The Xiaojiashan Tungsten deposit in the Barkol district, Xinjiang, China: geological features and ore-forming fluid composition

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Abstract. The Xiaojiashan Tungsten deposit is located in Barkol district, Xinjiang. The ore bodies occur in the Hercynian granite intrusions and contact between the intrusion and wallrock which consists of the second lithologic section of the first Sub-Formation in Middle Devonian Dananhu Formation (D²d₁). Quadrupole mass spectrometry reveals that fluid inclusions contain major vapor phase contents of CO₂, H₂O. Meanwhile, fluid inclusions contain major liquid phase contents of Cl⁻, Na⁺. It can be speculated that ore-forming fluid of the Xiaojiashan wolframite deposit is characterized by a CO₂-rich, low salinity, and H₂O-CO₂-NaCl system. During ore-forming process, the magmatic water had separated from magmatic intrusions and ore-bearing complex was taken to a portion where tungsten-bearing ores could be mineralized.

Keywords: geological features; wolframite-bearing quartz vein; fluid inclusions; quadrupole mass spectrometer; Xiaojiashan.

1 Introduction

The Xiaojiashan Tungsten deposit, located in the Barkol district of Xinjiang, is newly found by Beijing Sinotech Mineral Exploration Co., Ltd. The ore deposit is a tungsten-quartz vein type deposit. Tectonically, the deposit is located in the central south margin of east Junggar region. The ore bodies occur in a Hercynian granite intrusion and its contact zone with the surrounding rock of the second lithologic section of the first sub-Formation of Middle Devonian Dananhu Formation (D²d₁) (Fig. 1). On the basis of geological features and petrography of the tungsten deposit rocks, this paper studies on the lithgeochemistry in Xiaojiashan tungsten deposit and discusses the hydrogeochemical differences among all various rocks to completely understand the nature and characteristics of magmatic activity, which can provide basic information about the metallogenesis of Xiaojiashan tungsten deposit.
2 Geologic setting

2.1 Regional geology

The Xiaojiashan tungsten deposit of Barkol, Xinjiang is located in the southern margin of the central East Junggar orogenic belt which belongs to the Junggar Plate. Stratigraphically, it belongs to Bogda Mountains Sub-district, North Tianshan Branch, Tianshan-Xing'an District. Strata in the mineralization belt are mainly Devonian and Quaternary. The regional strata mainly include Devonian, Carboniferous and Quaternary in area from the early to late stages, respectively. The Permian and Ordovician strata is distributed sporadically. The Devonian and Carboniferous strata is mainly include the intermediate-basic and intermediate-felsic volcanic rocks are the most widespread; The regional strata is mainly Permian and Ordovician strata, which are mainly clastic sedimentary rocks petrologically; The Quaternary strata is primarily alluvial and diluvial sediments, which are primarily made up of conglomerate, sandstone, siltstone, mudstone and loose windborne sediments[1].

Figure 1. Sketch map of the Xiaojiashan region (After Sinotech Mineral Exploration Co., Ltd., Beijing, China, 2013)

1- Quaternary system; 2- The second lithologic siction of the first sub-Formation of the Dananhu Formation; 3- The first lithologic siction of the first sub-Formation of Middle Devonian Dananhu Formation; 4- Gneissic quartz diorite; 5-Biotite monzonitic granite; 6- K-feldspar granite; 7- The second sub-Formation of Middle Devonian Dananhu Formation; 8- Geological boundary; 9- Tungsten quartz veinlet belts; 10- Fault; 11- Anticlinal axis; 12- Geological section; F1- Northern fracture; F2- Southern fracture; AA'- The measured profile (line237)

2.2 Deposit Geology

The strata in the Xiaojiashan Tungsten deposit area are mainly composed of First and Second Sub-Formation of Middle Devonian Dananhu Formation (D2d1, D2d1′), as well as Quaternary alluvial sediments (Q4) (Fig. 1).

The first sub-Formation of Middle Devonian Dananhu Formation (D2d1′), mainly distributed in the north of mining area, comprise a north-dipping monoclinal structure. The first lithologic section of the first sub-Formation of Middle Devonian Dananhu Formation (D2d1′) is mainly composed of
metamorphic crystal tuff, tuffaceous sandstone and a small amount of alternation diorite. The second lithologic section of the first sub-Formation of the Dananhu Formation (D$_2d_1^2$) is mainly metamorphic crystal tuff and a small amount of intrusive diorite veins.

The second sub-Formation of the Dananhu Formation (D$_2d_2$), extending from east to west, is distributed in the south of mining area. The sub-formation lithology is mainly metamorphic crystal tuff, silty slate and a small amount of intrusive granite veins. The Quaternary sediments mainly covered in the south of mining area.

Tectonically, the deposit occurs in E-W striking Harlik anticlinorium. There are two faults (F$_1$ and F$_2$) striking E-W in the mine area, dipping to south with dip angle of 50°. The fault F$_1$ occurs in the north of mining area, located between the first lithologic section and the second lithologic section of the first sub-Formation of Middle Devonian Dananhu Formation. It is easy to observe that quartz veins intercalated in rocks on both sides along the fault line. Silicification, pyritization, and chloritization are relatively developed in the deposit area, and there are a few sporadic potashfeldspathization veinlets.

