Mineralogy, Fluid Inclusion and H-O-C-S Stable Isotopes of Mengqiguer Uranium Deposit in the Southern Yili Basin, Xinjiang: Implication for Ore Formation

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Abstract: The Mengqiguer deposit in southern Yili basin is a large interlayer-oxidation-zone type uranium deposit. In this paper, we applied multiple methods including microscopic observation, scanning electron microscope and electronic probe, to analyze the systematical alteration characteristics of the ore-bearing sandstone layer. Fluid inclusion and stable isotope studies on the ore-bearing sandstone have also been carried out to discuss the internal relations between fluid activities, epigenetic alteration and the uranium mineralization. Major epigenetic alteration include clay alteration, carbonatization and pyritization, of which biogenetic pyritization is most closely related to the uranium mineralization. This suggests the existence of microorganism during the uranium mineralization process. The mineralization fluids of low temperature, medium density but varied salinities are suggested to be derived from multi-source, including the meteoric water and organic acidic vapor components from coal-bearing strata. Uranium mineralization, grain-dispersed kaolinite, limonite, colloidal pyrite, and the carbonate cements associated with sulfate-reducing bacteria were formed by meteoric water and vermicular-shaped kaolinite, autologous pyrite, and the carbonate cementation associated with the dehydroxylation of organic matter was formed by organic acidic. Based on these results, we consider that the uranium mineralization and epigenetic alteration both resulted from the reciprocity of organic–inorganic fluid and fluid–rock during the formation of the interlayer oxidation zone.

Key words: The Mengqiguer sandstone type uranium deposit; Metallogenic fluid; Epigenetic alteration; Uranium metallicogen

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1. Introduction

The interlayer-sandstone-type uranium deposit refers to the uranium transported by groundwater as an ore-forming fluid and then deposited in the redox zone, which can be regarded as mineralization (Huang, 1994). Recently, many researchers have determined that this type of uranium mineralization is also likely related to basinal organic matter and the hydrocarbons it produced (P. Landais, 1996; Charles, 1996; Yang et al., 2004; Cai, 2008; Zhang et al., 2013). A series of related genetic models has also been produced (Quan et al., 2007; Li, 2009; Yang et al., 2009). Admittedly, basinal fluid activities play an essential role in the formation of sandstone-type uranium deposits, and they also resulted in special alterations under some certain conditions, i.e., bleached alteration (Wu et al., 2014), the green-colored alteration (Li et al., 2007) in the northeastern Ordos Basin, and the faded alteration in the Yili Basin (Li et al., 2004). Correspondingly, the stable isotope and fluid inclusion research of alteration minerals has provided important clues to our understanding of the source of related fluids, their influence on diagenesis (Hua, 1994; Lu et al., 2004), and their interaction processes (Wu, 2005; Yang et al., 2009; Xue et al., 2010; Wu et al., 2014).

The Yili Basin, which was formed in the Meso-Cenozoic, is generally considered to be the most important U-producing basin in northwestern China. The Mengqiguer deposit, one of the largest sandstone-type uranium deposits in China, is located roughly in the eastern part of the southern Yili uranium belt, and has been studied for decades. However, these studies have concentrated on the properties and sources of ore-forming fluids and their alteration characteristics (Li et al., 2004; Li, 2006; Wang et al., 2008; Zeng et al., 2013; Xiu et al., 2015; Liu et al., 2015; Ding et al., 2016; Ding et al., 2017; Ding et al., 2018). Few studies have addressed the genesis of related alterations, the interaction

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processes between basinal fluids and ore-bearing sandstones, and their relationship with uranium mineralization. In this paper, we mainly concentrate on the characteristics of the fluid inclusions in ore-bearing sandstone and their related alteration characteristics and stable isotopes to reveal the source of the fluids, genesis of the alteration types, the genetic relationship between fluid activities, and the epigenetic alteration and uranium mineralization in the rolling development of the interlayer oxidation zone.

2. Geological setting

Yili basin is formed based on the evolving of Carboniferous-Permian rift valley into a Meso-Cenozoic intermountain graben basin, which is sandwiched in the Tien Shan Orogen and is widen into Kazakhstan. Actually, the Yili basin is the major part of the Yili-Central Tien Shan microblock (Zhang et al., 1999), as shown in Fig. 1. In the southern slope belt, there are Honghaigou, Kujie’ertai, Wukuerqi, Zhajisitan, and Mengqiguer deposit, respectively, from west to east (Fig.1). These deposits extend about 70km in E-W striking, and are the important component of south balkhash-Yili sandstone type uranium province of Central Asia.

Fig. 1. The tectonic position and Uranium deposit distribution of Yili basin (modified from Zhang et al., 1999).

3. Ore deposit geology

The Mengqiguer deposit is located in the transitional zone between eastern tectonic activity belt and western stable belt of southern slope belt of Yili basin, mainly controlled by the NEE-striking basin-controlling fault in the south and Thajistan fault in the north. As shown in Fig.2, this deposit is generally bounded by NEE-striking F1 and F3, and structurally homed in the eastern part of Thajistan syncline. The ore-bearing strata are Middle-Lower Jurassic Shuixigou group which in lithology are mainly coal-containing clastic rocks. Upwardly, there are twelve coal seams named from M1 to M12, respectively, according to which the Shuixigou group was classified into Badaowan formation (J1b), Sangonghe formation (J1s), and Xishanyao formation (J2x). In Mengqiguer deposit, the ore-bearing strata is dominantly Sangonghe formation (J1s) and Xishanyao formation (J2x) (Fig. 3) between the coal seams of M5 and M12 spatially. The U orebodies are mainly contained in redox zone, and in roll, tabular and lense shape on profile, among of which the roll shape orebodies are the most developed. In orebodies, the U is mainly existed as the adsorption state, isomorphism, and uranium mineral which mainly occurred as pitchblende and then coffinite, with paragenesis of coals, pyrite, calcite and clay minerals (Liu et al., 2015).

