The Technological Mineralogical Research of Molybdenum in Skarn-type Ore of Huangshaping Polymetallic Mining Area, Hunan, China

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Abstract. Huangshaping is one of the most important polymetallic deposits in the south of Hunan Province. Through field investigation, chemical analysis, observation under the optical microscope, energy spectrum analysis of the SEM and X-ray diffraction, the author made a technological mineralogical research of molybdenum on skarn-type ore, and the result shows that the ore containing molybdenum is mainly on the contact of the granite porphyry and the impure limestone in the lower carboniferous Shidengzi group. Besides molybdenum, the ore minerals contain scheelite, native bismuth, bismuthinite, magnetite and so on; and the gangue minerals are mainly andradite, fluorite and wollastonite. Part of the molybdenum exists in the scheelite in form of isomorphism, and there is an obvious negative correlation between MoO₃ and WO₃. The molybdenite granularity is mainly located in the 0.04~0.08mm area, which accounts for 29.5% of the total and is the finely disseminated ore. For samples of 70%, 90%, and 100% with the particle size of more than 200 meshes, the maximum recovery of the molybdenite are 75.15%, 86.45% and 91.25% respectively. So there will be a better use of molybdenum if we properly improve the ground particle size of the comprehensive samples. As part of the molybdenum is distributed in the scheelite lattice, the actual recovery rate in this area may decline compared with the ideal value.

1 Preface

Huangshaping polymetallic deposit with a long history is one of the most representative deposits in the south of Hunan Province, and an important polymetallic origin of lead and zinc in our country [1-2]. In the early days, lead-zinc mine is the main mining object, but with the lead-zinc resource gradually decreasing, it is urgent to find new economical minerals to prolong the productive life. Tungsten molybdenum bismuth ore body produced from the acidic magma eroding in the carbonate rock becomes the research priority [3]. There are a lot of researches about Huangshanping deposit[4-7], but few about the systematical study of the minerals containing Mo. On the basis of principles and methods of process mineralogy[8-12], and with the help of microscope, scanning electron microscope and X-ray diffractometer to make a process mineralogical study of Mo-bearing minerals, the author provides a convincing
ground for further research on the mineral smelting.

2 Overview of the Deposit Geology

Huangshaping polymetallic deposit is located in the collision convergence belt of Neocathaysian plate and Yangtze plate, and in the complex area of the north of the Nanling WE and Leiyang-Linwu NS tectonic belt [3-4]. The main strata belong to the upper Devonian and lower Carboniferous, and the main ore-bearing stratum is the impure limestone belonging to the Shidengzi Formation of lower Carboniferous, secondly is the sandshale in the Ceshui Formation and the dolomite in the Xinmenqiao Formation. Affected by Yanshanian movement, the tectonic structure is very complicated with many folds and fractures inside. The magmatic rocks are mainly the Yanshanian hypabyssal - ultra shallow intrusions which contain the quartz porphyry granodiorite - porphyry, granite porphyry and granite. The deposit discussed in this paper is a skarn-type polymetallic one in the contact zone of the granite porphyry and the impure limestone in the Shidengzi Formation of lower Carboniferous. (Figure 1).

Figure 1. 16 m middle geological map of Huangshaping deposit
3 Types of Ores

| Mineral          | Granularity (mm) | Average Content (wt.%) | Mineral          | Granularity (mm) | Average Content (wt.%) |
|------------------|------------------|------------------------|------------------|------------------|------------------------|
| Scheelite        | 0.01-10          | 0.4                    | Magnetite        | 0.01- >10        | 3                      |
| Molybdenite      | 0.01-10          | 0.3                    | Pyrite           | 0.01-0.2         | 1                      |
| Bismuthinitne    | 0.005-0.07       | 0.05                   | Fluorite         | 0.01- >10        | 12                     |
| Native bismuth   | 0.005-0.1        | 0.06                   | Andradite        | 0.1 - >10        | 40                     |
| Chalcopyrite     | 0.005-0.1        | 0.01                   | Diopside         | 0.05-5           | 5                      |
| Galena           | 0.005-0.1        | 0.04                   | Calcite          | 0.05-5           | 8                      |
| Sphalerite       | 0.005-0.1        | 0.1                    | Quartz           | 0.1-0.5          | 5                      |
| Pyrrotite        | 0.005-0.1        | tiny                   | Epidote          | 0.05-0.5         | 8                      |
| White iron ore   | 0.01-0.1         | 0.1                    | Wollastonite     | 0.05-0.5         | 12                     |
| Cassiterite      | 0.001-0.01       | tiny                   | Potash feldspar  | 0.05-0.1         | 5                      |

