Mineralogical characteristics of scheelite in the Xi’an tungsten deposit, western Hunan

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Abstract. The Xi’an tungsten deposit, located in the middle of Xi’an gold antimony tungsten metallogenic belt, western Hunan, is an important tungsten deposit in South China. In order to place emphasis on mineralogy of the scheelite, based on the previous researches, using mineralogical, this dissertation documents the geological feature of the studied deposit. This study investigated the scheelite deposit is hosted in the Madiyi Formation of Proterozoic Banxi Group. Its ore bodies, occurring as stratiform and stratoïd, are strictly controlled by strata, lithology and structure. The chemical formula of scheelite collected from the studied deposit is C₉₀,₉₆W₁,₀₂O₄,₀₂, and its content of CaO is less than the theoretical value, while the content of WO₃ is bigger, and the latter tends to increase with depth from deep to shallow. The crystal parameters for scheelite are close to the theoretical value.

1. Introduction
The Tungsten deposit in Western Hunan Province are mainly stratabound deposits which are not directly related to magmatism[¹]. The orebodies are mainly hosted in the Mesoproterozoic and Neoproterozoic Lengjiaxi group and Banxi group in the form of scheelite bearing quartz veins, and most of them are concentrated in the Madiyi formation of the Neoproterozoic Banxi group. The ore bodies are mainly layered and stratabound quartz vein type scheelite[²]. Although the deposit is unique in this area, few people have carried out special research on it, and its significance for Scheelite mineralization is still unclear. This study attempts to improve the indicative significance of scheelite and guide the prospecting by studying the geological characteristics, petrographic characteristics and mineralogical characteristics of scheelite in Xi’an, Western Hunan Province, and lay a foundation for the geological prospecting and theoretical research of stratabound scheelite deposits in the future.

2. Geological features
The Xi’an tungsten deposit in Western Hunan is located in the Xi’an Au-sb-w ore belt in the middle part of Xuefeng archeformed structural uplift zone, which is composed of Guojiaochong, Zhoujiaochong, Dianchang and Lijiachong deposit (Fig. 1). The strata in the area are simple except the quaternary system, all of them are light metamorphic rocks of the Lengjiaxi group and the Madiyi formation of the Banxi group. The relationship between them is angular unconformity. The Lengjiaxi group is composed of grayish green slate, sandy slate and metamorphic fine sandstone. The Madiyi formation of Banxi group is composed of purplish red slate, sandy slate with gray green slate and metamorphic fine sandstone. There are two layers of dolomitic marl in the lower part, which is the main
occurrence layer of scheelite ore body in this area. The orebody is mainly produced in purplish red slate of Madiyi formation in Banxi group, which is controlled by interlayer fracture zone. There is no magmatic rock exposed in the mining area and nearby\[3\].

Figure 1 Geological Sketch map of Xi'an tungsten ore district, Western Hunan Province (revised according to Geological Survey Center for nonferrous metals and minerals, 2005).

According to the occurrence form, the ore body of the mine can be divided into network vein and fracture vein. Net vein is the main ore bearing vein in the deposit, accounting for about 90% of the total reserves. The ore bodies are enriched in the ore bearing bed in the form of plate columnar, cystic, wedge-shaped and lenticular. The strike length of single ore body is 10~300m, and the dip extension is 20~360m. The fracture vein ore body is vein or lenticular, and the ore body is short, extending 10~70m\[4\]. The upper part of the fault surface is purplish red slate without vein; the lower part is discolored altered slate, and the vein occurrence is controlled by structure.

The mineral composition is simple, metal minerals are mainly scheelite, pyrite, chalcocite, etc; Non-metallic minerals are quartz, calcite, ankerite and a small amount of apatite and feldspar. According to the difference of ore composition, the ore can be divided into the following types: scheelite-quartz type, scheelite-quartz-carbonate vein type, scheelite-quartz vein-altered slate type. The composition ratio of ore is also different in different structures, among which scheelite quartz type ores are common in tungsten ore bodies.