Fig. 2. Generalized geological map of Mengqiguer area (modified from Ding et al., 2016).
4. Sampling and analyzing

Samples of ores, altered and unaltered sandstone were collected mainly from drillcore in the Mengqiguer deposit. All samples were polished into thin sections and were examined using transmitted and reflected light to determine the alteration characteristics and mineral paragenesis. After petrographic analyses, these thin sections were analysed using the polarizing microscope, scanning electron microscope, and electronic probe analysis. In addition, a few samples were washed with distilled water, dried under ambient conditions, and crushed for mineral separation. The pyrite was handpicked under a binocular stereomicroscope to obtain 1 g fractions for isotope analyses. Few crushed samples were mixed with 500 ml distilled water in a beaker, stirred for 3 min, and stood for 6 min, then the upper suspend fluid were exported into another beaker for later drying to get the clay minerals. In addition, the altered and unaltered sandstone were crushed to powder for carbon and oxygen isotope analyses.

More than twenty doubly polished thin sections were prepared from the ore and alteration samples. The microthermometric measurements and laser Raman experiments of fluid inclusions on the doubly polished thin sections were performed using a LABHR–VIS LabRAM HR800 and a Linkam TH600 heating-cooling stage, respectively, using standard techniques (Shepherd et al., 1985) and standard artickraft fluid inclusion samples of FLUIDINC company for calibration at the Geological Analysis and Testing Center, Beijing Research Institute of Uranium Geology, China.

Sulfur isotopic compositions of pyrite were measured using the method of Robinson and Kusakabe (1975) and a Finnigan MAT 253 mass spectrometer. The results are reported in δ notation in units of per mil (‰) relative to CDT. Replicate δ34S_VCDT values were reproducible to ±0.2‰, as demonstrated by analysis of Chinese national standards GB04414 (δ34S_VCDT = −0.07 ± 0.13‰) and GB04415 (δ34S_VCDT = 22.15 ± 0.14‰).

After the C clastic and organic matters eliminated, some sandstone samples were conducted using the carbon and oxygen analyses. Oxygen and carbon isotopic compositions were measured using the methods of McCrea (1950) and Clayton and Mayeda (1963), respectively. The results are reported in δ notation in units of per mil (‰) relative to V_PDB. Replicate δ13C_V_PDB and δ18O_V_PDB values were reproducible to ±0.1‰ and ±0.2‰, respectively, as demonstrated by analysis of Chinese national rock standards GB04416 (δ13C_V_PDB = 1.61 ± 0.03‰; δ18O_V_PDB = −11.59 ± 0.11‰) and GB04417 (δ13C_V_PDB = −6.06 ± 0.06‰; δ18O_V_PDB = −24.12 ± 0.19‰). All the O and C isotope analyses were performed using a Finnigan MAT 253 mass spectrometer.

From the results of XRD analysis, samples with a high kaolinite content were selected for further tests. After cleaning, the selected bulk samples were crushed and passed through a 60-mesh sieve into a beaker filled with 500 ml distilled water, stirred for 3 min, and kept for 10 min. The suspension in the beaker was then moved to another beaker and dried to obtain the separation product (the main component was kaolinite). Based on XRD data, products with a kaolinite content of more than 50% were selected for H-O isotopic analysis. Oxygen isotopic compositions measured using the BrF5...
method of Clayton and Mayeda (1963). The results are reported relative to VSMOW, and the analytical precision and accuracy are both ±0.2‰, as demonstrated by the analysis of Chinese national quartz standards GBW-04416 (δ18O = 11.11 ± 0.06‰) and GBW-04417 (δ18O = -1.75 ± 0.08‰). Hydrogen isotopic compositions of clay-hosted waters were determined using the method of Kyser and O’Neil (1984). The results are reported in δ notation in units of per mil (‰) relative to VSMOW. Replicate δD analyses were reproducible to ±1‰, and we used the Peking University (δD = –64.8‰) and Lanzhou (δD = –84.55‰) standards. These O and H isotope analyses were performed using a Finnigan MAT 251 mass spectrometer. These analyses were performed at the Geological Analysis and Testing Center, Beijing Research Institute of Uranium Geology, Beijing, China.

5. Results

5.1 Alteration Characteristics

Using the polarizing microscope, scanning electron microscope, and electronic probe, we determined the types of epigenetic alteration in the ore-bearing Mengqiguer uranium deposit to be mainly clayization, carbonatization, silicification, and pyritization. The clayization is mainly kaolinite, then petrochemical, montmorillon, and greenwood. The silicification mainly includes quartz overgrowth and self-generated microcrystalline quartz, and the metallic mineralization is mainly lignite and pyrite etc. Furthermore, the kaolinization, carbonation, and pyritization were related to uranium mineralization.

