In situ trace elements and Sr isotopes in scheelite and S-Pb isotopes in sulfides from the Shiweidong W–Cu deposit, giant Dahutang ore field: Implications to the fluid evolution and ore genesis

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A R T I C L E   I N F O

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A B S T R A C T

The Shiweidong W–Cu polymetallic deposit, with resources of 300,000 tWO3 and 200,000 t Cu, is one of the major tungsten polymetallic deposits in the giant Dahutang ore field. This study conducted a series of in-situ analyses on scheelite and sulfides, aiming to provide some new insights into the sources, hydrothermal ore-forming processes, fluid evolution history and genesis of this deposit, which is of importance to understand the formation of the super-large Dahutang ore field. Quartz vein- and veinlet-disseminated-type tungsten ore bodies are mainly hosted in Neoproterozoic granodiorite and/or the Yanshanian porphyritic two-mica granites. Four stages of mineralization from early to late are identified in this deposit: 1) pegmatite stage; 2) silicate-oxide stage; 3) oxide-sulfide stage; and 4) sulfide stage. The δ13C-CDT values of stage 3 chalcopyrite and pyrite are from −1.73‰ to −1.46‰ and from −1.66‰ to −0.31‰, respectively, indicating a magma-related hydrothermal origin. The 206Pb/204Pb, 207Pb/204Pb and 208Pb/204Pb ratios of pyrite range from 18.169 to 18.295, 15.650 to 15.679, and 38.496 to 38.525, respectively, revealing a crust origin for the Pb. Trace element compositions of scheelite show that the both stage 2 scheelite (scheelite-II) and stage 3 scheelite (scheelite-III) have high contents of Nb and REEs. The scheelite-II has a narrow range of the Y/Ho ratios (16.2–18.3), whereas those of scheelite-III shows variable Y/Ho ratios of 29.2–41.0, obviously high 87Sr/86Sr ratios of 0.72640–0.73336, whereas scheelite-III shows variable Y/Ho ratios of 20.6–96.9, positive Eu anomalies (Eu/Eu* = 1.31–7.11) and relatively high 87Sr/86Sr ratios of 0.73496–0.76098. These data indicated that the Eu anomalies and Sr isotopic compositions of scheelite-II were inherited from magmatic-hydrothermal fluids, whereas those of scheelite-III were sourced from modified fluids due to intense fluid-rock interaction and input of meteoric fluids. Our data also reveal that the REEs of scheelite-II and scheelite-III are mainly controlled by the substitution mechanism of $3Ca^2+ = Ca + 2REE^{3+}$. The W-rich reduced fluids and intense fluid-rock interactions, which could provide enough W and Ca, are likely the key factors for the formation of scheelite in the Shiweidong tungsten deposit.

1. Introduction

South China, one of the most significant metallogenic domains in the world, holds abundant tungsten and other rare metal resources (Zhai et al., 1999; Mao et al., 2008; Chen et al., 2014; Hu et al., 2017; Zhou et al., 2018). Formerly, tungsten resources are mainly located in the Nanling range, which hosts a large number of tungsten deposits e.g., Shizhuyuan, Yaogangxian, Xitian and Dengfuxian in Hunan Province, and Xihuashan and Taoxikeng in Jiangxi Province. (Peng et al., 2006; Guo et al., 2011; Cai et al., 2012; Hu et al., 2012; Chen et al., 2016; Cao et al., 2018a,b, 2020a,b). Recently, a series of tungsten deposits were identified in the Jiangnan Orogenic Belt of South China, including, Zhuxi, Dahutang, Dongyuan, Zhuxiling, Shangjinshan and Xiaoyao (Table 1; Zhou et al., 2011; Mao et al., 2013; Jiang et al., 2015; Huang, 2017; Mao et al., 2017; Dai et al., 2018; Song et al., 2018a; Su et al., 2018; Tang et al., 2019). The discovery of these giant deposits shows the great metallogenic potential in the Jiangnan Orogenic Belt. It has been proposed that the giant tungsten polymetallic mineralization in...
Table 1