3. Mineralogical characteristics of Scheelite
Scheelite, known as calcium tungstate, Colorless, white rare, mostly gray, light yellow, light purple or light brown, sometimes with green, orange or red. Generally, scheelite with little or no molybdenum is white or nearly white. The chemical formula is Ca(WO$_4$)$_2$, mainly composed of CaO and WO$_3$. Theoretically, CaO and WO$_3$ are 19.4% and 80.6% respectively\[5\]. Light blue to yellow fluorescence under UV irradiation.

3.1. Sample selection
This study adopts the method of combining macro and micro. First of all, through the routine observation in the field and indoor watchbook and identification under the light slice microscope, the minerals with fine particles and difficult to be identified were confirmed by using electron probe microanalysis (EPMA), and the composition quantitative and image analysis of scheelite in Xi'an scheelite deposit were emphatically carried out. EPMA-1720H electron probe was used in the laboratory of electron probe and Geophysics of South Central University. The test conditions of EPMA are as follows: accelerating voltage 15.0kV, probe current 10.0nA, beam spot diameter 1.0um, ZAF correction method, ambient temperature of 20°C, the standard materials used for the analysis of samples are Ca and W.
3.2. Mineral composition

The chemical composition of scheelite was analyzed by electron probe microanalysis (Table 1). The results show that the crystal chemical formula of scheelite is $\text{Ca}_{0.96}\text{W}_{1.02}\text{O}_{4.02}$ according to the calculation of the total number of atoms=6 and the two cations in the general formula of minerals. It can be concluded that there is a lack of Ca in scheelite in the mining area. The Ca content is lower than the theoretical value due to isomorphic substitution of Ca with REE, Sr, Pb, Ba and other elements in hydrothermal fluid.

The composition of scheelite quartz type, scheelite quartz carbonate type and scheelite quartz altered rock type in Xi’an tungsten deposit is analyzed by means of electron probe microanalysis. According to the results of scheelite quartz type determination (Table 1), the content of CaO is 17.93% ~ 18.79%, and the average content is 18.49%, which are all lower than the theoretical value; the content of WO$_3$ is 80.375% ~ 82.162%, with an average value of 81.24%, and the average value is greater than the theoretical value. For Scheelite in scheelite quartz carbonate type, the EPMA analysis results (Table 2) show that CaO content of scheelite is 18.33% ~ 18.8%, with an average value of 18.52%, which are all lower than the theoretical value; WO$_3$ content is 80.274% ~ 82.206%, with an average value of 81.203%, and the average value is greater than the theoretical value. For Scheelite quartz altered wall rock type, the results of EPMA analysis (Table 3) show that CaO content of scheelite is 18.24%~18.81%, with an average value of 18.49%, which are all lower than the theoretical value; WO$_3$ content is 79.643%~ 82.211%, with an average value of 81.114%, and the average value is greater than the theoretical value.

| Table 1 | Electron probe analysis results of scheelite in scheelite quartz type (wt.%). |
|---------|--------------------------------------------------------------------------------|
| number  | location | Point site | CaO  | WO$_3$ | CaWO$_4$ |
| 15-1A   | rim      | 283m       | 18.708 | 81.51 | 100.218 |
| 15-2I   | rim      | 283m       | 18.58  | 81.664 | 100.244 |
| 15-2H   | rim      | 283m       | 17.97  | 82.082 | 100.052 |
| 15-3A   | rim      | 283m       | 18.578 | 81.19  | 99.768  |
| 15-3B   | rim      | 283m       | 18.655 | 81.145 | 99.8    |
| 15-4F   | core     | 283m       | 18.694 | 81.29  | 99.84   |
| 15-4G   | core     | 283m       | 18.396 | 81.619 | 100.015 |
| 15-4J   | core     | 283m       | 18.778 | 81.242 | 100.019 |
| 57-1A   | rim      | 273m       | 17.934 | 82.162 | 100.096 |
| 57-2E   | rim      | 273m       | 18.53  | 81.039 | 99.569  |
| 57-2F   | rim      | 273m       | 18.465 | 80.718 | 99.183  |
| 57-2G   | rim      | 273m       | 18.504 | 80.504 | 99.008  |
| 57-1C   | core     | 273m       | 18.219 | 81.12  | 99.338  |
| 57-1D   | core     | 273m       | 18.207 | 80.793 | 99      |
| 57-2A   | core     | 273m       | 18.728 | 81.222 | 99.95   |
| 57-2B   | core     | 273m       | 18.791 | 81.178 | 99.969  |
| 57-2C   | core     | 273m       | 18.713 | 80.375 | 99.089  |
| 57-2D   | core     | 273m       | 18.653 | 81.075 | 99.728  |
Table 2: Electron probe analysis results of scheelite in quartz carbonate type (wt.%).

