Isotope Geochemistry of the Shimensi Deposit, Northern Jiangxi and Its Analysis

Zhanghuang Ye1,* and Peng Wang2

1Jiangxi Science and Technology Normal University, Nanchang, 330083, Jiangxi, China
2School of Earth Science and Resources, Chang’an University, Xi’an, China

*Corresponding author e-mail: chuckverna@sina.com

Abstract. The Shimensi deposit is located in the Lower Yangtze metallogenic province. It is a recently-discovered world-class tungsten-polymetallic deposit, accompanied by Cu and Mo. The orebodies are thick with gentle dipping, mainly distributed along the contact zone between the Cretaceous porphyritic biotite granite and the Neoproterozoic biotite granodiorite. The mineralization was closely linked with the zoned hydrothermal alteration, including silicification, greisenization, chloritization, carbonatization and K-feldsparization. Based on ore geology and C, H, O isotope, this paper has studied the origin and evolution of the ore-forming fluids. The $\delta^{13}C_{\text{V-PDB}}$ values of calcite range from -10.26‰ to -3.26‰, with an average of -7.3‰, indicating that hydrothermal fluids from which calcites precipitated were derived from the granitic magma. The H and O isotopic compositions of the quartz veins ($\delta^{18}D_{\text{SMOW}}=-106‰$ to -86‰, $\delta^{18}O_{\text{SMOW(H2O)}}=2.2‰$ to 4.5‰) suggest that the ore-forming fluids mainly had a magmatic-hydrothermal origin, but to some extents, mixed with meteoric water. The subduction of the Paleo-Pacific Plate beneath the Eurasian Plate resulted in lithospheric thickening and subsequent delamination, and the main N-S stress field in East China changed progressively to an E-W orientation during 170-135Ma. Maximal lithospheric thinning happened in the Late Mesozoic, which led to the direct contact between the crust and asthenospheric mantle. Consequently the heating from the asthenosphere on the crust triggered and widespread development of extensional structures, the intensive magmatism and mineralization in eastern China in Mesozoic.

The isotopic chemistry indicates that the ore mineralization in the Shimensi deposit was closely linked with Early Cretaceous magmatism in East China.

1. Introduction

Recently several granite-related W-Cu-Mo deposits have been discovered to the south of Yangtze River, along the Yangxing-Changzhou Fault [1], including the Shimensi tungsten deposit in Wuning County, Jiangxi Province. It is a world-class deposit, with an estimated reserve of 742.5 thousand tons $WO_3@0.196\%W$, accompanied by 28 thousand tons Mo and 403.6 thousand tons Cu in the Shimensi deposit.

The article systematically analyses C isotope composition of calcite and H, O isotope composition of quartz veins in the deposit, and discusses its constraints on ore genesis and the source of ore-
forming fluid, which has an important theoretical significance for a deeper understanding of the mineralization mechanism.

2. Regional Geological Setting
Southeast China includes the Cathaysia Block in the southeast and the Yangtze Block in the northwest. The Shimensi deposit lies in the northern part of Mount Jiuling, the center of the Jiangnan Orogen. It is surrounded by the Xiangshan district of the Qin-Hang Belt in the south and the Jiuwei region of the Middle-Lower Yangtze Valley Mineralization Belt in the north. Its tectonic location is in the middle of the southeast margin of the Yangtze Block.

The ca. 1500km long NE-trending Proterozoic Jiangnan Orogen extends along the southeast margin of the Yangtze Block. The Jiangnan Orogen was mainly defined based on the distribution of meta-sedimentary sequences and Proterozoic magmatic rocks between the two blocks [2]. There are two series of metamorphic rocks separated by an unconformity in the Jiangnan Orogen. Metamorphic rocks above the unconformity include the Dengshan Group in Jiangxi Province. Metamorphic rocks below the unconformity include the Shuangqiaoshan Group. These two suites of low-grade metamorphic rocks have been formed separately in the Meso- and Neoproterozoic.