<table>
<thead>
<tr>
<th>Province</th>
<th>Deposit Type of mineralization</th>
<th>Ore-forming age</th>
<th>Rock-forming age</th>
<th>Host rocks</th>
<th>Major ore minerals</th>
<th>References</th>
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<tbody>
<tr>
<td>Jiangxi</td>
<td>Quartz vein-, and veinlet-disseminated-type</td>
<td>140.9 ± 3.6 Ma</td>
<td>144.0 ± 0.6 Ma</td>
<td>Neoproterozoic Biotite granodiorite and Yanshanian granitoids</td>
<td>Wolframite, scheelite and pyrite</td>
<td>Fan et al. (2019), Feng et al. (2012) and Xiang et al. (2013)</td>
</tr>
<tr>
<td>Dalingshang</td>
<td>Quartz vein-, veinlet-disseminated-, and cryptoexplosion breccia-type</td>
<td>133.7 ± 0.5 Ma</td>
<td>143.7 ± 1.2 Ma</td>
<td>Neoproterozoic Biotite granodiorite and Yanshanian granitoids</td>
<td>Wolframite, scheelite and pyrite</td>
<td>Peng et al. (2018) and Huang and Jiang (2014)</td>
</tr>
<tr>
<td>Zhuxi</td>
<td>Skarn type</td>
<td>150.6 ± 1.5</td>
<td>153.5 ± 1.0 Ma</td>
<td>Skarn rocks between Yanshanian granitoids and Neoproterozoic carbonatite</td>
<td>Scheelite and molybdenite</td>
<td>Pan et al. (2017, 2018)</td>
</tr>
<tr>
<td>Anhui</td>
<td>Porphyritic type</td>
<td>149.4 ± 1.3 Ma</td>
<td>149.5 ± 1.3 Ma</td>
<td>Skarn rocks between Yanshanian granitoids and Neoproterozoic carbonatite</td>
<td>Scheelite and molybdenite</td>
<td>Chen et al. (2013) and Kong et al. (2016)</td>
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Scheelite (CaWO₄), the important W-bearing mineral in the tungsten deposits, is also the associated mineral in the hydrothermal Au, Sn and Mo deposits (Ghaderi et al., 1999; Brugger et al., 2002; Guo et al., 2016; Hazarika et al., 2016; Raju et al., 2016; Fu et al., 2017; Mackenzie et al., 2017; Orhan, 2017; Liu et al., 2019). Due to its crystal structure, scheelite has the ability to host high concentrations of some specific elements (e.g., REEs, Mo, Nb, Na and Sr) via substitution of Ca²⁺ or W⁶⁺ in the crystals, which could provide essential information about the source, physico-chemical conditions and evolutionary history of the ore-forming fluids (Bell et al., 1989; Raimbault et al., 1993; Ghaderi et al., 1999; Brugger et al., 2000, 2002, 2008; Song et al., 2014; Kozlik et al., 2016). High Sr concentration and low Rb concentration are unique properties of scheelite which makes it possible to use Sr isotopic compositions as a valid tracer to provide information about the tungsten source and the evolution of fluids (Li et al., 2018; Zhao et al., 2018). Recently, the in-situ laser ablation (multi-collector) inductively coupled plasma-mass spectrometry (LA–(MC) ICP–MS) has been widely used in the analyses of the trace element compositions and Sr isotopes of scheelite (e.g., Fu et al., 2017; Sun and Chen, 2017; Li et al., 2018; Peng et al., 2018; Zhao et al., 2018; Liu et al., 2019). With the help of these highly precise analysis techniques, the change in physico-chemical conditions of the ore-forming fluids could be reconstructed based on REE behaviors (Zhao et al., 2018). In addition, the interaction between the fluids and rocks during the ore-forming process could also be identified from the REE patterns, especially Eu anomalies (Brugger et al., 2008; Sun and Chen, 2017; Peng et al., 2018). Some authors have argued that REEs in scheelite could be inhomogeneous, even in a single grain containing a few crystals, and that this might result from the dynamic nature of hydrothermal systems (Brugger et al., 2000; Peng et al., 2010). Therefore, more detailed studies of the geochemical and isotopic compositions of scheelite can potentially provide an effective tool for better understanding of the tungsten mineralization process.

The Shiweidong tungsten deposit, located in the Middle Jiangnan Orogenic Belt, is an important part of the giant Dahutang ore field with resources of 300,000 t WO₃ and 200,000 t Cu (Feng et al., 2012). Previous studies mainly focused on the geological features, rock- and fluid evolution history and genesis of the Shiweidong tungsten deposit. Combined with the previously published geochemical data for other tungsten deposits in the Dahutang ore field, the present study aims at providing some new insights into the source, hydrothermal ore-forming processes, fluid evolution history and genesis of the Shiweidong tungsten deposit.