5.1.1 Kaolinization

In the Mengqiguer deposit, the kaolinization is extensively developed, especially in the weak oxidation and redox zones (Liu et al., 2017). Our microscopic and scanning electron microscope observations indicate that the kaolinite is commonly primary kaolinite occurring in fine-grained, page, slice, laminated, and vermicular shapes, with fewer occurring in dispersed granular or irregular shape in granular pores or feldspar-leached holes (Fig. 4). The paragenetic minerals of kaolinite are mainly self-generated microcrystalline quartz (Fig. 4e, j), gypsum (Fig. 4a, c, j, i), pyrite (Fig. 4d, f), and uranium (Fig. 4i), and then dolomite (Fig. 4b), hematite (Fig. 4b), and illite–montmorillonite (Fig. 4e). Occasionally, we observed slice-shaped kaolinite in association with primary U minerals (Fig. 4i). The grains of fine-grained kaolinite are commonly 1–2 μm in size (Fig. 4a). The page-shaped and slice-shaped grains are generally 2–5 μm in size, coat the quartz grain within, and have irregular margins and corrosion (Fig. 4b, d, f, g, h, i). The vermicular-shaped grains commonly occur in pseudo six-crystalline form and range from 10–20 μm in size (Fig. 4c, e).

Fig. 4. The microscopic morphology and its common minerals about kaolinite in ore-bearing sandstone of Mengqiguer uranium deposit.
(a) Gray-white sand conglomerate, fine grain and kaolinite and gypsum aggregate in the leached hole of K-feldspar. (b) Yellow sand conglomerate, intergranular lamellar kaolinite and acicular hematitei on the particle. (c) Gray fine-grain sandstone, intergranular lamellar, vermicular kaolinite. (d) Gray griststone, vermicular kaolinite and framboidal pyrites in the leached hole of feldspar. (e) Gray-white medium sandstone, intergranular lamellar kaolinite, honeycomb illite-montmorillonite and self-generated microcrystalline quartz. (f) Gray-white sand conglomerate, intergranular slice kaolinite, octahedron pyrite and columnar gypsum aggregate. (g) Gray-white griststone, intergranular slice kaolinite and rhomboid dolomite. (i) Gray gristone, intergranular slice kaolinite, uranite and gypsum aggregate.

5.1.2 Carbonatization

In the Mengqiguer deposit, carbonation is present due to the occurrence of calcite (Fig. 5a, b, c, g, h, i), dolomite (Fig. 5d), and siderite (Fig. 5e, f), all of which are concentrated in the oxidation and redox zones. These carbonate minerals are commonly understood to have replaced clastic rocks (Fig. 5a) and clay minerals (Fig. 5e), which occur in fine and shining grains (Fig. 5b, c). Our microscopic and scanning electron microscope observations indicate that these carbonate minerals commonly occur as cemented clastic rocks and minerals in association with pyrites (Fig. 4i), and that fewer are associated with U minerals (Fig. 5g, h). The fine-grain calcite is generally 0.01–0.3 μm in size and is always coated with clastic minerals, whereas shining grain calcite is 0.05–0.1 mm in size and occurs in fractures and corrosion pores (Fig. 5b, c).

![Fig. 5. The microscopic morphology and its common minerals about carbonate cement in ore-bearing sandstone of Mengqiguer uranium deposit.](image)

(a) The shine grain calcite metasomatism and filling the feldspar fissure. (b) The shine grain calcite and the fine grain calcite. (c) The shine grain calcite occurred in the outside of the fine grain calcite. (d) Intergranular rhomboid dolomite. (e) Rhomboid siderite and slice kaolinite. (f) Globular siderite occurred on the surface of partial. (g) Calcite occurred in the uraninite. (h) Uraninite occurred on the surface of the shine grain calcite. (i) Globular pyrite occurred in the shine grain calcite.

5.1.3 Pyritization

The pyrites in the Mengqiguer deposit can be classified into three groups according to their crystal type, which are euahedral, framboidal, and anhedral. (1) Euahedral pyrites commonly occur in cube (Fig. 6a, b), pyritohedron (Fig. 6d), octahedron, and tetrahedron (Fig. 6c, d) shapes, and we observed U minerals on their surfaces. The cube pyrites are generally 2–200 μm in size and are dispersed in the pores of clastics rocks, whereas the pyritohedron, octahedron, and tetrahedron pyrites commonly occur in groups and are 0.5 μm in size. (2) Framboidal pyrites generally range from 5–20 μm in size and are composed of fine octahedron pyrite grains. These grains are arranged in irregular patterns similar in size to a framboidal group. We found U minerals to occur on the surfaces of octahedron pyrite grains (Fig. 6e, f). (3) Anhedral pyrites are commonly disseminated in the fractures of sandstones (Fig. 6h), and are all closely associated with U minerals.

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5.2 Stable isotopes

The hydrogen isotopic compositions of water released via kaolinization range from −93.0‰ to −48.3‰. The oxygen isotope compositions range from 11.8‰ to 13.7‰, with an average value of 12.7‰, as shown in Table 1. Using the equations $10^3\text{ln}a = 4.29 \times 10^5 / T^2 - 6.44 \times 10^4 / T + 2.03$ (T is Kelvin) and $10^3\text{ln}a = \delta^{18}O_{\text{kaolinite}}_{\text{V-SMOW}} - \delta^{18}O_{\text{H}_2\text{O}}_{\text{V-SMOW}}$ (Zheng Yongfei et al., 2000), the oxygen isotopic compositions of water-forming kaolinite range from −10.3‰ to −5.1‰.

The carbon isotopic compositions of carbonate minerals range from −10.9‰ to −7.2‰ (V-PDB), and the oxygen isotopic compositions range from −13.2‰ to −5.8‰ (V-PDB), as shown in Table 2. Using the equation $\delta^{18}O_{\text{V-SMOW}} = 1.03086\delta^{18}O_{\text{V-PDB}} + 30.86$ (Turner et al., 1993; Friedman et al., 1987), the carbon isotopic compositions of carbonate minerals range from 17.6‰ to 24.9‰ (V-SMOW).