3. Ore Deposit Geology

Figure 1. Geological sketch map of the Shimensi deposit.
In the Shimensi deposit, there are no other strata except Quaternary residual. Magmatic activities in the deposit were very frequent. Exposed Neoproterozoic biotite granodiorite in the deposit is one part of the Jiuling composite batholiths, and the main rock unit of the deposit. The predominantly gray, medium- and coarse-grained granodiorite is composed of 28-35% quartz, 25-35% plagioclase, 10-15% K-feldspar, 5-10% biotite, 2-5% muscovite and 1-5% cordierite. Garnet, magnetite, zircon and apatite are the most common accessory minerals. Magmatite in Early Cretaceous includes porphyritic biotite granite ($b\gamma^{2}_{5}(\gamma^{2}_{5}2a)$), gray fine-grained biotite granite ($b\gamma^{2}_{5}(\gamma^{2}_{5}2b)$), gray granite porphyry ($\gamma\pi^{2}_{5}(\gamma^{2}_{5}2b)$) (Fig. 1).

They have intruded regularly in time (from early to late) and in space (from bottom to top), mainly as stocks or dykes. The porphyritic biotite granite is gray to white with ca. 55% plagioclase, ca. 37% quartz, ca. 8% biotite phenocrysts. The average length of plagioclase phenocrysts is 1 cm, and the largest crystals reach up to 2 cm. The gray fine-grained granite includes ca. 40% quartz, ca. 35% K-feldspar, ca. 20% plagioclase and ca. 5% biotite. The subhedral tabular plagioclase crystals are between 0.8×0.6 mm and 2.5×1.5 mm in length and generally exhibit compound carlsbadalbite twins and polysynthetic twins. The gray granite porphyry has ca. 20% quartz, ca. 15% plagioclase and ca. 5% biotite in phenocrysts, and K-feldspar, quartz and sericite in matrix. They resulted from three magmatism events from 148.3±1.9 Ma to 143.0±0.76 Ma [3], suggesting the characteristic of comagmatic evolution. A pegmatite shell with ca. 1.5×2.7 cm pink K-feldspar phenocrysts, is distributed along the contact zone between the Neoproterozoic biotite granodiorite and the Cretaceous granite.

According to the ore body feature, the mineral assemblage, the mineralization zoning and the wall rock alteration, mineralization in the Shimensi deposit can be further divided into three types: firstly, the veinlet disseminated type—distributed around the contact zones between Neoproterozoic biotite granodiorite and Early Cretaceous porphyritic biotite granite (ca. 300-800 m), mainly scheelite at the external contact zone; secondly, the hydrothermal crypto-explosive breccia type—distributed in the central mining area, punching into biotite granodiorite; thirdly, the thick quartz vein type—a relatively broad distribution, cutting all the rock units and the two ore bodies mentioned above.

### 4. Sampling And Testing Methods

Samples for the study were collected from underground tunnels and drill cores in the Shimensi mining area. At least three types of veins have been recognized after careful field study: (1) sulfide-quartz veins, disseminated or concentrated with pyrite, pyrrhotite and chalcopyrite; (2) early barren quartz veins; (3) late calcite veins. Among them, only the sulfide-quartz veins, which include the majority of W (or Cu, Mo) mineralization, and calcite veins have been used for isotope study. The samples used for H, and O isotope test were collected from sulfide-quartz veins, while samples used for C isotopic analysis from the calcite veins. The samples were crushed and a binocular microscope was used to pick up the minerals. The test has been carried out by the Isotope Laboratory of Wuhan Geological Survey Center.

The C isotope was analyzed by using the 100% phosphoric acid method. The minerals have been reacted with 100% phosphoric acid at 25°C; CO$_2$ released from the reaction was collected, condensed, and separated in a liquid nitrogen-alcohol cooling trap (-70°C), and then carbon isotope was tested on a MAT251 type mass spectrometer. PDB was taken as a standard for δ$^{13}$C.