Huangshaping Polymetallic deposits with molybdenum are mainly divided into three types. The first, also the main type is the skarn-type molybdenum polymetallic ore body in the contact zone, and its main output (figure 1) is 301 # granite porphyry. The output of single ore body with the highest industrial value goes up to 200 - 200 tons. The second type, a small-scale one, is the skarn-type tungsten molybdenum ore body in the outside of the contact zone. The third type is the vein polymetallic ore body in the fracture tectonic belt, a high grade one, but with low degree of thickness. The research of this study is mainly focused on the first type of ore body.

In order to find out the types and contents of minerals in molybdenum polymetallic ore of the deposit, the ore samples are observed by a polished-thin microscope, supplemented by electric energy spectrum quantitative analysis and X-ray diffraction analysis of typical samples. The statistics of the main minerals contents and the estimated secondary mineral contents based on chemical analysis are shown in Table 1. As listed in the table, the main ore minerals in the molybdenum polymetallic ore are molybdenite, scheelite, natural bismuth, bismuthinite and magnetite, and the ore also contains a small amount of pyrite, sphalerite, white iron ore, galena and chalcopyrite. Gangue minerals are mainly andradite, fluorite, wollastonite, and there are also a small amount of calcite, and epidote, etc.

According to the natural endowment and characteristics of element combination, molybdenum polymetallic ore in the deposit can be divided into the skarn-type containing molybdenum and diopside-magnetite skarn-type ore, and the latter accounts for the vast majority. The results of multielement composition analysis of ore samples (see Table 2.) are: the grade of molybdenum in skarn type ore are 0.073% to 0.073%, and the average is 0.485%; molybdenum grades in diopside magnetite skarn type ore, skarn type surrounding ore and comprehensive deputy samples in different particle sizes are 0.42%, 0.13%, 0.11% (80 - 200 meshes) and 0.22% (> 200 meshes) respectively. In addition, it can be seen that besides molybdenum, the ore sample also contains much tungsten and bismuth, and small amounts of lead, zinc, tin and other metal elements.
| Number | Ore Type               | Cu/10⁶ | Pb/10⁶ | Ag/10⁶ | Zn/10⁶ | Bi/10⁶ | Au/10⁹ | W/10² | Sn/10² | Mo/10² | S/10²  |
|--------|------------------------|--------|--------|--------|--------|--------|--------|-------|-------|-------|-------|
| 200-36 | Skarn-type ore         | 6.1    | 48.3   | 0.58   | 130    | 375    | 10.06  | 1.96  | 0.35  | 0.17  | 0.045 |
| 165-Mo | Skarn-type ore         | 4.5    | 56     | 0.1    | 267    | 51.2   | 12.44  | 0.13  | 0.023 | 0.57  | 0.37  |
| GK54-176| Skarn-type ore        | 3.5    | 29.6   | 0.2    | 64     | 33.3   | 8.18   | 0.54  | 0.04  | 0.14  | 0.072 |
| 56-21-5| Skarn-type ore         | 4.4    | 47.9   | 0.23   | 82     | 85.2   | 9.3    | 0.33  | 0.14  | 1.47  | 0.88  |
| GK100-11| Skarn-type ore       | 2.6    | 30.7   | 0.5    | 320    | 500    | 9.48   | 0.29  | 0.85  | 0.073 | 0.014 |
| 92-57 | Diopside magnetite skarn ore | 22    | 39.4   | 2.4    | 314    | 1565   | 5.72   | 0.29  | 0.26  | 0.42  | 0.75  |
| 56-171| Skarn surrounding rock| 1.5    | 11.1   | 0.1    | 152    | 38     | 4.34   | 0.012 | 0.0084| 0.13  | 0.08  |
| heald+200| Comprehensive deputy samples(granularity 80-200 section) | 204 | 281.4 | 1.53 | 1800 | 487 | 20.26 | 0.21 | 0.27 | 0.11 | 0.73 |
| heald-200| Comprehensive deputy samples(granularity >20 section) | 267.4 | 760 | 1.65 | 3700 | 699 | 20.8 | 0.37 | 0.18 | 0.22 | 0.91 |