2. Geological settings

2.1. Regional geology

The South China Block (SCB) is composed of the Yangtze Block to the northwest and the Cathaysia Block to the southeast. The Jiangnan Orogenic Belt, with a length of about 1500 km and a NE orientation, was formed by the collision between the Yangtze Block and Cathaysia Block at ca. 860–820 Ma, which may be related to the formation of the...
Rodinia supercontinent (Charvet, 2013; Yao et al., 2013; Xu et al., 2017). The Middle- and Eastern-Jiangnan Orogenic Belt is adjacent to the Middle-Lower Yangtze River Belt in the northeast which is bounded by the Yangxing-Changzhou fault (Fig. 1). The Middle-Lower Yangtze River Belt is famous for its world-class porphyry- and skarn-type Cu-Au polymetallic mineralization, whereas the Middle- and Eastern-Jiangnan Orogenic Belt contains the giant W–Cu–Mo polymetallic mineralization (Table 1; Mao et al., 2006, 2017; Mao et al., 2013; Jiang et al., 2015; Wang et al., 2015; Xie et al., 2015; Yan et al., 2015; Huang, 2017; Dai et al., 2018; Song et al., 2018a; Su et al., 2018). Numerous large and super large tungsten deposits were located in the Middle to Lower Yangtze River Valley Belt in the northeast which is bounded by the Yangxing-Changzhou fault (after Mao et al., 2017). 1-Middle Jurassic to Cretaceous paralic clastic rocks; 2-Cambrian to Early Triassic strata marine clastic and carbonates rocks and Middle Triassic to Early Jurassic paralic clastic rocks; 3-Jiulong Massif: Neoproterozoic epimetamorphic and sedimentary rocks; 4-Cretaceous granitoids; 5-Jurassic granitoids; 6-Neoproterozoic granite; 7-Neoproterozoic ophiolite; 8-River and lake; 9-W deposits; 10-Sn deposits; 11-Cu deposits; 12-Au deposits; 13-Pb-Zn deposits; 14-Research deposits.

![Geological map of the Distribution of the Middle-Lower Yangtze River Valley Belt in the north and the Middle- and Eastern-Jiangnan Orogenic Belt in the south, showing the location of the W–Cu–Au–Mo–Pb–Zn deposits.](image)

2.2. Geology of ore deposit

The Shiweidong deposit, located in the southern part of the giant Dahutang ore field, is one of the large-scale tungsten polymetallic deposits in this ore field. Neoproterozoic Shuangqiao basin Group metamorphic rocks, mainly composed of gray-green/dark-gray phyllite and slate, are well-exposed in this district (Fig. 2b). A series of NE-trending faults and/or fracture zones were developed in these metamorphic rocks, with these fault fracture zones being mostly filled by breccia, cataclase and mylonite. The intrusions include the Jiuling Neoproterozoic granitic batholith (ca. 850 Ma) and the Yanshannian granitoids (144.2–130.3 Ma). The Jiuling Neoproterozoic granitic batholith is mainly composed of medium to coarse-grained biotite granodiorites, whereas the Yanshannian granitoids are fine to coarse-grained porphyritic biotite granites, fine grained biotite (muscovite) granites and granite porphyries (Huang and Jiang, 2012, 2013, 2014; Sun et al., 2017). The Neoproterozoic granodiorite is mainly comprised of quartz, plagioclase, K-feldspar, biotite, muscovite, and cordierite, with minor zircon, apatite, and ilmenite (Sun et al., 2017). The Yanshannian granitoids mostly occur as stocks, bosses and apophyses and were intruded into the Neoproterozoic Shuangqiao basin Group metamorphic rocks and Neoproterozoic granodiorite batholith. Rock-forming minerals consist of quartz, plagioclase, K-feldspar, biotite, muscovite, with accessory minerals of apatite, zircon, monazite, fluorite, titanite and ilmenite (Fan et al., 2019).

Two types of ore bodies, quartz vein- and veinlet-disseminated-type, are identified in the Shiweidong deposit (Feng et al., 2012) and 117 wolframite-bearing quartz veins are exploited (Jiang et al., 2015). These wolframite-bearing ore veins can be subdivided into two groups in terms of the attitude. The Group 1 ore veins are mainly EW- or NE-trending, with a maximum length of 573 m, maximum dipping depth of 522 m, an average thickness of 0.53 m and an average grade of 1.81% WO3 (Jiang et al., 2015). The quartz vein-type ore minerals are mainly composed of wolframite, scheelite,
molybdenite, chalcopyrite, pyrite, and magnetite (Fig. 3). The veinlet-disseminated-type ore bodies are mostly hosted in the Neoproterozoic granodiorite and the Yanshanian porphyritic two-mica granites (Jiang et al., 2015; Song et al., 2018b). A total of 36 ore bodies were discovered, and they have lengths of 100–600 m, dipping depths of 122–770 m, thicknesses of 2.81–80.3 m and ore grades of 0.066–0.291% WO₃, respectively (Jiang et al., 2015; Song et al., 2018b). Ore minerals include scheelite, wolframite, chalcopyrite, molybdenite, pyrite, and magnetite (Fig. 3). Based on field investigation, mineral assemblages and mineral paragenesis, four stages of mineralization, from early to late, were identified: 1) pegmatite stage; 2) silicate-oxide stage; 3) oxide-sulfide stage; and 4) sulfide stage. The silicate-oxide stage and oxide-sulfide stage are the main mineralization stages.
In the silicate-oxide stage, ore veins are predominantly composed of quartz with wolframite, scheelite and molybdenite (Fig. 3a, d, e and h). Abundant wolframite and scheelite occur in this stage, making it a significant mineralization stage. Wolframite commonly occurs in large quartz ore veins, exhibiting coarse and euhedral crystals and tabular structure (Fig. 3a, d, e and h). However, some chalcopyrite and magnetite occur in the inner part of the wolframite (Fig. 3d). The scheelite in this stage (scheelite-II) commonly coexists with the wolframite, with euhedral and/or subhedral crystals (Fig. 3e and h). In addition, a small number of molybdenite forms in this stage (Fig. 3a).