The H and O isotopic compositions of the 20 samples were further analyzed on a MAT 252 mass spectrometer. The analytical error for δD$_{V,SMOW}$ was ±1‰ and the analytical precision for δ$^{18}$O was ±0.2‰.

### 5. Test Results

#### 5.1. C isotopic composition

Calcite veins in this deposit are very common, which can be seen from the outcrops to the deep drillings, with big and pure crystals. The veins do not contain quartz, pyrite, which clearly shows that the calcite was formed after the mineralization stage.
As demonstrated in Table 1, the $\delta^{13}C_{V-PDB}$ values of calcite range from -10.26‰ to -3.26‰, which mainly focus from -8‰ to -7‰, and the average value is -7.30‰.

| Sample No. | location | mineral      | $\delta^{13}C_{V-PDB}$ (‰) |
|------------|----------|--------------|-----------------------------|
| SMS-cal-1  | calcite  | calcite      | -10.20                      |
| SMS-cal-2  | calcite  | calcite      | -7.60                       |
| SMS-cal-3  | calcite  | calcite      | -7.73                       |
| SMS-cal-4  | calcite  | calcite      | -7.41                       |
| SMS-cal-5  | calcite  | calcite      | -3.26                       |
| SMS-cal-6  | calcite  | calcite      | -5.32                       |
| SMS-cal-7  | calcite  | calcite      | -7.89                       |
| SMS-cal-8  | calcite  | calcite      | -5.56                       |
| SMS-cal-9  | calcite  | calcite      | -7.19                       |
| SMS-cal-10 | calcite  | calcite      | -7.92                       |
| SMS-cal-11 | calcite  | calcite      | -10.26                      |

5.2. H and O isotopic composition
Hydrogen and oxygen isotopes can be used to trace the evolution of ore fluids. $\delta^{18}O_{SMOW(H_2O)}$ values were calculated by using the formulas: $1000 \ln \alpha = \delta^{18}O_{SMOW} - \delta^{18}O_{SMOW(H_2O)} = 3.38 \times 10^6 T^{-2} - 3.4$. The values of $\delta^{18}O_{SMOW(H_2O)}$ and $\delta D_{SMOW}$ from quartz fluid inclusions range from 2.2‰ to 4.5‰ and from $-106‰$ to $-86‰$, respectively.

6. Discussion

6.1. Geological implication of C isotope
As calculated, the $\delta^{13}C_{V-PDB}$ values of calcite range from -10.26‰ to -3.26‰, with an average value of -7.3‰. All data fall within the magmatic range (-10.3 ‰ to 2.9 ‰) (Table 1), indicating that hydrothermal fluids from which calcites precipitated were derived from the granitic magma. They are mainly distributed from -8‰ to -7‰, which indicates the ore-forming fluids may come from the lower crust or upper mantle (-5 ‰ to -8 ‰). But there are two samples whose values are at the edge of -10.3‰, suggesting that strong isotope fractionation occurred when deep source fluid migrated in the form of methane. Methane in metallogenic field was oxidized to carbon dioxide, further precipitated to form calcite.

6.2. Geological implication of H and O isotope
The $\delta^{18}O_{SMOW(H_2O)}$ values of fluid inclusions in quartz from the Shimensi deposit vary from 2.2‰ to 4.5‰, with a peak from 3.0‰ to 4.0‰, which fall in the range for magmatic water and suggests a magmatic-hydrothermal origin. The $\delta D$ values of the fluids vary from $-106.0‰$ to $-86.0‰$. The values are lower than those for magmatic water ($-85‰$ to $-50‰$). Because H prefers to link with the $H_2O$ vapour, low $\delta D$ effect can happen through a magma-degassing process, which suggests that the magmatic fluids can be linked with low $\delta D$ values. Thus, a magmatic–hydrothermal origin, but mixing with heated meteoric groundwater and magmatic water can account for the H versus O isotope diagram from the Shimensi deposit.