4 Endowment State of Molybdenite

A. Symbiosis of molybdenite (Mo) and scheelite (W), produced in the garnet (Gt) and fluorite (Fl); B. Molybdenite (Mo) plate shaped distributed in the garnet (Gt) and quartz (Qz); C. Molybdenite (Mo) plate shaped distributed in the garnet (Gt) - magnetite (Mt) - fluorite (Fl); D. Molybdenite (Mo) distributed in diopside (Dp) - magnetite (Mt) - quartz (Qz) - fluorite (Fl); E. Symbiosis of molybdenite (Mo) and white tungsten (W), produced in magnetite (Mt) and garnet (Gt); F. Symbiosis of flake molybdenite (Mo), natural bismuth (Bi), and calcite (Cc), distributed in diopside (Dp);

Figure 2. The Endowment State of Huangshaping Molybdenite

From the field research, it can be seen the molybdenite is usually a vein aggregate filled in the crack of the skarn whit a width of 1-10 mm and a length of 10 cm. Figure 2 is the endowment state of the molybdenite samples observed under microscope and scanning electronic microscopy. The molybdenite in this area are 0.01-0.1 mm granules or patchy
distributed in the skarn, part of which contain scheelite (Figure 2. a, E) and a small amount of natural bismuth (Figure 2. f). The paragenetic minerals are mainly magnetite, garnet, diopside, calcite, and fluorite, etc.

**Figure 3. X-ray Diffraction Diagram of Huangshaping Molybdenite**

The samples of molybdenite have been researched through X-ray diffraction, analyzed and tested by Changsha Research Institute of Mining and Metallurgy. The instrument used is Dmax / 2200 - gamma A10 X-ray diffractometer produced by Ricoh company of Japan and the test conditions are as follows: copper target for the X-ray tube, the pipe pressure is 50 kv, the pipe flow is 100 mA, 4°/min, and automatic slit system. The test result is in Figure 3, showing the fact that there is no solid impurity component existing in the molybdenite, which is the feature of the 2H type. Previous studies have pointed out that molybdenite polymorphism is associated with Re contained, which can reflect different metallogenic temperatures [13], therefore it can be concluded the molybdenite in this area is formed at high temperatures. Former studies also proved that the mineralization temperature of skarn type molybdenum polymetallic ore is about 300-400 °C [14], which is consistent with the conclusion drawed in this article.

A. Scheelite (W) produced in magnetite (Mt) and garnet (Gt). It’s darker with high content of molybdenum (C) and brighter with low content of molybdenum (B);

B. Scheelite (W) produced in magnetite (Mt), symbiosis with calcite (Cc). It’s darker with high content of molybdenum (B) and brighter with low content of molybdenum (D)

**Figure 4. SEM Image of Huangshaping’s Molybdenum in Scheelite**

During the spectroscopy quantitative analysis of the scheelite on this deposit, it was found that scheelite generally contains a certain amount of molybdenum oxide (Table 3), whose content is 0.64% -21.74% with an average content of 7.21%. The analysis under the scanning electron microscopy shows that scheelite with more molybdenum is much less bright than that with less molybdenum (Figure 4). Through cluster analysis of various components in scheelite, the author got the following results, as shown in Table 4, that related index between
WO$_3$ and MoO$_3$ in scheelite is -0.950, which is a negative correlation, showing that the content of WO$_3$ in scheelite decreases while the content of MoO$_3$ increases. Since 6+ ion valence of the tungsten molybdenum elements has similar atomic radius and the same charge, it’s easy for the Mo$^{6+}$ to get into the lattice of scheelite to replace W$^{6+}$ in the process when the minerals separate out from the ore fluid, causing part of the molybdenum to exist in scheelite in the form of isomorph [15].