The $\delta^{18}S_{\text{V-CDT}}$ values for pyrite range from −17.3‰ to 1.2‰. In addition, the $\delta^{34}S_{\text{V-CDT}}$ values for pyrite in the oxidizing sandstone range from −17.3‰ to −1.4‰ and the $\delta^{34}S_{\text{V-CDT}}$ values for pyrite in the reducing sandstone range from −9.2‰ to 1.2‰, as shown in Table 3.

Table 1. The analysis of H-O isotopes about kaolinite and forming kaolinite fluid of Mengqiguer uranium deposit

<table>
<thead>
<tr>
<th>The number of samples</th>
<th>Lithology</th>
<th>Kaolinite content (%)</th>
<th>$D_{-\text{SMOW}}$ (%)</th>
<th>$^{18}O_{\text{SMOW}}$ (%)</th>
<th>$^{18}O_{\text{H}<em>2\text{O}}</em>{\text{SMOW}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P4108-4</td>
<td>Gray-white sandstone conglomerate</td>
<td>87</td>
<td>-59.0</td>
<td>11.8</td>
<td>-10.3 to -7.0</td>
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<tr>
<td>P4108-5</td>
<td>Red gritstone</td>
<td>86</td>
<td>-79.8</td>
<td>12.4</td>
<td>-9.7 to -6.4</td>
</tr>
<tr>
<td>P5147-1</td>
<td>Yellow sandstone conglomerate</td>
<td>83</td>
<td>-64.4</td>
<td>11.8</td>
<td>-10.3 to -7.0</td>
</tr>
<tr>
<td>P5147-3</td>
<td>Gray gritstone</td>
<td>89</td>
<td>-69.6</td>
<td>12.6</td>
<td>-9.5 to -6.2</td>
</tr>
<tr>
<td>P5147-4</td>
<td>Gray-white medium sandstone</td>
<td>83</td>
<td>-58.8</td>
<td>12.8</td>
<td>-9.3 to -6.0</td>
</tr>
<tr>
<td>P5147-5</td>
<td>Red sandstone conglomerate</td>
<td>88</td>
<td>-52.6</td>
<td>12.7</td>
<td>-9.4 to -6.0</td>
</tr>
<tr>
<td>P3504-1</td>
<td>Yellow-white sandstone conglomerate</td>
<td>58</td>
<td>-72.1</td>
<td>13.70</td>
<td>-8.4 to -5.1</td>
</tr>
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</table>
Table 2 The results of C-O isotopes of carbonate cement from ore-bearing of Mengqiguer uranium deposit

<table>
<thead>
<tr>
<th>The number of samples</th>
<th>Lithology</th>
<th>δ¹³C_{V-PDB}(‰)</th>
<th>δ¹⁸O_{V-PDB}(‰)</th>
<th>δ¹⁸O_{V-SMOW}(‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P731-7</td>
<td>Red gritstone</td>
<td>-9.3</td>
<td>-10.9</td>
<td>19.7</td>
</tr>
<tr>
<td>P731-8</td>
<td>Yellow gritstone</td>
<td>-9.1</td>
<td>-10.9</td>
<td>19.7</td>
</tr>
<tr>
<td>P731-11</td>
<td>Red gritstone</td>
<td>-9.7</td>
<td>-10.8</td>
<td>19.8</td>
</tr>
<tr>
<td>P731-13</td>
<td>Maroon gritstone</td>
<td>-9.8</td>
<td>-11.5</td>
<td>19.1</td>
</tr>
<tr>
<td>P1915-11</td>
<td>Maroon gritstone</td>
<td>-7.2</td>
<td>-12.7</td>
<td>17.8</td>
</tr>
<tr>
<td>P1911-7</td>
<td>Yellow gritstone</td>
<td>-7.5</td>
<td>-12.9</td>
<td>17.6</td>
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<tr>
<td>P731-20</td>
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<td>-8.5</td>
<td>22.1</td>
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<tr>
<td>P731-29</td>
<td>Gray-white conglomerate</td>
<td>-10.2</td>
<td>-5.8</td>
<td>24.9</td>
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<td>P731-41</td>
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<td>-8.5</td>
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<td>18.7</td>
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<td>P731-22</td>
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<td>-10.1</td>
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<td>-7.4</td>
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<td>Gray gritstone</td>
<td>-9</td>
<td>-7.5</td>
<td>23.1</td>
</tr>
<tr>
<td>P1915-9</td>
<td>Gray sandstone conglomerate</td>
<td>-9.1</td>
<td>-13.2</td>
<td>17.3</td>
</tr>
<tr>
<td>Average value</td>
<td></td>
<td>-9.2</td>
<td>-10.3</td>
<td>20.3</td>
</tr>
</tbody>
</table>

Table 3 The analysis of S isotopes of sandstone in ore-bearing sandstone of Mengqiguer uranium deposit

<table>
<thead>
<tr>
<th>Sandstone zoning</th>
<th>The number of samples</th>
<th>Lithology</th>
<th>δ³⁴S_{V-CDT}(‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidizing sandstone</td>
<td></td>
<td>Gray-white medium sandstone</td>
<td>-3.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gray-white medium sandstone</td>
<td>-7.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gray-white conglomerate</td>
<td>-17.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gray-white gritstone</td>
<td>-1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yellow conglomerate</td>
<td>-10.3</td>
</tr>
<tr>
<td>Average value</td>
<td></td>
<td></td>
<td>-8.1</td>
</tr>
<tr>
<td>Reducing sandstone</td>
<td></td>
<td>Gray medium sandstone</td>
<td>-6.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gray medium sandstone</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gray gritstone</td>
<td>-9.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gray medium sandstone</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Gray siltstone</td>
<td>-3.5</td>
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<td></td>
<td></td>
<td>Gray siltstone</td>
<td>-2.6</td>
</tr>
<tr>
<td>Average value</td>
<td></td>
<td></td>
<td>-5.0</td>
</tr>
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</table>
5.3 Fluid inclusions

5.3.1 Occurrence and types
Based on preliminary optical microscopy observations, we identified three types of fluid inclusion, gas-hydrocarbon inclusions (Fig. 7a, b), liquid-hydrocarbon inclusions (Fig. 7c, d), and brine inclusions (Fig. 7e, f), which occurred in single clusters or trails in carbonate minerals or in trails that crosscut clastic quartz. All these fluid inclusions featured low vapor/aqueous ratios, of ≤5%.

