Abstract: The Shimensi tungsten deposit in northern Jiangxi is located in the Middle-Lower Yangtze River metallogenic belt. There have been many debates about the origin of metallogenic materials and genetic type. Three mineralization styles are present in the Shimensi deposit. The sulphur isotopic compositions of sulphides in the deposit indicate that the sulphur source was homogeneous and the origin was closely related to the magmatic sulphur. The lead isotopic compositions of sulfides suggest that the lead has multiple sources, and were closely related to magmatism. The carbon isotopic compositions of calcite indicate that hydrothermal fluids were derived from the granitic magma. The Hydrogen and Oxygen isotopic compositions of the quartz veins indicate that the ore-forming fluids had a magmatic-hydrothermal origin, but mixed with meteoric water. Analysis indicates that the mineralization was related to Early Cretaceous magmatism in eastern China. The subduction of the paleo-Pacific plate and subsequent lithospheric delamination resulted in the transition from a compressional to extensional tectonic regime. The upwelling of hot asthenosphere triggered the partial melting of the Neoproterozoic Shuangqiaoshan Group, with high W background concentrations. The ascent of the magma resulted in the exsolution of the ore-bearing magmatic hydrothermal fluid.

Keywords: stable isotopes; ore genesis; Cretaceous magmatism; the Shimensi tungsten deposit

1 Introduction

Several granite-related W and W-Cu-Mo deposits have recently been discovered in the northern Jiangxi, to the south of the Yangtze River, which formed a tungsten-oriented ore concentration area in Wuning County, northern Jiangxi. The Shimensi
deposit alone is now recognized as a world-class deposit, with an estimated reserve of 742,500 tons WO3@0.195%W, accompanied by 403,600 tons Cu and 28,000 tons Mo [1].

2 Regional Geological Setting

The deposit are located in the northern part of Mt. Jiuling, the center of the Jiangnan Orogen. It is bounded by the Jiurui area of the Middle-Lower Yangtze Valley Mineralization Belt to the north and the Xiangshan district of the Qin-Hang Belt in the south. Its tectonic location is in the middle of the southeast margin of the Yangtze Block (Fig. 1–a).

The Shimensi tungsten deposits lies in southwestern part of the E-W-trending Jiuling uplift area. The Strata of the Shuangqiaoshan Group are partly exposed in the district. They comprise a suite of low-grade metapelite, intercalated with lesser metamorphosed conglomerate. Magmatism was widespread in this region. Abundant felsic magmas, including the Jiuling biotite granodiorite batholith, intruded the metamorphic rocks of the Shuangqiaoshan Group. This batholith, with an area greater than 2500 km², is the largest intrusion in southeastern China. Mesozoic granitic rocks in the region occur mainly in two stages. The oldest stage is dominated by porphyritic two-mica granite sills and dikes. It include N-S dikes ranging from 100 m to several hundred meters in length and from several meters to tens of meters in thickness, intruding both the Neoproterozoic granodiorite batholith and rocks of the Shuangqiaoshan Group. The second magmatic stage includes medium- to fine-grained muscovite-bearing granite, porphyritic two-mica granite, fine-grained two-mica granite, and granite porphyry. The relative geological relationships between the phases of this stage are not clear, although the second stage granites cut the first stage granite and the Neoproterozoic granodiorite batholith. A number of SHRIMP U-Pb zircon ages for the late stage Mesozoic granites vary from 144.2±1.3 Ma to 134.6±1.3 Ma [2–3], suggesting that the emplacement in Early Cretaceous (Fig.1–b).
Fig. 1: (a) Tectonic location of the study area (modified after Zhou et al., 2006 [4]). The South China Block is comprised of two blocks: Yangtze Block and Cathaysia Block. The approximate position of the Jiangnan Orogenic Belt is at the edge of Cathaysia Block and belongs to Yangtze Block. The Jiuling ore concentration area is located in the Jiangnan Orogen. (b) Geological and mineral map of the Shimensi deposit, north Jiangxi

3 Sampling and Analytical Methods

Samples for the study were collected from drill cores and underground tunnels in the Shimensi deposit. At least three types of veins have been recognized after careful field study: (1) early barren quartz veins; (2) sulfide-quartz veins, disseminated or concentrated with pyrite, pyrrhotite and chalcopyrite; (3) late calcite veins. Among them, only the sulfide-quartz veins, which account for the majority of W (or Cu, Mo) mineralization, and calcite veins have been used for isotope study. The samples used for S, Pb, 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 the minerals were handpicked under a binocular microscope. The test has been carried out by the Isotope Laboratory of Wuhan Geological Survey Center.

The S isotope test has been conducted as follows: monomineral (from metal sulphides) and cuprous oxide were exposed to an oxidized reaction after full grinding and mixing according to a certain proportion; generated SO₂ was collect by a freezing method; and then the sulphur isotopic composition was analyzed with a MAT251 gas isotope mass spectrometer. In terms of the standard sample, V-CDT was adopted for measured results, with an analysis precision better than ± 2 ‰.