In the oxide-sulfide stage, ore veins consist of quartz, scheelite, molybdenite, pyrite and chalcopyrite. In this stage, scheelite (scheelite-III) as subhedral and/or anhedral crystals always coexists with chalcopyrite and pyrite (Fig. 3b, c and g). Pyrite follows tungsten deposition, and then is mostly replaced by chalcopyrite (Fig. 3g). Chalcopyrite is abundant, and largely occurs as replacement and/or rimming of the early formed minerals (e.g., wolframite, scheelite, molybdenite and pyrite) (Fig. 3b, d, f and g). The sulfide stage mainly forms pyrite and chalcopyrite (Fig. 3i).

3. Sampling and analytical techniques

A large number of tungsten-bearing ores were collected from the Shiweiudong deposit. Thin sections of ores were prepared, and then observed and photographed using an electron microscope. Pyrite and chalcopyrite from the oxide-sulfide stage were chosen for in-situ LA–MC–ICP–MS sulfur and lead isotopic analyses. In addition, scheelite from the silicate-oxide stage were chosen for in-situ LA–MC–ICP–MS sulfur and lead isotopic analyses. In addition, scheelite (scheelite-III) as subhedral and/or anhedral crystals always coexists with chalcopyrite and pyrite (Fig. 3b, c and g). Pyrite follows tungsten deposition, and then is mostly replaced by chalcopyrite (Fig. 3g). Chalcopyrite is abundant, and largely occurs as replacement and/or rimming of the early formed minerals (e.g., wolframite, scheelite, molybdenite and pyrite) (Fig. 3b, d, f and g). The sulfide stage mainly forms pyrite and chalcopyrite (Fig. 3i).

3.1. In-situ LA–MC–ICP–MS sulfur isotopic analyses

In situ sulfur isotopic analyses of pyrite and chalcopyrite were performed using the RESolution M-50 laser ablation system (ASL, Australia), which was equipped with a 193 nm ArF CompexPro102 excimer laser and Nu Plasma 1700 multi-collector inductively coupled plasma mass spectrometer (MC–ICP–MS, NP-1700) in the State Key Laboratory of Continental Dynamics, Northwest University, Xi’an, China. Laser spot sizes of 25–37 µm were used at an energy density of 3.6 J/cm² and a repetition rate of 3 Hz. Each analysis included 30 s baseline and 60 s of ablation, with He gas (gas flows = 0.86 L/min) as the carrier gas during the analytical process. Sixteen Faraday cups and three ion counters were used to determine the sulfur isotopic compositions, with a H5 cup for 34S, an Ax cup for 33S, and a L4 cup for 32S. In-house sulfur reference material (PY-4, δ34S_CDT = 1.7 ± 0.3‰, Bao et al., 2017) was used for external standard bracketing. The measurement accuracy was within the range of 0.23–0.41‰ (Bao et al., 2017). The detailed procedures used for sulfide in-situ sulfur isotopic analyses were reported in Yuan et al. (2018) and Chen et al. (2017).

3.2. In-situ LA–MC–ICP–MS lead isotopic analyses

In situ lead isotopic analyses of pyrite from the oxide-sulfide stage were conducted on polished sections, using a Nu Plasma™ multi-collector ICPMS with a femtosecond laser ablation system (fsLA–MC–ICPMS) at the State Key Laboratory of Continental Dynamics, Northwest University, Xi’an, China. Argon and helium were used as the carrier gases for laser ablation. The Ti aerosol and the sample aerosol was mixed homogeneously in a glass container, and then introduced into the ICP for atomization and ionization. During the analysis, Faraday collectors L4, L3, L2, L1, AX, H1, H2 were used to collect the ion beam 204Hg, 203Tl, 202Hg + 204Pb, 205Tl, 206Pb, 207Pb, 208Pb, respectively. Thallium was used to monitor and correct the instrumental mass discrimination, and 206Hg was used to correct for the isobaric overlap of 204Hg on 206Pb. The time-resolved analysis (TRA) mode with an integration time of 0.2 s was employed to obtain Pb isotopic ratios, and laser ablation was performed in the line scan ablation mode at a speed of 5 µm/s. Each line scan analysis consisted of background collection for 40 s followed by an additional 50 s of ablation for signal collection and 40 s of wash time to reduce memory effects and to allow the instrument to stabilize after each gas addition. To ensure the accuracy of the 206Pb signal obtained from different samples with disparate Pb concentrations, samples were ablated with laser line scans approximately 120 µm in length and 30–65 µm in width with adjustable laser frequency. NIST 610 was used as a quality control sample and was analyzed once for every five sample points. The measurement accuracy of lead isotopic compositions for pyrite were better than 0.057% (Bao et al., 2017). Detailed description of the measuring procedures is available in Bao et al. (2017) and Chen et al. (2017).