The sizes of the gas-hydrocarbon inclusions typically vary from <2×5 μm to >20×25 μm even within one cluster, and they can have oval, irregular, or negative crystal shapes. These gas-hydrocarbon inclusions commonly occur in the fractures that crosscut the quartz or calcite grains in trails. Brine inclusions typically measure 4×10 μm, have a bubble fill (vapor H₂O) of less than 5%, and generally have oval, irregular, or negative crystal shapes. The liquid-hydrocarbon inclusions range in size from 3×5 μm to 40×60 μm, and generally have oval, irregular, or negative crystal shapes. The occurrences of these brine and liquid-hydrocarbon inclusions are similar to the gas-hydrocarbon inclusions.

5.3.2 Component
In the Mengqiguer deposit, using a UV laser fluorescence microscope, we observed only a few hydrocarbons as faint blue or yellow-green fluorescences in the intergranular pores of sandstone (Fig. 7g, h, i). Then, based on the laser Raman spectrum, we analyzed the components of the gas-hydrocarbon inclusions, which were mainly CH₄ (Fig. 8). The above research shows that hydrocarbon (CH₄) took part in the ore formation process in the Mengqiguer uranium deposit.

Fig.7. The feature of the fluid inclusions in ore-bearing sandstone of Mengqiguer uranium deposit. (a) The brownness and graygas-hydrocarbon+ brine inclusions incarbonate cement in a line way; (b) The graygas-hydrocarbon inclusions in quartz; (c) The dark-brownness liquid-hydrocarbon inclusions inquartz microcracks; (d) The dark-brownness liquid-hydrocarbon inclusions incarbonate cement in a group way; (e) The colourless and graybrine inclusions inquartz microcracks in a line way; (f) The yellow and graybrine inclusions inquartz microcracks in a line way; (g) The faint blue fluorescence in quartz hole; (h) The faint yellow-green fluorescence in quartz hole; (i) The faint blue fluorescence in quartz hole.

Fig.8. Laser Raman spectra of gas-hydrocarbon inclusions in quartz grain microcracks in ore-bearing sandstone of Mengqiguer uranium deposit.
5.3.3 Microthermometry

The homogenization temperatures of the brine inclusions range from 56°C to 76°C, with an average of 67.9°C. The salinity of brine inclusions can be calculated by freezing point temperature (Tm) conversion with equation ω(NaCl)=0.00+1.78(Tm−4.42×10²Tm²+5.57×10⁻³Tm³ (Hall et al., 1988). The salinities range from 1.23% to 19.84% (NaCl eq), with an average value of 6.0%. According to the above temperature and salinity data, the density was calculated by using the functional relationship between the density of hydrothermal solution and temperature and salinity (Liu et al., 1987). The salinities range from 1.23% to 19.84% (NaCl eq), with an average value of 6.0% (Tab 4).

### Table 4 Results of microthermometric study of fluid inclusions of Mengqiguer uranium deposit

<table>
<thead>
<tr>
<th>Stratum, Lithology</th>
<th>Number</th>
<th>Mineral</th>
<th>Homogenization temperature (°C)</th>
<th>ω(NaCl eq) (%)</th>
<th>Bulk Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper member of Xishanyao</td>
<td>7</td>
<td>quartz</td>
<td>67–71</td>
<td>3.71–5.56</td>
<td>1.0 – 1.02</td>
</tr>
<tr>
<td>formation, coarse grained sandstone</td>
<td>53</td>
<td>quartz</td>
<td>56–76</td>
<td>1.4 – 18.8</td>
<td>0.99 – 1.12</td>
</tr>
<tr>
<td>Lower member of Xishanyao</td>
<td>8</td>
<td>Calcite</td>
<td>70–76</td>
<td>1.23 – 6.59</td>
<td>0.99 – 1.02</td>
</tr>
<tr>
<td>formation, coarse grained sandstone</td>
<td>14</td>
<td>quartz</td>
<td>58–73</td>
<td>2.24 – 14.04</td>
<td>1.00 – 1.08</td>
</tr>
</tbody>
</table>

6. Discussion

### 6.1 Genesis of alteration types

#### 6.1.1 Kaolinite

The primary kaolinite resulted from the interaction between fluid and sandstone, which can be simplified as the interaction of acidic fluid with low K’ and Na’ contents with the plagioclase and K-feldspar minerals in sandstone. Details of these reactions are as follows.

1. 2KAlSiO₄(K-feldspar) + 2H⁺ + H₂O = Al₂Si₂O₅(OH)₄(Kaolinite) + 4SiO₂ + 2K⁺
2. 2NaAlSiO₄(Albite) + 2H⁺ + H₂O = Al₂Si₂O₅(OH)₄(Kaolinite) + 4SiO₂ + 2Na⁺
3. CaAl₂Si₂O₆(Anorthite) + 2H⁺ + H₂O = Al₂Si₂O₅(OH)₄(Kaolinite) + Ca²⁺

The acidic fluid was probably sourced from the meteoric water and hydrocarbon fluid of the source rocks. In addition, the presence of kaolinite may also reflect the genesis, environment, tectonic setting, and evolution of related fluids, i.e., the slice- and vermicular-shaped primary kaolinite in strata commonly formed in the subsidence process of the basin, and the fine-grained and dispersed kaolinite usually formed during the leaching processes between surficial meteoric water and rocks.

