchblende |
| Q4.37-03 0.09 0.05 6.68 7.53 0.03 0.01 70.07 0.15 3.67 1.68 / | 0.00 0.53 0.02 90.50 | Pitchblende |
| Q4.37-04 0.09 0.00 0.49 1.98 0.00 0.00 81.72 0.20 3.89 0.57 / | 0.90 0.71 0.13 90.69 | Pitchblende |
| Q4.37-06 0.03 0.22 8.12 8.29 0.00 0.02 66.89 0.18 2.69 2.12 / | 0.04 0.15 0.00 88.75 Silicon-rich pitchblende |
| Q4.37-08 0.16 0.23 2.37 2.61 0.00 0.00 76.52 0.29 3.56 0.61 / | 0.61 1.75 0.11 88.82 | Pitchblende |
| Q4.37-09 0.09 0.17 1.49 2.47 0.00 0.00 82.04 0.20 3.27 0.67 / | 0.77 0.44 0.02 91.62 | Pitchblende |
| Q4.41-01 0.19 0.04 1.80 3.07 0.01 0.03 79.77 0.14 2.79 0.55 / | 0.09 2.88 0.03 91.39 | Pitchblende |
| Q4.41-02 0.21 0.10 7.52 7.89 0.00 0.14 67.85 0.17 4.99 0.82 / | 0.06 0.29 0.00 90.04 | Pitchblende |
| Q4.41-03 0.02 0.13 7.42 8.43 0.00 0.06 67.94 0.12 2.01 1.64 / | 0.00 0.69 0.00 88.47 | Pitchblende |
| Q4.41-04 0.04 0.05 5.89 6.53 0.00 0.08 76.89 0.17 2.69 1.46 / | 0.00 0.33 0.00 94.13 | Pitchblende |
| Q4.41-05 0.06 0.13 6.42 8.46 0.00 0.22 70.25 0.19 1.06 0.64 / | 0.02 0.85 0.00 88.29 | Pitchblende |
| Q4.41-09 0.09 0.19 10.35 7.52 0.00 0.21 66.38 0.11 1.96 0.85 / | 0.00 0.35 0.00 88.02 | Cathline |
| Q3.27-01 0.00 0.05 0.37 2.37 0.06 0.01 88.99 0.20 0.45 0.84 1.36 / / / | 93.32 | Pitchblende |
| Q3.27-02 0.00 0.02 0.46 2.34 1.98 0.00 87.90 0.17 0.52 0.70 1.41 / / / | 94.08 | Pitchblende |
| Q3.93-03 0.08 0.26 5.97 6.78 0.00 0.06 71.13 0.15 1.35 1.62 2.70 / / / | 87.40 | Pitchblende |
| Q3.93-04 0.00 0.00 0.90 3.00 0.00 0.01 89.19 0.18 0.46 1.04 2.10 / / / | 94.78 | Pitchblende |
| Q4.05-01 0.13 0.16 1.91 7.26 0.00 0.05 69.85 0.23 4.08 0.97 0.99 / / / | 91.93 | Cathline |
| Q4.05-02 0.10 0.11 9.12 6.74 0.00 0.01 72.40 0.22 3.64 1.78 0.64 / / / | 94.12 | Cathline |
| Q4.05-03 0.09 0.10 9.28 6.54 0.08 0.00 71.90 0.21 3.43 2.30 1.44 / / / | 93.93 | Cathline |
| Q4.09-01 0.09 0.16 8.41 6.32 0.07 0.00 73.94 / 1.22 1.50 0.20 / / / | 91.69 | Silicon-rich pitchblende |
| Q4.09-02 0.00 0.17 7.83 7.08 0.06 0.08 74.16 / 0.86 1.41 1.43 / / / | 91.65 | Silicon-rich pitchblende |