| number | location | Point site | CaO | WO$_3$ | CaWO$_4$ |
|--------|----------|------------|-----|--------|----------|
| 34-1F  | rim      | 283m       | 18.398 | 80.977 | 99.375   |
| 34-1G  | rim      |            | 18.51  | 80.693 | 99.203   |
| 34-2E  | rim      |            | 18.522 | 81.09  | 99.612   |
| 34-2H  | rim      |            | 18.383 | 81.202 | 99.585   |
| 34-3D  | rim      | 103m       | 18.38  | 80.933 | 99.312   |
| 34-3E  | rim      |            | 18.804 | 80.274 | 99.078   |
| 34-2D  | core     |            | 18.634 | 80.817 | 99.451   |
| 34-2F  | core     |            | 18.477 | 81.208 | 99.685   |
| 34-3A  | core     |            | 18.604 | 80.76  | 99.364   |
| 34-3B  | core     |            | 18.478 | 81.45  | 99.928   |
| 50-1A  | rim      |            | 18.674 | 81.302 | 99.975   |
| 50-2A  | rim      |            | 18.453 | 81.327 | 99.78    |
| 50-3A  | rim      | 103m       | 18.524 | 81.889 | 100.414  |
| 50-3B  | rim      |            | 18.562 | 81.964 | 100.526  |
| 50-3D  | rim      |            | 18.602 | 81.769 | 100.371  |
| 50-1D  | core     |            | 18.523 | 81.036 | 99.56    |
| 50-2G  | core     |            | 18.407 | 80.919 | 99.326   |
| 50-2F  | core     | 103m       | 18.602 | 80.92  | 99.522   |
| 50-2E  | core     |            | 18.328 | 82.206 | 100.534  |
| 50-3G  | core     |            | 18.546 | 81.333 | 99.879   |

Table 3: Electron probe analysis results of scheelite in quartz altered rock type (wt.%).

| number | location | Point site | CaO | WO$_3$ | CaWO$_4$ |
|--------|----------|------------|-----|--------|----------|
| 26-3E  | rim      | - 107m     | 18.301 | 81.052 | 99.353   |
| 26-3F  | rim      |            | 18.446 | 80.776 | 99.222   |
| 26-3C  | rim      |            | 18.309 | 81.254 | 99.563   |
| 26-3E  | rim      | - 107m     | 18.301 | 81.052 | 99.353   |
| 26-4C  | rim      |            | 18.466 | 81.736 | 100.202  |
| 26-5A  | core     |            | 18.561 | 81.958 | 100.52   |
| 26-5B  | core     |            | 18.523 | 81.829 | 100.352  |
| 26-5C  | core     |            | 18.641 | 81.404 | 100.045  |
| 26-5D  | core     |            | 18.493 | 81.758 | 100.251  |
| 26-5E  | core     |            | 18.753 | 80.85  | 99.603   |
| 221-1H | rim      | - 77m      | 18.373 | 82.124 | 100.497  |
| 221-1J | rim      |            | 18.555 | 81.584 | 100.139  |
| 221-1C | core     | - 77m      | 18.659 | 80.562 | 99.221   |
| 221-1E | core     |            | 18.491 | 81.732 | 100.223  |
| 221-1F | core     |            | 18.814 | 80.549 | 99.363   |
| 56-1G  | rim      | 223m       | 18.478 | 80.328 | 98.807   |
The variation of WO₃ content in scheelite quartz type, scheelite quartz carbonate type and scheelite quartz altered wall rock type in Xi'an tungsten deposit is shown in Fig. 2. From the graph analysis, the WO₃ content in scheelite quartz type is the highest, followed by scheelite quartz altered wall rock type, and scheelite quartz carbonate type is the lowest. The WO₃ content of the three types of scheelite increases from the core to the edge, which may be due to the change of hydrothermal fluid composition or physicochemical conditions during the mineralization process.