In the Mengqiguer deposit, the kaolinite occurs in fine-grained, slice, page, and vermicular shapes, and corrosion could be observed in the plagioclase and K-feldspar grains, both of which demonstrate that the fine-grained slice-shaped kaolinite formed in the leaching processes of meteoric water flow into the ore-bearing sandstone. However, the vermicular-shaped kaolinite resulted from the interaction between acidic hydrocarbon fluid and the sandstone. In addition, the plot of δ¹⁸Oᵥ−SMOW against δ¹⁹Oᵥ−SMOW (Xubutai, 1986) shows that all these values are in the area of the weathered kaolinite line of 17°C and hydrothermal kaolinite line of 100°C (Fig. 9), which also supports the idea that the kaolinite in ore-bearing sandstone is formed in the leaching process of surficial meteoric water by the interaction between acidic hydrocarbon fluid and the sandstone.

![Fig. 9](image-url)

**Fig. 9.** The figure about δDᵥ−SMOW = δ¹⁸Oᵥ−SMOW of kaolinite in ore-bearing sandstone of Mengqiguer uranium deposit (modified from Xu, 1986).

### 6.1.2 Carbonate minerals

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The carbon isotopic composition of cemented carbonate minerals can be used to reveal their genesis, i.e., the $\delta^{13}$C$_{VPDB}$ ratio of biogenic carbonate minerals is $-25\%$, that of carbonate minerals related to CH$_4$ ranges from $-5\%$ to $15\%$ (Klein et al., 1999), that of carbonate minerals from biogenic enzymatic processes is $15\%$, that of carbonate minerals from the thermal decomposition of organic matter is $-20\%$ (Wang et al., 2010; Irwin, 1977), and that of carbonate mineral from dissolved CO$_2$ in water is $-7\%$.

In the Mengqiguer deposit, the $\delta^{15}$N$_{VPDB}$ values range from $-10.9\%$ to $-7.2\%$, with an average value of $-9.2\%$, which indicates that the carbonate minerals probably resulted from a combination of the above processes. In addition, the plot of $\delta^{18}$O$_{VPDB}$ vs. $\delta^{13}$C$_{VPDB}$ shows that most of the carbonate minerals are genetically related to thermal decompositions of organic matter, and fewer are related to the reduction process of sulfate (Fig. 10) (Wang et al., 2000). Considering that U mineralization must be an open system, we prefer to think that CO$_2$ in the atmosphere and oxidized from organic matter would also influence the formation of carbonate minerals.

6.1.3 Pyrites

The S sources of the pyrites in sandstone can be classified into four groups: (1) the biogenic reduction of sulfate (BSR), (2) thermal decomposition of organic sulfur (oil and karogen), (3) hydrothermal reduction process of sulfate (TSR), and (4) inorganic sulfur from the mantle. The $\delta^{34}$S$_{CDT}$ values of pyrites range from $-7.3\%$ to $1.2\%$, with an average value of $-6.4\%$. These values indicate that the sulfur of pyrites in sedimentary rocks is reduced from sulfate in coal seams, gasline, and sedimentary sulfate minerals (Cao et al., 2000; Mao et al., 2002; Fig. 11). In addition, Min et al. (2003) discovered that U minerals are spatially associated with microorganisms, which means that these pyrites are probably genetically related with microbes. The $\delta^{34}$S$_{CDT}$ values of pyrites in the oxidation zone range from $-17.3\%$ to $-1.4\%$ (average value of $-8.1\%$), which are lower than those of primary sandstone that range from $-9.2\%$ to $1.2\%$ (average value of $-5.0\%$). This indicates that the biogenic pyrites generally have higher $\delta^{34}$S$_{CDT}$ values than primary pyrites. The biogenic reduction process is actually an important fractionation process (Faure, 1986; Lloyd, 1968; Mizutani et al., 1973; Fritz et al., 1989; Chang et al., 2007; Canfield et al., 1996; Habicht et al., 1997). In the Mengqiguer deposit, sulfur occurs mainly from the compaction of the Shuixigou group, which released a significant amount of U-bearing oxidizing groundwater into ore-bearing sandstone. When this released groundwater flowed into the redox zone, the S$^8$ sulfate was reduced into S$^2-$ via a biogenic process, during which the sulfur suffered great fractionation, which resulted in the enrichment of $^{34}$S in pyrites (Wu, 2005; Chen et al., 2007). During this reduction, the U$^{4+}$ was also reduced to U$^{6+}$, which resulted in the spatial association of pyrites and U minerals (Chen et al., 2007).

6.2 Sources and properties of fluids

The homogenization temperatures of the brine inclusions range from 56°C to 76°C (average 67.9°C), and are concentrated in the range of 65–75°C, which indicates that the U-mineralization temperature is generally low. In fact, this deposit is typically a low-temperature hydrothermal U deposit (Fig. 12a). The salinities of the ore-forming fluid range from 1.23% to 19.84% (NaCl-eq) (average 6.0%) and are concentrated in two bands of 2%–6% and 12%–18%. However, the 2%–6% band is pervasive and probably represents the fluid characteristics of the main ore-forming fluid (Fig. 12c). The bulk densities of ore-forming fluids range from 0.99 g/cm$^3$ to 1.12 g/cm$^3$ (average value is 1.02 g/cm$^3$) (Fig. 12b). These microthermometric results are generally consistent with the results of Wu et al. (2007). Although it is difficult to distinguish the stages of this fluid inclusion, the histogram of their homogenization temperatures and salinities indicates that there are two kinds of fluid: one is meteoric
water corresponding to the low salinities and the other is basinal hydrocarbon fluid corresponding to the high salinities (Fig. 13). In summary, the ore-forming fluid is characterized by low temperature, a wide salinity range, medium density, and multiple superimpositions of ore-forming fluid.