In the north-central part of mining area, there are quartz diorite, K-feldspar granite, monzonitic granite and a small amount of intermediate-acid granodiorite veins. Granite intrusion is controlled by the EW-trending fault. The contact metamorphism is developed.

Figure 2 is a typical geological profile, located in exploratory line 237, showing the characteristics of strata and intrusion in the north of Xiaojiashan Tungsten deposit area.

3 Mineralizing ore veins

Exploratory trenches reveal that tungsten mineralizing zones are mainly EW-extending, while wolframite quartz veins occur in S-N and E-W to land in the grid distribution. Two types of wolframite quartz veins can be identified: grey quartz vein (Q$_1$) (Fig. 3A) and white quartz vein (Q$_2$) (Fig. 3B).

The main minerals in the ores are wolframite and quartz. Ore texture occurs as euhedral to subhedral, and metasomatic textures and fragmentation are commonly observed (Fig. 3C). The wolframite distribute in quartz veins as elongated, flaggy or disseminated. The gangue mineral is quartz which is of oily luster, and commonly occurring in limonitization, and they are dense block and closely associated with wolframite.

Wall rock alterations mainly include silicification, potassic feldspathization, as well as chloritization in the late stage.
Figure 3. The photos showing wolframite-bearing quartz veins of the Xiaojiashan in field (A) EW-trending and S-leaning gray limonite wolframite quartz vein in groove, 83 meter distance in the south of TC3; (B) SN-trending and E-leaning white limonite wolframite quartz vein in groove, 56 meter distance in the south of TC2; (C) Ore hand specimens of wolframite(W) quartz veins(Q)

4 Composition of ore fluids

In order to understand ore-forming progress, the compositions of fluid inclusions were measured using Quadrupole Mass Spectrometry at the Institute of Geology and Geophysics, Chinese Academy of Sciences. Seven samples contain five quartz veins and two wolframites. The RG202 quadrupole mass spectrometer and HTC-6A type ion chromatograph are respectively used to measure the compositions of vapor and liquid phase of fluid inclusions. The test are processed with the sample vapor flow rate of 1.04L/min, auxiliary vapor flow rate of 0.96L/min, cooling air flow rate of 14.0L/min, analysis room vacuum 6×10⁻⁶Pa. Repeat measurement accuracy was <5%. The grain sizes of sample are +60~ - 40 mesh. The weight of quartz samples are 2 -5g, and wolframite sample have the weight of 0.5g. The purity single mineral sample is >99%.

Quadrupole mass spectrometer is producted by Japanese vacuum technology co., LTD production, SME voltage of -1.22V, ionization ways is IE, ionization energy 50eV, measurement speed is 50ms/amu [2,3]. RG202 quadrupole mass spectrometer was used to measure the compositions of vapor phase of fluid inclusions. The results are shown in table 1.

Table 1. Analysis results of quartz fluid inclusion vapor phase composition(mol%)

<table>
<thead>
<tr>
<th>Sample no</th>
<th>H₂O</th>
<th>N₂</th>
<th>Ar</th>
<th>CO₂</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>H₂S</th>
<th>CO₂/H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC2-3 (Quartz)</td>
<td>93.41</td>
<td>0.121</td>
<td>0.009</td>
<td>5.977</td>
<td>0.416</td>
<td>0.059</td>
<td>-</td>
<td>-0.064</td>
</tr>
<tr>
<td>TC2-5 (Quartz)</td>
<td>96.33</td>
<td>0.078</td>
<td>0.012</td>
<td>3.269</td>
<td>0.259</td>
<td>0.047</td>
<td>-</td>
<td>-0.034</td>
</tr>
<tr>
<td>TC3-2B (Quartz)</td>
<td>91.39</td>
<td>0.212</td>
<td>0.006</td>
<td>7.770</td>
<td>0.588</td>
<td>0.015</td>
<td>-</td>
<td>-0.085</td>
</tr>
<tr>
<td>TC3-4 (Quartz)</td>
<td>95.90</td>
<td>-</td>
<td>0.022</td>
<td>3.359</td>
<td>0.183</td>
<td>0.532</td>
<td>-</td>
<td>-0.035</td>
</tr>
<tr>
<td>TC3-6 (Quartz)</td>
<td>90.38</td>
<td>0.163</td>
<td>0.09</td>
<td>8.719</td>
<td>0.619</td>
<td>0.097</td>
<td>-</td>
<td>-0.096</td>
</tr>
<tr>
<td>TC3-2B (Wolframite)</td>
<td>89.63</td>
<td>0.184</td>
<td>0.0004</td>
<td>9.964</td>
<td>0.165</td>
<td>-</td>
<td>-</td>
<td>-0.111</td>
</tr>
<tr>
<td>TC3-4 (Wolframite)</td>
<td>91.65</td>
<td>0.221</td>
<td>0.022</td>
<td>7.723</td>
<td>0.363</td>
<td>-</td>
<td>-</td>
<td>-0.084</td>
</tr>
<tr>
<td>Average</td>
<td>92.67</td>
<td>0.163</td>
<td>0.011</td>
<td>6.683</td>
<td>0.371</td>
<td>0.150</td>
<td>-</td>
<td>0.072</td>
</tr>
</tbody>
</table>