3.3. The crystal structure
Scheelite belongs to tetragonal crystal system, space group C₄ᵥ-I4₁/a. a₀ = b = 5.25, c₀ = 11.40, Z = 4. Scheelite has a simple crystal structure with tetrahedron [WO₄]²⁻ group and Ca²⁺ arranged in phase along the c-axis (Fig. 3). Atomic spacing: W-O(4) = 1.78, Ca-O(8) = 2.46 Å.
X-ray diffraction analysis (XRD) was carried out on 5 scheelite samples from different ore segments according to their spatial positions. This analysis was performed on a micro-area diffractometer, Rigaku Rapid IIR, in the School of geosciences and info-physics of Central south university. First target particles under a microscope chosen, then the samples into the sample stage, and through the CCD vision positioning, set to 40 kv X-ray generator voltage, electric current is 250 ma, X-ray collimator tube diameter is 0.03 mm, the exposure time of 15 minutes, the diffraction effect of samples recorded in 2D cylindrical IP imaging plate, through Rapid XRD instrument random software converts 2D diffraction pattern to common 2θ-I, then background subtraction by Jade, peak and phase matching processing, and calculate the crystal cell parameters. The analysis and test results are shown in Table 5, and the scheelite diffraction pattern is obtained (Fig. 4).

The analysis of the diffraction pattern shows that the selected mineral has high purity and good crystallization degree, and it is determined that the mineral conforms to scheelite crystal structure characteristics.

Comparing the results of this measurement (Table 5) with the cell constants of the ideal minerals of scheelite, it is shown that the cell parameters of scheelite in this mine area are close to the theoretical values.

| Number | 2θ  | d(Å) | I%  | Number | 2θ  | d(Å) | I%  |
|--------|-----|------|-----|--------|-----|------|-----|
| 1      | 18.673 | 4.7479 | 5   | 5      | 58.095 | 1.5864 | 30.9 |
| 2      | 28.762 | 3.1014 | 100 | 9      | 59.631 | 1.5492 | 18.2 |
| 3      | 34.248 | 2.6161 | 26.4| 10     | 64.717 | 1.4392 | 7.4  |
| 4      | 39.285 | 2.2914 | 43.6| 11     | 76.413 | 1.2454 | 17.1 |
| 5      | 45.543 | 1.9901 | 20.1| 12     | 80.867 | 1.1877 | 10.1 |
| 6      | 47.292 | 1.9205 | 19.4| 13     | 90.764 | 1.0821 | 14.9 |
| 7      | 49.233 | 1.8492 | 26.5| 14     | 117.09 | 0.903 | 10.3 |

Figure 3 Crystal structure of scheelite. (Zhaolu P, 1994)
Table 5 Scheelite cell parameters.

| cell parameters | GJC-17 | GJC-22-1 | GJC-29 | GJC-30 | GJC-56 | Scheelite | Yangchuling |
|-----------------|--------|----------|--------|--------|--------|-----------|-------------|
| a0 (Å)          | 5.23247| 5.23263  | 5.23506| 5.2327 | 5.2351 | 5.245     | 5.248       |
| c0 (Å)          | 11.35682| 11.36829 | 11.35254| 11.36477| 11.36217| 11.37     | 11.364      |
| c0/a0           | 2.170451| 2.172577 | 2.16856| 2.171875| 2.170383| 2.167779  | 2.165396    |

4. Conclusions
Xi 'an tungsten deposit occurs in the Madiyi Formation of Banxi Group. The ore body is layered and like a layered, which is controlled by stratigraphy, lithology and structure.

The chemical formula of scheerite is Ca$_{0.96}$W$_{1.02}$O$_{4.02}$. The content of CaO in scheerite is less than the theoretical value, and the content of WO$_3$ is greater than the theoretical value. The content of WO$_3$ increases slightly with the depth from deep to shallow. The cell parameters of scheelite are close to the theoretical values.

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