![Fig. 12 The histogram of the homogenization temperature-density-salinity of fluid inclusions](image)

In summary, the ore-forming fluid is characterized by low temperature, a wide salinity range, medium density, and multiple superimpositions of ore-forming fluid.

![Fig. 13 The temperature-salinity correlation diagram of fluid inclusions](image)

Microscopic characteristics and stable isotopic compositions can be used as a basis for deducing the source and properties of ancient fluid (Boles et al., 2004; Cai et al., 2008; Guo et al., 2013). With the consideration of hydrogen and oxygen isotopic fractionation and the water–rock interaction, a plot of the H and O isotopic compositions of kaolinite shows that the ore-forming fluid is mainly meteoric water (Fig. 14) (Chen et al., 1997; Zheng et al., 2000; Li et al., 2006), likely with a mixture of hydrothermal or metamorphic water (Taylor, 1997). A plot of δ¹⁸Oᵥ-SMOW against δ¹³Cᵥ-PDB shows that most of the values are located in the area of the thermal decomposition of organic matter, which indicates that the oxidation of organic matter may have provided the carbon source for carbonation (Liu et al., 1997; Mao et al., 2003; Fig. 15). Research on mature organic matter indicates that when Ro > 0.35, the decarboxylation of organic matter will occur (with the help of microbes) and result in the release of organic acid, H₂S, and CH₄ (Min et al., 2003). Xiu et al. (2015) found that the Ro value of coal seams in the Mengqiguer deposit ranges from 0.4–0.74%, which means that the organic matter is generally immature, and the coal seam is undergoing decarboxylation, during which a lot of organic acid, CO₂, CH₄, and H₂S are released to facilitate U transport and deposition (Min et al., 2003). Considering the carbon isotopic composition (Wu, 2005), we prefer the idea that CH₄ in U-bearing sandstone is sourced from the coal seam.

![Fig. 14. The figure about δDᵥ-SMOW−δ¹⁸Oᵥ-SMOW of water in metallogenic fluid of Mengqiguer uranium deposit (modified from Taylor, 1997).](image)

![Fig. 15. The figure about δ¹⁸Oᵥ-SMOW−δ¹³Cᵥ-PDB of carbonate cement in ore-bearing sandstone of Mengqiguer uranium deposit. Fields for magmatic, marine carbonates, and sedimentary organic matter are from Ohmoto (1986) and Vezier and Hoefs (1976), respectively.](image)

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6.3 Process of formation of Mengqiguer uranium deposit

The above statements strongly suggest that the ore-forming fluid comprises two kinds of fluid, i.e., inorganic brine and organic hydrocarbon fluid. The inorganic brine is sourced from the surficial meteoric water, whereas the organic hydrocarbon fluid is sourced from the decarboxylation of organic matter. In this section, we try to explain the relationship between fluid activities, alteration, and U mineralization (Fig. 16).

We determined the pH of the groundwater by the pH of the surficial meteoric water, which is related to the climate. Actually, an arid–semi arid climate would result in the meteoric water being alkaline (Zhang et al., 2015). However, since the Late Jurassic, the ancient climate of Yili Basin transformed into desert or arid–semi arid up to the present (Liu et al., 2015), thus the groundwater of this period is generally weak alkaline. When the ore-bearing of the Mengqiguer uranium deposit was lifted to the surface, the oxidizing groundwater from the source area containing U4+ flowed continuously into the primary sandstone and the interlayer-oxidation-zone development process began.

In this process, O₂ would oxidize the Fe²⁺-bearing minerals (pyrite, siderite) and convert them into limonite or hematite. Meanwhile, the biotite was probably converted to a brown color, releasing K⁺ and Mg²⁺, both of which could be used to form montmorillonite. The oxidation of the organic matter would result in the occurrence of CO₂ and CO₃²⁻, both of which would activate the metals, thus causing the U to be transported as [UO₂(CO₃)₃]⁴⁺. CO₂ and CO₃²⁻ could also have combined with Ca²⁺ to form calcite. In addition, the clay minerals in sandstone would be transformed into montmorillonite by their interaction with the meteoric water, and the kaolinite and montmorillonite could be transformed into illite or a mixture of illite and montmorillonite in the K⁺-enriched environment.

\[
\begin{align*}
C \text{ (organic matter)} + O₂ + H₂O + CO₂ & \rightarrow Fe^{2+} (Pyrite, siderite) + O₂ + H₂O \rightarrow FeO(OH) + H₂O (Goethite, limonite) → Fe₂O₃ (hematite) \\
K₂Fe₃O₆ + SiAlO₅(OH)₂ (biotite) + O₂ → Fe^{2+} + K⁺ + Mg^{2+} + OH⁻ & \rightarrow U^{4+} + CO₂ + H₂O → [UO₂(CO₃)₃]^{2+} (Uranyl) \\
CO₂ + H₂O + Ca²⁺ → CaCO₃ (Calcite with organic matter oxidation) & \rightarrow \text{Clay minerals} + H₂O → Smectite
\end{align*}
\]