The vapor phase of fluid inclusion mainly contain H₂O and CO₂, followed by N₂, CH₄, as well as minor Ar, C₂H₆. The molar concentration of H₂O vary from 89.63% to 96.33%, and the molar concentration of CO₂ vary from 3.269% to 9.964%.
The liquid phase compositions of fluid inclusions from quartz veins are measured by HTC-6A type ion chromatograph. The results are shown in Table 2.

### Table 2. Analysis results of quartz fluid inclusion liquid phase composition (μg/g)

<table>
<thead>
<tr>
<th>Sample no</th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Na⁺/Ca²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC2-3 (Quartz)</td>
<td>-</td>
<td>53.6</td>
<td>-</td>
<td>38.5</td>
<td>-</td>
<td>-</td>
<td>1.57</td>
<td>24.522</td>
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<tr>
<td>TC2-5 (Quartz)</td>
<td>-</td>
<td>54.5</td>
<td>-</td>
<td>40.2</td>
<td>-</td>
<td>-</td>
<td>1.15</td>
<td>34.957</td>
</tr>
<tr>
<td>TC3-2B (Quartz)</td>
<td>-</td>
<td>58.0</td>
<td>-</td>
<td>42.0</td>
<td>-</td>
<td>-</td>
<td>3.60</td>
<td>11.667</td>
</tr>
<tr>
<td>TC3-4 (Quartz)</td>
<td>-</td>
<td>51.4</td>
<td>-</td>
<td>36.7</td>
<td>-</td>
<td>-</td>
<td>0.627</td>
<td>58.533</td>
</tr>
<tr>
<td>TC3-6 (Quartz)</td>
<td>-</td>
<td>65.5</td>
<td>-</td>
<td>48.0</td>
<td>-</td>
<td>-</td>
<td>3.09</td>
<td>15.534</td>
</tr>
</tbody>
</table>

Test at the Institute of Geology and Geophysics, Chinese Academy of Sciences. "-" not detect

The liquid phase compositions of fluid inclusions mainly contain Cl⁻, Na⁺, followed by Ca²⁺. The ion number ratios of Na⁺/Ca²⁺ vary from 11.667 to 58.533. The contents of Cl⁻, Na⁺ are far more than other ions, indicating that the salt compounds in ore-forming fluid are mainly NaCl, as well as a spot of Ca-compounds.

### 5 Discussion

Quadrupole mass spectrometry reveals that fluid inclusions contain major vapor phase contents of CO₂, H₂O. In addition, there is a little variable component of Ar, C₂H₆ in vapor phase. Meanwhile, fluid inclusions contain major liquid phase contents of Cl⁻, Na⁺ and a little variable positive ion component of Ca²⁺. For the quartz veins containing CO₂ component inclusions in the tungsten mining area, some researchers suggest that the precipitation of CH₄ components could cause an unmixing of NaCl-H₂O-CO₂ fluids in vein quartz at the bottom of tungsten deposit [4]. Liquid unmixing plays an important role in tungsten precipitate from hydrotherm [5].

The late stage medium-low temperature fluid activities indicate the natural cooling process of fluids. The natural cooling process of the fluid system plays as an important role in the hydrothermal decomposition and precipitation of tungsten clathrate [6]. In the major tungsten ore-forming stage, magmatic hydrothermal fluids are driven under temperature and pressure differences. Transporting fracture structures and ore-forming fluids were cooled during tungsten element migration. Because the NaCl-H₂O-CO₂ fluid in the quartz vein was unmixing, the tungsten clathrate was decomposed and precipitated.

### 6 Summary

The mineralizing belt of the Xiaojiashan tungsten mining area occur as East-West trending zone, which are characterized by tungsten-bearing quartz vein system. Ore minerals are primarily composed of quartz and wolframite. Two types of tungsten-bearing quartz veins can be found in the deposit, including grey wolframite-quartz vein and white quartz vein.

Quadrupole mass spectrometry reveals that fluid inclusions contain major vapor phase contents of CO₂, H₂O. Meanwhile, fluid inclusions contain major liquid phase contents of Cl⁻, Na⁺. It can be speculated that ore-forming fluid of the Xiaojiashan wolframite deposit is characterized by a CO₂-rich, low salinity, and H₂O-CO₂-NaCl system.

The ore-forming fluids of the tungsten deposit had a source of magmatic water, and mixing of magmatic and meteoric water happened in the late stage. During ore-forming process, magmatic water had separated from magmatic intrusion and brought tungsten complex to a portion where tungsten-bearing ores could be mineralized.
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References