The Pb isotope samples were firstly decomposed by mixed acid, and then Pb was separated by a resin exchange method. After evaporation, the Pb isotope was measured using the hot surface method by a MAT–261 type mass spectrometry. The
measurement precision is the value of $^{204}\text{Pb}/^{206}\text{Pb}$ less than 0.05 %, $^{208}\text{Pb}/^{206}\text{Pb}$ generally no more than 0.005 % for 1 μg Pb.

The C isotope was analyzed using the 100 % phosphoric acid method. The samples have been reacted with 100 % phosphoric acid at 25 °C; CO₂ released from the reaction was collected, condensed and separated in a liquid nitrogen-alcohol cooling trap, and then carbon isotope was tested on a MAT251 type mass spectrometer. PDB was taken as a standard for $\delta^{13}\text{C}$.

The H and O isotopic compositions of the 20 samples were analyzed on a MAT 252 mass spectrometer. The analytical error for $\delta D_{V-SMOW}$ was ±1‰ and the analytical precision for $\delta^{18}\text{O}$ was±0.2 ‰.

4 Results and discussion

S isotopic composition: The S isotope from molybdenite, pyrite and chalcopyrite are tested. Among them, $\delta^{34}\text{S}$ values of 6 molybdenite samples vary from –2.51‰ to –1.12%, with an average value of –1.91 ‰, while $\delta^{34}\text{S}$ values of 6 chalcopyrite samples vary from –1.98 % to –0.91 ‰, with an average value of –1.42 ‰; $\delta^{34}\text{S}$ values of 5 pyrite samples vary from –1.67 ‰ to –1.27 ‰, with an average value of –1.48 ‰. These data indicate that the variation range of $\delta^{34}\text{S}$ sulfide value is small, from –2.51 ‰ to -0.91‰, with an average value of –1.61 ‰.

Most of The $\delta^{34}\text{S}$ isotope composition is within the range of –2 ‰ to –1.5 ‰, showing an obvious “peak” distribution, which means the sulphur source was homogeneous. The $\delta^{34}\text{S}$ values of sulfides vary from –2.51 ‰ to –0.91 ‰, with an average value of –1.61 ‰, indicating sulphur origin is closely related to the magmatic sulphur [5–6].

Pb isotopic composition: As can be seen from the lead isotope data, the variation ranges from 17 samples are small, indicating that the lead isotope composition in the deposit is fairly homogeneous. Taking the Pb isotope of pyrite as an example, $^{206}\text{Pb}/^{204}\text{Pb}$: 18.155–18.259, $^{207}\text{Pb}/^{204}\text{Pb}$: 15.586-15.709, $^{208}\text{Pb}/^{204}\text{Pb}$: 38.227–38.717. The $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of sulfides vary from 18.155 to 18.277, with an average of 18.189; $^{207}\text{Pb}/^{204}\text{Pb}$ ratios vary from 15.586 to 15.709, with an average of 15.640; $^{208}\text{Pb}/^{206}\text{Pb}$ ratios vary from 38.227 to 38.717, with an average of 38.420.

The parameters of lead isotope, especially $\mu$ value and $\omega$ value can provide information on the geological process that the geologic body has gone through. Among the 17 samples of metal sulphide lead isotope composition from the deposit, 12 pieces have $\mu$ values below 9.58, and 5 pieces have $\mu$ values that are slightly higher than 9.58. The calculated $\omega$ values are between 37.145–39.621, all of which are higher than the average value of the mantle (36.84). Therefore, the characteristics of low $\mu$, high $\omega$ of lead isotope composition in the deposit indicate that the lead has the
characteristics of the lower crustal sources, but some may come from the upper crust [7].

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 and pyrite, which clearly shows that the calcite was formed after the mineralization stage. The \( \delta^{13}C_{\text{VPDB}} \) values of calcite range from -10.26 ‰ to -3.26 ‰, which mainly focus from -8 ‰ to -7 ‰, and the average value is -7.30 ‰.

The C isotope geochemistry of calcite has been used previously to trace the origin of hydrothermal fluids. As calculated, the \( \delta^{13}C_{\text{VPDB}} \) 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 ‰), 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 ‰)[8]. But there are two samples whose values are at the edge of -10.3 ‰, suggesting that strong isotope fractionation occurred when deep source fluids migrated in the form of methane. Methane in metallogenic field was oxidized to carbon dioxide, further precipitated to form calcite.