3.3. In-situ LA–ICP–MS trace element analyses of scheelite

Trace element analysis of minerals was conducted by LA-ICP-MS at the Wuhan SampleSolution Analytical Technology Co., Ltd., Wuhan, China. Detailed operating conditions for the laser ablation system and the ICP-MS instrument and data reduction are the same as described by Zong et al. (2017). Laser sampling was performed using a GeolasPro laser ablation system that consists of a COMPexPro 102 ArF excimer laser (wavelength of 193 nm and maximum energy of 200 mJ) and a MicroLas optical system. An Agilent 7700e ICP-MS instrument was used to acquire ion-signal intensities. Helium was applied as a carrier gas. Argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP. This laser ablation system also includes a “wire” signal smoothing device (Hu et al., 2015). The spot size and frequency of the laser were set to 32 mm and 5 Hz, respectively, in this study. Trace element compositions of minerals were calibrated against various reference materials (BHVO-2G, BCR-2G and BIR-1G) without using an internal standard (Liu et al., 2008). Each analysis incorporated a background acquisition of approximately 20–30 s followed by 50 s of data acquisition from the sample. An Excel-based software ICPMSDataCal was used to perform off-line selection and integration of background and analyzed signals, time-drift correction, and quantitative calibration for trace element analysis (Liu et al., 2008).

3.4. In-situ LA–MC–ICP–MS strontium isotopic analyses of scheelite

Sr isotope ratios of scheelite were measured by a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Bremen, Germany) in combination with a Geolas HD excimer ArF laser ablation system (Coherent, Göttingen, Germany) at the Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China. The Neptune Plus was equipped with nine Faraday cups fitted with 1011 Ω resistors. The Faraday collector configuration of the mass system was composed of an array from L4 to H3 to monitor Kr, Rb, Er, Yb and Sr. The combination of the high-sensitivity X-skimmer cone and Jet-sample cone was employed. In the laser ablation system, helium was used as the carrier gas for the ablation cell. For a single laser spot ablation, the spot diameter ranged from 60 to 160 μm dependent on Sr signal intensity. The pulse frequency was from 8 to 15 Hz, but the laser fluence was kept constant at ~10 J/cm². The data reduction for LA–MC–ICP–MS analysis was conducted using ICPMSDataCal (Liu et al., 2010). The interference correction strategy was the same as the one reported by Tong et al. (2016). First, the regions of integration for both gas background and sample were selected. Following background correction, which removes the background Kr⁺ signals, no additional Kr peak stripping was applied. Interferences were corrected in the following sequence:

(1) The interferences of 166Er⁺ on 84Sr, 170Er⁺ and 179Yb⁺ on 86Rb, 172Yb⁺ on 86Sr, and 174Yb⁺ on 87Sr were corrected based on the measured signal intensities of 166Er⁺, 172Yb⁺ and the
natural isotope ratios of Er and Yb (Berglund and Wieser, 2011); (2) The isobaric interference of \(^{87}\text{Rb}\) on \(^{87}\text{Sr}\) was corrected by monitoring the \(^{85}\text{Rb}\) signal intensity and a user-specified \(^{87}\text{Rb}/^{85}\text{Rb}\) ratio using an exponential law for mass bias. The user-specified \(^{87}\text{Rb}/^{85}\text{Rb}\) ratio was calculated by measuring reference materials with a known \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio. Following the interference corrections, mass fractionation of Sr isotopes was corrected by assuming \(^{88}\text{Sr}/^{86}\text{Sr}\) = 8.375209 (Tong et al., 2016) and applying the exponential law. Two natural samples of apatite, Durango and MAD were used as the (unknown) samples for in situ Sr isotope analysis of apatite. The chemical and Sr isotopic compositions of Durango and MAD have been reported by Yang et al. (2014).

4. Results

4.1. Sulfur isotopes of sulfides

The in-situ LA–MC-ICP–MS sulfur isotopic compositions of chalcopyrite and pyrite from the Shiweidong tungsten deposit are shown in Table 2. The measured \(^{34}\text{S}_\text{VCDT}\) values of chalcopyrite and pyrite range from \(-1.73\%\) to \(-1.46\%\) and from \(-1.66\%\) to \(-0.31\%\), respectively (Fig. 4). These data are consistent with the previously reported sulfur isotopic compositions in the Dalingshang deposit, giant Dahutang ore field (Peng et al., 2018).