Upon the exhaustion of O₂, the groundwater became more and more acidic, and the environment more and more reducing. This acidic groundwater caused the clastic rocks and plagioclase to become unstable (Huang et al., 2009; Zhang et al., 2015), which resulted in the formation of fine-grained, dispersed kaolinite and the release of K⁺, Ca²⁺, Mg²⁺, Fe²⁺, and SiO₂. This reaction would raise the pH, which favors the deposition of U minerals and the enlargement of quartz grains. When U-bearing groundwater encountered the organic reducing matter, the U⁶⁺ would have reduced into U⁴⁺ to form stable U minerals in the redox zone. In addition, the infiltration of groundwater into the sandstone would bring in many microbes (sulfate reducing bacteria), which would then have reduced the SO₄²⁻ to H₂S to form framboidal pyrites. These pyrites made the sandstone in the redox zone more reducing, which could result in the future enrichment of U to form orebodies and the spatial association of pyrite and U minerals (Chen et al., 2007).

\[
\begin{align*}
Ca₂Al₄Si₄O₁₀ (Anorthosite) + 2H⁺ + H₂O & → Al₂SiO₅(OH)₄ (Kao aluminate) + Ca²⁺ + 2Na⁺ & \rightarrow \text{Clay minerals} + H₂O → Smectite \\
2Na₂Al₄Si₄O₁₀ (Albite) + 2H⁺ + H₂O & → Al₂SiO₅(OH)₄ (Kao aluminate) + 2SiO₂ + 2Na⁺ & \rightarrow \text{Clay minerals} + H₂O → Smectite \\
2K₂Al₄Si₄O₁₀ (K-feldspar) + 2H⁺ + H₂O & → Al₂SiO₅(OH)₄ (Kao aluminate) + 2SiO₂ + 2K⁺ & \rightarrow \text{Clay minerals} + H₂O → Smectite
\end{align*}
\]

When the released K⁺, Ca²⁺, Mg²⁺, Fe²⁺, and CO₂ from the redox zone were transported into the reduction zone by the groundwater, the environment became weakly alkaline, which is favorable for the deposition of framboidal pyrites and carbonate minerals and the transformation of biotite into chlorite.

\[
\begin{align*}
3Al₂SiO₅(OH)₄ (Kao aluminate) + 2K⁺ → 2KAl₂Si₃O₈(OH)₄ (Illite) + 2H⁺ + 3H₂O & \rightarrow \text{Clay minerals} + H₂O → Smectite \\
3Al₂SiO₅(OH)₄ (Kao aluminate) + 4Mg²⁺ + 4Fe²⁺ + 9H₂O & → Fe₂Mg₂Al₂Si₃O₁₀ (OH)₄ (Chlorite) + 14H⁺ & \rightarrow \text{Clay minerals} + H₂O → Smectite
\end{align*}
\]

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In addition, research on mature organic matter shows that when Ro > 0.35, decarboxylation will occur in organic matter (with the help of microbes) and result in the release of organic acid, H2S, and CH4 during the formation of the Mengqigu uranium deposit (Min et al., 2003; Liu et al., 2009). The interaction between organic acid and ore-bearing sandstone would result in the formation of vermicular-shaped kaolinite, and CH4 would react with SO42− with the assistance of sulfate-reducing microbes (Chen et al., 2007), thus forming biogenic pyrites and CO2, which could be used to form carbonate minerals.

C (Organic matter) + CO2 + H2O + H2S + Organic acid → 2CH4 + 2H2O (24)
CalSiO3(OH)2 (Albite) + Organic acid + H2O → Al2SiO5(OH)4 (Kaolinite) + SiO2 + Na+ + Ca2+ (25)
NaAlSi2O5 (K-feldspar) + Organic acid + H2O → Al2SiO5(OH)4 (Kaolinite) + SiO2 + K+ (26)
CO2 + H2O + Ca2+(organically decarboxylated) → CaCO3 (Calcite with organic manure decarboxylation) (28)
SO42− + 2CH4 → (Reducing microbes) H2S + 2HCO3− (29)
H2S + Fe2+ → FeS (Marcasite) + 2H+ (30)
4FeS(Marcasite) + 4H+ + O2 → 2FeS2 (Framboidal pyrite) + 2H2O + 2Fe2+ (31)

7. Conclusions

(1) The alterations related to U mineralization mainly include clayization, carbonatization, and pyritization. Clay minerals are typically primary kaolinite in fine-grained, page, slice, and vermicular shapes, which resulted from the bleaching of surficial meteoric water and interaction between organic acid and ore-bearing sandstone. Carbonate cements are mainly fine-grained or euhedral calcite, with fewer occurrences of siderite and dolomite, all of which resulted from the reduction of sulfate and the decarbonation of organic matter. The pyrites in the Mengqigu deposit can be classified into three groups based on their crystal types, which are euhedral, frambooidal, and anhedral. All these pyrites are biogenic and closely associated with U minerals.

(2) Ore-forming fluid is mainly composed of brine and hydrocarbons. The brine is predominantly sourced from meteoric water, however, the hydrocarbons are CH4 mainly from the decarbonation of organic matter contained in the ore-bearing strata. This ore-forming fluid is generally characterized by being low in temperature and having a wide salinity range, medium density, and multiple superimpositions.

(3) Uranium mineralization and related alterations resulted from the interaction of interlayer brine–hydrocarbon fluid and ore-bearing sandstone. Uranium mineralization, grained and dispersed kaolinite and limonite, carbonate cements associated with sulfate-reducing bacteria, and colloidal pyrite alterations were formed by meteoric water and vermicular-shaped kaolinite and autologous pyrite, and the carbonate cementation associated with the dehydroxylation of organic matter was formed by hydrocarbons.
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