H and O isotopic composition: Hydrogen and oxygen isotopes are important indicators for the evolution of ore fluids. \( \delta^{18}O_{\text{SMOW(H2O)}} \) values were calculated by using the formulas: \( 1000 \ln{\alpha} = \delta^{18}O_{\text{SMOW}} - \delta^{18}O_{\text{SMOW(H2O)}} = 3.38 \times 10^6 T^{-2} - 3.4 \)[9]. The \( \delta^{18}O_{\text{SMOW(H2O)}} \) and \( \delta D_{\text{SMOW}} \) values of quartz fluid inclusions range from 2.3‰ to 4.6‰ and from -107‰ to -85‰, respectively.

The \( \delta^{18}O_{\text{SMOW(H2O)}} \) values of the quartz from the deposit vary from 2.3 ‰ to 4.6 ‰, with a peak from 3.0 ‰ to 4.0 ‰, which fall in the range for magmatic water[10] and suggest a magmatic-hydrothermal origin. The \( \delta D \) values of the fluids vary from -107 ‰ to -85 ‰, which are lower than those for magmatic water (-85‰ to -50 ‰). If an H\(^+\) or CH\(^+\) bearing hydrothermal fluid encounters an oxidizing environment, the H\(_2\)O will become depleted in deuterium. However, this effect is small in natural hydrothermal systems because the volume of H\(_2\)O involved is enormous. Thus, a magmatic-hydrothermal fluid, but with mixing between the magmatic water and heated meteoric groundwater, can account for the stable isotope data derived from the deposit.

5 Conclusion

The mineralization age of the Shimensi deposit occurred at the same time as other Early Cretaceous deposits of the Middle-Lower Yangtze Valley mineralization belt, Lower Yangtze metallogenic province, ranging from 150–121 Ma. The deposits are
spatially close and temporally coeval with the Middle-Lower Yangtze Valley mineralization belt. Mineralization in the Lower Yangtze metallogenic province occurred at the subduction zone of two paleo-blocks and triggered by the tectonic transition.

The subduction of the Paleo-Pacific Plate beneath the Eurasian Plate resulted in lithospheric thickening and subsequent delamination, and consequently the principal N-S stress field in eastern China changed progressively to an E-W orientation from 170 Ma to 135 Ma [11]. Maximum lithospheric thinning occurred in the late Mesozoic, which resulted in the interaction between the asthenospheric mantle and crust. The resulting crustal heating caused intense magmatism, mineralization, and widespread development of extensional structures in eastern China. The eastern part of the Eurasian continent was an active continental margin at ca. 180 Ma, as the Izanagi Plate subducted orthogonally beneath the continent. At ca. 160 Ma this plate rotated clockwise towards the north, with the subduction orientation becoming oblique with respect to the continental margin. This movement was associated with metallic mineralization controlled by regional NE-SW strike-slip faults. Asthenospheric upwelling along the subducting slab window between 150 and 126 Ma, triggering partial melting of the overlying continental crust with a high W background content in the back-arc setting, resulting in a highly-fractionated, volatile-rich, peraluminous magma.

The highly fractionated S-type granites in the deposit are strongly peraluminous and highly alkalic, with high Ga/Al ratios. These rocks are enriched in LILEs, such as Rb, and are depleted in HFSEs, such as Zr, Nb, Ti. These granites formed at relatively low temperatures (679–760 °C) according to the zircon saturation temperatures. These εNd(t) values of the granites varied from −7.78 to −7.47, with the two-stage modal ages of 1568 Ma to 1543 Ma [2]. The tungsten concentrations of metapelitic rocks of the Shuangqiaoshan Group are as high as 12 ppm [12], which is much higher than that of typical crustal rocks at 1–2 ppm [13]. Tungsten is a strongly incompatible element, and partial melting and extreme fractional crystallization can lead to additional enrichment of the element. These observations indicate that the Shuangqiaoshan Group metapelite, with high W background concentrations, is the most likely source for the ore components in the Shimensi deposit.

The ascent of the volatiles-rich magma resulted in exsolution of the ore-bearing magmatic hydrothermal fluid, large-scale alkaline replacement in the wallrocks, and greisenization, silification and K-feldspar alteration of wall rocks in the deposit. The existence of volatiles, such as F and B, can increase the solubility and enrichment of tungsten in magma. Ore-forming fluid filled joints and fractures, forming the veinlet-disseminated style of orebodies. The Jiuling batholith, which is rich in calcium, contributed the Ca²⁺ that combined with the WO₄²⁻ in the ore-forming fluid to form scheelite along the contact between the Cretaceous biotite granite and the Neoproterozoic biotite granodiorites. When fractures in the region penetrated the top of the porphyritic biotite granites, the exsolving high-temperature liquid released a vapor and a crypto-explosion occurred, resulting in the formation of ore-
bodies of the hydrothermal crypto-explosive breccia style of mineralization. The quartz vein style orebodies formed last, because they cut both igneous rock units and the two other styles of orebodies (Fig. 2).

Fig. 2: Metallogenic model of the Shimensi deposit

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References