4.2. Lead isotopes of sulfides

The Pb isotopic compositions of pyrite are listed in Table 3. The measured \(^{206}\text{Pb}/^{204}\text{Pb}\), \(^{207}\text{Pb}/^{204}\text{Pb}\) and \(^{208}\text{Pb}/^{204}\text{Pb}\) ratios range from 18.169 to 18.295, 15.650 to 15.679, and 38.496 to 38.525, respectively.

4.3. Trace element compositions of scheelite

The trace element compositions of scheelite are presented in Table 4. Generally, the scheelite-II and scheelite-III in the Shiweidong deposit have relatively low concentrations of Na, Cu, Zn, Ga, Rb, Zr, and Sn (Fig. 5). Specifically, the scheelite-II has low Na (0.26–4.60 ppm) and Rb (0.01–0.81 ppm) concentrations which are similar to that of the scheelite-III with Na content of 0.17–8.16 ppm and Rb content of 0.01–0.53 ppm, respectively (Fig. 5). The Mo content of scheelite-II is 0.29 ppm to 29.6 ppm (mean = 6.2 ppm), higher than scheelite-III of 0.22–4.09 ppm (mean = 1.67 ppm). Scheelite-II has Sr contents of 92.1–1636 ppm (mean = 269 ppm), lower than the

![Fig. 4. Histogram of the S isotopic values of the sulfides in the Shiweidong and Dalingshang tungsten deposits. The data of the Dalingshang deposit were from Peng et al. (2018).](image-url)
sulfur-bearing minerals in the Shiweidong deposit are molybdenite, the adjacent Dalingshang deposit (Peng et al., 2018; Fig. 4). The major tungsten deposit are listed in Table 5. Both scheelite-II and scheelite-III have relatively low 87Rb/86Sr ratios, ranging from 0.00002 to 0.00579 and from 0.00243 to 0.018477, respectively, indicating that the radiogenic 87Sr/86Sr can be ignored. The 86Sr/86Sr ratios of the scheelite-II and scheelite-III are of 0.72640–0.73496 and 0.73137–0.76098, respectively, and represent the initial Sr isotopic compositions of the scheelite (Fig. 7).

### 4.4. Strontium isotopes of scheelite

Strontium isotopic compositions of scheelite in the Shiweidong tungsten deposit are listed in Table 5. Both scheelite-II and scheelite-III have relatively low 87Rb/86Sr ratios, ranging from 0.00002 to 0.00579 and from 0.00243 to 0.018477, respectively, indicating that the radiogenic 87Sr/86Sr can be ignored. The 86Sr/86Sr ratios of the scheelite-II and scheelite-III are of 0.72640–0.73496 and 0.73137–0.76098, respectively, and represent the initial Sr isotopic compositions of the scheelite (Fig. 7).

### 5. Discussion

#### 5.1. Sources of sulfur and lead

Sulfides formed in different geochemical systems have different isotopic compositions. Therefore, the sulfur isotopes of sulfides in the hydrothermal deposits can be used as a key tracer in determining the sources of metallic mineral deposits (e.g., Ohmoto and Goldhaber, 1997; Jin et al., 2015; Laflamme et al., 2018; Peng et al., 2018; Tsang et al., 2019). The δ34S values for both pyrite and chalcopyrite in this study, ranging from −1.66% to −0.31% and from −1.73% to −1.46% (Table 2), respectively, are consistent with published data for the adjacent Dalingshang deposit (Peng et al., 2018; Fig. 4). The major sulfur-bearing minerals in the Shiweidong deposit are molybdenite, pyrite and chalcopyrite with few occurrences of sulfate. The pyrite has higher δ34S values than the chalcopyrite, which suggests that the sulfur isotopes of these sulfides could reflect the sulfur isotopic signatures of the ore-forming fluids (Ohmoto and Goldhaber, 1997). The sulfide sulfur isotope data falls within the range of granitic rocks, indicating a magmatic origin (Fig. 8).

The lead isotopes of the pyrite in the Shiweidong deposit show narrow ranges for 206Pb/204Pb, 207Pb/204Pb and 208Pb/204Pb ratios, which are 18.169–18.295, 15.650–15.679 and 38.496–38.525, respectively. These Pb isotopic ratios are similar to those in the Dalingshang deposit and the related ore-forming Yanshannian granites in Dahutang giant ore field, indicating that both the Shiweidong deposit and Yanshannian granites share a similar lead source, both showing a distinctly crustal origin (Fig. 9).