**Means below the detection limit.**

5. Discussion
Sandstone type uranium deposits are usually formed in open systems with shallow burial. After a long period of mineralization or transformation, uranium minerals with different morphological characteristics and chemical composition are formed. The study of the characteristics of uranium minerals and their symbiotic relationship with other minerals is the direct evidence to explore the mechanism of uranium mineralization. The uranium minerals in the Qianjiadian uranium deposit mainly include several types, such as independent uranium minerals, uranium minerals symbiotic with pyrite and carbonate, and uranium minerals adsorbed by clay minerals. The most common type is the symbiotic association of uranium minerals with minerals such as pyrite and carbonate. By analyzing the interpenetration relationship between minerals, it can be divided into two categories: one is that the uranium minerals develop around the edge of pyrite, forming a ring edge, like the ring edge, filling in the gap between pyrite and other particles in a colloidal form. In this interpenetration relationship, iron dolomite often develops around the periphery of pyrite. The other is that the uranium minerals are veined in the pyrite and have no carbonate to associate with them. This indicates that at least two periods of different properties of uranium bearing fluids are involved in mineralization. Previous studies have also shown that pre-existing pyrite can react with water to form H₂S and reduce U⁵⁺ in an anaerobic environment, and all uranium minerals will be enriched on the surface of pyrite [9].

At the same time, adsorption of clay minerals and plant carbon chips also plays an important role in uranium mineralization. Uranium is often found in rocks and minerals in the epigenetic zone in the form of adsorption, which is an important feature of uranium geochemistry. The positively charged uranyl ions in the epigenic zone are easy to be adsorbed by clay minerals, organic matter and other highly absorbent particles due to their weak hydrolysis ability and poor migration ability. The study area is mainly composed of kaolinite adsorbed uranium minerals (Fig. 2e). No other clay minerals are directly related to uranium minerals. In clay minerals, the adsorption capacity of montmorillonite and illite is greater than that of kaolinite, which is in contradiction with the observed phenomenon. Therefore, whether the specific cause of the close symbiosis between uranium minerals and kaolinite in space is adsorption or fluid remains to be further studied.
Abundant phosphorus in uranium minerals is a favorable evidence of bioreuranium mineralization [4,10]. Electron probe data indicate that phosphorus is enriched in uranium minerals (Table 1). Generally, the accumulation of phosphorus in sedimentary strata is considered to be the product of microorganisms. When bacteria degrade organic matter, they will break the bonds in organophosphates and release the phosphorus. At the same time, in the process of bacterial sulfate reduction, bacterial activities can produce organic acids and other substances, reduce the pH value of the environment, and lead to the dissolution of phosphate-rich minerals such as apatite. Therefore, it is speculated that these phosphorus-rich granular uranite aggregates are probably mineralized microorganisms, which are the products of UO\textsubscript{2} metasomatization of microorganisms during metabolism or after death [11]. Combined with the main fluid temperature in the mine area, this may indicate that microorganisms under low temperature fluid are involved in uranium mineralization.

All in all, the uranium minerals and their symbiotic mineral assemblages in the Qiandaidian uranium mine have the conditions of low temperature genesis. It is undeniable that a small number of titanium-bearing minerals representing hydrothermal origin exist in the study area. However, such minerals only develop locally and are not the product of major metallogenic events.

6. Conclusion

(1) The occurrence forms of uranium in Qiandaidian uranium mining area include uranium minerals, adsorption uranium. The uranium in low-grade ore is mainly in the form of dispersive adsorption, which is clay mineral and organic matter adsorption. The high-grade ore mainly exists in the form of uranium mineral, the type of uranium mineral is mainly pitchblende, followed by coffinite, a small amount of uranium mineral containing titanium.

(2) Uranium minerals are often closely symbiotic with pyrite, carbonate and so on, most of them develop in the pyrite, carbonate margin and fractures in the form of colloidal, there are also granular, pellet independent distribution.

(3) Uranium minerals are rich in Phosphorus, and there is an obvious positive correlation between Phosphorus and Silicon. It has been found that some samples contain phosphorus-rich uranium aggregates in microspheres, which is considered as a strong evidence that microorganisms are involved in uranium mineralization at low temperature.

Acknowledgments
This work was financially supported by the National Key Research and Development Plan of China [grant No.2018YFC0604200], the National Important Basic Research Program of China [grant No.2015CB453000] and the Geological Survey Project of China [grant No.DD20190472].

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