Table 3. Molybdenum Content in Scheelite of Huangshaping Deposit

| number | WO$_3$ | CaO | MoO$_3$ | FeO | number | WO$_3$ | CaO | MoO$_3$ | FeO |
|--------|--------|-----|--------|-----|--------|--------|-----|--------|-----|
| 5#-A   | 80.16  | 19.84 | 12#b-c | 68.56 | 15.93 | 14.93 | 0.23 |
| 5#-H   | 80.64  | 19.35 | 12#b-f | 79.92 | 16.16 | 3.91  |     |
| 6#-a   | 77.11  | 16.3  | 6.58   | 12#b-g | 83.8  | 14.29 | 1.53  |
| 6#-b   | 81.78  | 16.48 | 1.74   | 12#b-h | 76.29 | 10.54 | 12.7  | 0.2 |
| 6#-c   | 74.32  | 17.18 | 7.54   | 12#b-l | 80.62 | 16.35 | 2.15  | 0.54 |
| 11#-a  | 63.23  | 18.13 | 18.63  | 12#b-j | 80.72 | 16.22 | 3.05  |     |
| 11#-b  | 67.34  | 17.45 | 15.19  | 12#b-k | 83.17 | 15.92 | 0.64  | 0.27 |
| 11#-c  | 83.44  | 15.36 | 1.19   | 12#b-l | 81.83 | 13.77 | 4.4   |     |
| 11#-d  | 77.79  | 12.37 | 9.83   | 12#b-m | 69.71 | 18.23 | 12.05 |     |
| 11#-e  | 72.44  | 17.89 | 9.66   | 12#b-n | 57.49 | 20.31 | 21.74 | 0.05 |
| 12#b-a | 69.66  | 15.23 | 14.72  | 0.38 | 12#b-o | 74.81 | 15.21 | 9.73  |     |
| 12#b-b | 83.27  | 14.47 | 2.25   | 12#b-p | 79.87 | 14.39 | 4.95  | 0.78 |
| 12#b-d | 82.14  | 16.41 | 1.07   | 0.37 |     |     |     |     |

Table 4. Cluster Analysis of Various Components in Scheelite of Huangshaping Deposit

|        | WO$_3$ | CaO   | MoO$_3$ | FeO |
|--------|--------|-------|---------|-----|
| WO$_3$ | 1      |       |         |     |
| CaO   | -0.413 | 1     |         |     |
| MoO$_3$| -0.950 | 0.111 | 1       |     |
| FeO   | 0.103  | -0.230| -0.066  | 1   |

Figure 5. Distribution Features of Particle Content of Molybdenite in Huangshaping Deposit
5 Particle Feature Analysis of Molybdenite

Table 5. Measuring Results of Molybdenite’s Particle Size

| Sequence of Particle size | size range /mm | ratio size /d | particles /n | content ratio/n*d | content distribution/% | content distribution/% |
|---------------------------|----------------|---------------|--------------|-------------------|------------------------|------------------------|
| I                         | 2.56~1.28      | 256           | 3            | 768               | 5.06                   | 5.06                   |
| II                        | 1.28~0.64      | 128           | 8            | 1024              | 6.74                   | 11.8                   |
| III                       | 0.64~0.32      | 64            | 15           | 960               | 6.32                   | 18.12                  |
| IV                        | 0.32~0.16      | 32            | 54           | 1728              | 11.38                  | 29.5                   |
| V                         | 0.16~0.08      | 16            | 165          | 2640              | 17.39                  | 46.89                  |
| VI                        | 0.08~0.04      | 8             | 560          | 4480              | 29.5                   | 76.39                  |
| VII                       | 0.04~0.02      | 4             | 589          | 2356              | 15.52                  | 91.91                  |
| VIII                      | 0.02~0.01      | 2             | 513          | 1026              | 6.76                   | 98.66                  |
| IX                        | 0.01~0.005     | 1             | 203          | 203               | 1.34                   | 100                    |
| Total                     |                |               | 2110         | 15185             | 100                    |                        |

The composition and distribution of the subject mineral’s particles in ore have a determining impact on the grinding fineness and the process of mineral separation[16]. Due to the prominent optical character, the natural particle size of molybdenite calculated under the reflective light microscope was divided by a power of 2. For those particularly small particles (eg. particle size less than 50 microns), might be neglected, thus the results might miss the micro-fine fractions. Statistical results are shown in Table 5 and Figure 5. It shows that the particles are relatively small mainly between 0.01 ~ 0.08mm, the number is 1662, 78.77% of the total number 2110. The largest particle size ranges form 0.04 ~ 0.08mm, 29.5% of the total number; then followed by 0.08 ~ 0.16mm, 17.39% of the total. Molybdenite particle size is relatively less in coarse and microgranular area, over 200 mesh (0.074mm), up to about 47% of the total, and is the fine grain disseminated.