### 5.2. Fluids evolution history

As shown in Table 4, both the scheelite-II and scheelite-III have high Sr concentrations and extraordinarily low Rb concentrations, with negligibly low Rb/Sr ratios (mostly lower than 0.001), thus the measured 87Sr/86Sr ratios could reflect the initial 87Sr/86Sr ratios. The 87Sr/86Sr ratios of scheelite-II (0.72640–0.733496) are lower than those of scheelite-III (0.73137–0.76098), but both are characterized by high 87Sr/86Sr ratios. The 87Sr/86Sr ratios of scheelite-II are consistent with those of related ore-forming granites (0.719650–0.736520), indicating that the early stage scheelite shares a similar 87Sr/86Sr isotopic composition with the ore-forming granites (Mao et al., 2015; Fig. 7). Therefore, the scheelite-II might be formed in fluids which were likely inherited from the initial magmatic-hydrothermal fluids. However, the scheelite-III has much higher 87Sr/86Sr ratios than those of the related ore-forming granites and the scheelite-II, which indicates that the high 87Sr/86Sr ratios of scheelite-III were not inherited from initial magmatic-hydrothermal fluids. The variation of 87Sr/86Sr ratios in scheelite from early stage to late stage likely reflects a change in the Sr isotopic composition of the ore-forming fluids. Several models have been proposed to explain Sr isotopic heterogeneities in various hydrothermal systems, including: 1) mixing of magmatic-hydrothermal fluids and meteoric fluids (Luders et al., 2009), 2) modification of the Sr
Fig. 5. Chemical covariation of the scheelite from the Shiweidong tungsten deposit.

Fig. 6. Rare earth element chondrite-normalized patterns of the scheelite in the Shiweidong deposits. Normalized values are from Taylor and McLennan (1985). Data of the ore-forming granites are from Mao et al. (2015).
isotopic compositions in hydrothermal fluids due to infiltration into chemically heterogeneous lithologies (Kempe et al., 2001; Bau et al., 2003), and 3) release of $^{87}$Sr of some specific minerals into the hydrothermal fluids caused by fluid-rock interaction (Glodny and Grauert, 2009; Kozlik et al., 2016). The first model is not the key reason in this case, since meteoric fluids commonly have relatively low $^{87}$Sr/$^{86}$Sr ratios ($^{87}$Sr/$^{86}$Sr = 0.70456, 2003), and 3) release of $^{87}$Sr of some specific minerals into the hydrothermal fluids caused by fluid-rock interaction (Kempe et al., 2001; Bau et al., 2009). Since Y/Ho ratios are fairly stable in the hydrothermal system, it could be used as the efficient tracer to reflect the source fluids (Bau and Moeller, 1992; Irber, 1999). The Y/Ho ratios of scheelite-II are concentrated in a relatively narrow range of 16.2–31.0, whereas the scheelite-III has more variable Y/Ho ratios of 20.6–96.9. The relatively uniform Y/Ho ratios of the scheelite-III indicate that it might have precipitated from a single hydrothermal fluid, whereas the variable Y/Ho ratios of the scheelite-III suggest mixed hydrothermal fluids (Fig. 10). This conclusion was fully supported by the H–O isotopic signatures of fluid inclusion studies on the other tungsten deposits in the Dahutang ore field, indicating that the primary magmatic-hydrothermal fluids and mixed hydrothermal-meteoric fluids were involved in the major and latter metallogenic stages, respectively (Peng et al., 2018).

In conclusion, we propose that the early stage fluids originated from magmatic-hydrothermal fluids, whereas the latter stage fluids were modified by fluid-rock interaction and the involvement of meteoric fluids. In addition, the rise of $^{87}$Sr/$^{86}$Sr ratios in scheelite-III was mainly controlled by the fluid-rock interactions.

### 5.3. Mechanism of REE substitution

Since the ionic radii of trivalent REEs are similar to that of the bivalent Ca, REE$^{3+}$ can substitute for Ca$^{2+}$ in scheelite (Ghaderi et al., 1999). Substitution of REE$^{3+}$ for Ca$^{2+}$ in scheelite is mainly through the following mechanisms:

$$2Ca^{2+} + Na^+ + REE^{3+}$$
$$Ca^{2+} + W^{6+} + Nb^{5+} + REE^{3+}$$
$$3Ca^{2+} = Ca + 2REE^{3+}$$

where □ is a site vacancy.

In terms of Eq. (1), if Na provides the charge balance in scheelite, MREEs would preferentially enter the lattice by substitution in the Ca site because of their similar ionic radii, which results in MREE-rich patterns and high Na concentration (Ghaderi et al., 1999; Brugger et al., 2002). Eq. (2) would result in the high Nb concentration, which is nearly equal to the 2REE content and a positive correlation of Nb$^{5+}$ and Nd$^{3+}$ (Dostal et al., 2009). In this study, Eq. (1) is not applicable, since (1) both the scheelite-II and scheelite-III in the Shiweidong deposit contain relatively low Na concentrations of 0.74–3.0 ppm and

![Table 5](image)

<table>
<thead>
<tr>
<th>Spot No.</th>
<th>$^{87}$Rb/$^{86}$Sr</th>
<th>2σ</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
<th>2σ</th>
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</thead>
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</table>