6.3. Ore genesis
The subduction of the Paleo-Pacific Plate beneath the Eurasian Plate resulted in lithospheric thickening and subsequent delamination, and consequently the stress field in East China transfer from the main N-S to E-W orientation progressively during 170-135Ma. Large scale lithospheric thinning happened in the Late Mesozoic, which resulted in the direct contact between the crust and asthenospheric mantle. The heating from the asthenosphere on the crust subsequently led to the
widespread development of extensional structures, intensive mineralization and magmatism in East China in Mesozoic [4].

Re-Os isochron age dating on molybdenite from the Shimensi deposit is 143.7±1.2 Ma [5], which is right within the transitional period of these two geodynamic systems, and also the production of the second large-scale mineralization in Mesozoic.

The Shimensi deposit is temporally coeval and spatially close with the metallogenic belt in the middle and lower reaches of the Yangtze River. The isotopic compositions and geochemistry also suggest that the ore mineralization in the Shimensi deposit was associated with Early Cretaceous magmatism (i.e. Late Yanshan Movement) in East China. Some metapelites abound with W, Sn and LILE. Tungsten concentrations on metapelitic rocks of the Shuangqiaoshan Group can be as high as 12 ppm) [6]. However the average tungsten contents in the crustal rocks are 1-2 ppm. Tungsten is a strongly incompatible element, and partial melting and extreme fractional crystallization can result in the additional concentration of such metal. These indicate that metapelite Shuangqiaoshan Group with high W background can mostly account for the source of the Shimensi tungsten deposit.

The ascent of the highly fractionated volatiles-rich magma led to the exsolution of the magmatic hydrothermal fluid [7-8], resulting in large-scale alkaline replacement with the wall rocks, and alteration such as greisenization, silification and K-feldspar. The existence of volatile elements, such as F, can increase the solubility and enrichment of tungsten in magma. Ore-forming fluid filled along the joints and fractures, forming the orebodies of veinlet-disseminated type along the contact zone between Cretaceous biotite granite and Neoproterozoic biotite granodiorites. When fractures of Jiuling ore concentration area have penetrated the top of porphyritic biotite granites under where the high temperature fluid was shielded, liquid volatile component was gasified instantly and crypto-explosion occurred, resulting in the forming of orebodies of hydrothermal crypto-explosive breccia type. The orebodies of thick-vein type should mineralize at last, because they cut various rock units and the two mentioned orebodies in the ore concentration area shown in Figure 2. The cause-effect relationship between the Shimensi deposit and Late Cretaceous magmatism in East China is convincing.

![Figure 2. Metallogenic model of the Shimensi deposit.](image)

7. Conclusion
The $\delta^{13}$C$_{VPDB}$ values of calcite range from -10.26‰ to -3.26‰, with an average of -7.3‰, indicating that hydrothermal fluids from which calcites precipitated were derived from the granitic magma. The calculated and measured H and O isotopic composition of quartz vein ($\delta^{18}$D$_{SMOW}$=-106‰ to -86‰, $\delta^{18}$O$_{SMOW(H2O)}$=2.2‰ to 4.5‰) indicates that ore-forming fluids had a magmatic-hydrothermal origin, but mixed with meteoric water.
Large-scale lithospheric thinning happened in the Late Mesozoic, which resulted in the direct contact between the crust and asthenospheric mantle. Consequently the heating from the asthenosphere from the crust led to the widespread development of extensional structures, intensive magmatism and mineralization in eastern China in Mesozoic. The partial melting of the Shuangqiaoshan Group, which is characterized with their high W background and the high fractional crystallization of volatiles-rich magma can be associated with the ore-genesis of the Shimensi tungsten deposit. The isotopic geochemistry also suggests that the ore mineralization in the Shimensi deposit was closely related to Late Cretaceous magmatism in East China. The cause-effect relationship between the Shimensi deposit and the Cretaceous magmatism in East China is convincing.

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