Table 6 Determination of molybdenite’s monomer dissociation degree

| sample            | fractions/ mesh | Monomer particles | Interlocked particles | fractions dissociation degree |
|-------------------|----------------|-------------------|-----------------------|-------------------------------|
| Composite samples | 80~200mesh     | 367               | 92                    | 58                            | 11                           | 78.46%                   |
|                   | >200mesh       | 628               | 69                    | 15                            | 4                             | 91.25%                   |

The amounting granulation method was used in determining the molybdenite’s monomer dissociation degree of composite samples of the ore, which were classified into two fractions, i.e., 80 to 200 mesh level, and> 200 mesh level. According to the relative value of volume molybdenite occupied in the interlocked particle, the interlocked particle was divided into 3/4, 2/4 and 1/4 level, then the number of the monomer particle and interlocked particle was recoded under the microscope, and the results are shown in Table 6.

According to Table 6, when the composite samples are grinded to 80 to 200 mesh, the number of the monomer particles is 367, the interlocked particles is 161, most of which is of 3/4 level, and the monomer dissociation degree of the molybdenite is 78.46%; when more than 200 mesh, the number of the monomer particles is 628, the interlocked particles is 88,
and most of them is also of 3/4 level, the monomer dissociation degree is of 91.25%. On the basis of the analysis in Table 2, the grade of molybdenum is 0.11% in the samples of 80 to 200 mesh, but 0.22% in > 200 mesh. Thus, the appropriately increased grinding degree of particles can raise the monomer dissociation degree of molybdenite and its grade as well. What’s more, it’s favorable to mineral recycle.

Therefore, the monomer dissociation degree of molybdenite is high in the composite sample of > 200 mesh, which is considered as the ideal recovery rate. When 70% of the composite sample is grinded to the particles of bigger than 200 mesh, the maximum ideal recovery rate (R70%) of molybdenum is: \[ R70\% = \left[ \frac{0.22 \times 0.7}{(0.11 \times 0.3 + 0.22 \times 0.7)} \right] \times 0.9125 = 75.15\%; \]
when 90% is grinded to > 200 mesh, it’s R90%: \[ R90\% = \left[ \frac{0.22 \times 0.9}{(0.11 \times 0.1 + 0.22 \times 0.9)} \right] \times 0.9125 = 86.45\%; \]
when 100% is grinded to > 200 mesh, it’s R100%: \[ R100\% = 91.25\%. \]
Therefore, the appropriately increased grinding degree of the composite sample can guarantee a better recovery prospects. Furthermore, since the inner part of the molybdenum mine is isomorphous existed in scheelite lattice (Table 3), this region's actual recovery rate of molybdenum will be reduced compared with the ideal one. In addition, the relations between the 2H multi-type and its flotation performance should be considered in the actual production process.

6 Conclusion

(1) Huangshaping ore body with molybdenum is mainly located on the contact belt of granite porphyry and lower Carboniferous Shidengzi Formation with pure limestone, which is a skarn type deposit. In addition to the fine granular, there are also scheelite, natural bismuth and magnetite in the ore molybdenite, among which gangue minerals are mainly andradite, fluorite, wollastonite, etc.

(2) Part of the molybdenum mine exists in scheelite in the form of isomorphism, where is negative correlation between MoO₃ and WO₃.

(3) The molybdenite granularity is mainly distributed in the 0.04 ~ 0.08 mm mining area, accounting for 29.5% of the total. Over 200 mesh (0.074 mm) accounts for about 47% of the total, which is the finely – disseminated ore.

(4) When 70%, 90%, 100% of the mineral composite samples are grinded to > 200 mesh, the most ideal molybdenum recovery rate is 75.15%, 86.45% and 91.25% respectively, so appropriately improving the grinded particle size of comprehensive samples can increase the recovery rate of molybdenite. As part of molybdenum exists in scheelite in the form of isomorphism, the actual recovery rate of molybdenite in this area will be relatively reduced compared with the ideal value.

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