![Fig. 7](image)

Fig. 7. Sr isotopic compositions of the Shiweidong tungsten deposits. The data of the Dahutang ore-related deposit were from Mao et al. (2015).
0.74–8.16 ppm, respectively; (2) they did not display MREE-rich patterns (Fig. 6); and (3) they both show poor correlation between Na versus ∑REE + Y–Eu (atom; Fig. 11a). In terms of the Eq. (2), it is unlikely the major substitution mechanism for the REE patterns of scheelite in this study, since no evidence for 1:1 correlation of Nb versus ∑REE + Y–Eu (atom) (Fig. 11b) and no clear correlation of Nb versus Nd were identified in this study (Fig. 11c).

In terms of the Eq. (3), this substitution mechanism could be the more applicable interpretation for the high REEs concentrations than that for Eq. (1) or Eq. (2). Commonly, Eq. (3) would lead to a relatively flat chondrite-normalized REE pattern (Fig. 6; Ghaderi et al., 1999). In addition, scheelite could inherit the REE compositions of the ore-forming fluids since Eq. (3) removes the ionic radii restrictions. Scheelite-II and scheelite-III are both enriched in LREE and have flat chondrite-normalized REE patterns, characteristics similar to that of the ore-forming granites in the Shiweidong tungsten deposit (Fig. 6; Huang and Jiang, 2014; Mao et al., 2015). Therefore, the substitution of REE3+ for Ca2+ into the scheelite-II and scheelite-III appear to be primarily controlled by the mechanism of Eq. (3).

5.4. Eu anomalies of scheelite

Scheelite Eu anomalies are mainly influenced by redox conditions, primary magmatic-hydrothermal fluids characteristics and modification by fluid-rock interaction (Ghaderi et al., 1999; Brugger et al., 2008; Peng et al., 2018; Sun et al., 2019). Eu can enter the scheelite lattice with other REE3+ through substitution in a Ca vacancy site as either Eu2+ or Eu3+ (Ghaderi et al., 1999). In addition, Eu2+ is preferentially
more incorporated than Eu\textsuperscript{3+}, therefore, it will cause negative Eu anomalies under highly oxidized conditions and positive Eu anomalies under reducing environment in scheelite, respectively (Ghaderi et al., 1999). A simple model, proposed by Ghaderi et al. (1999), could identify whether Eu\textsuperscript{2+} or Eu\textsuperscript{3+} dominates in scheelite. In this study, most of data from both of the scheelite-II and scheelite-III were plotted in the fields between the 1:1 to 10:1 ratio lines and 1:1 to 1:10 ratio lines (Fig. 11d), respectively, indicating that the Eu\textsuperscript{2+} in both the scheelite-II and scheelite-III were dominant and that they were crystallized in a reducing fluid (Ghaderi et al., 1999). Previous studies show that Mo could enter scheelite by substituting for W\textsuperscript{6+} as Mo\textsuperscript{6+} under oxidizing conditions (Hsu and Galli, 1973). Therefore, scheelite which crystallized from oxidized fluids would exhibit high Mo concentration (mostly higher than 10,000 ppm; e.g., Song et al., 2014; Fu et al., 2017). Both scheelite-II and scheelite-III have relatively low Mo concentrations, which are 0.29–29.6 ppm and 0.22–1.67 ppm, respectively, also indicating a reducing environment.

However, scheelite-II exhibits negative Eu anomalies which is inconsistent with a reducing condition, indicating that the redox condition is not the dominant factor causing the negative Eu anomalies. Since no fluid-rock interaction has been identified in the early stage mineralization, the fluid-rock interaction should be ruled out. The remaining possible explanation is that the negative Eu anomalies of scheelite-II were inherited from the primary magmatic-hydrothermal fluids. Since the substitution of REE\textsuperscript{3+} for Ca\textsuperscript{2+} in scheelite-II and scheelite-III is

Fig. 10. Plots of La/Lu ratios versus Y/Ho ratios scheelite from the Shiweidong tungsten deposit, modified from Irber (1999).

Fig. 11. Plots of (a) Na versus \(\sum\)REE + Y - Eu (as 100 atoms per CaWO\textsubscript{4} formula unit), (b) Nb versus \(\sum\)REE + Y - Eu (as 100 atoms per CaWO\textsubscript{4} formula unit), (c) Nb and Nd and (d) Eu\textsubscript{n} versus Eu*\textsubscript{n} for the scheelite from the Shiweidong and Dalingshang tungsten deposit. Note: (a), (b) and (d) are modified from Ghaderi et al., 1999). Eu*\textsubscript{n} = (Sm\textsubscript{n} × Gd\textsubscript{n})\textsuperscript{1/2}. Symbols are the same as those in Fig. 5.
mainly controlled by the mechanism of Eq. (3), we conclude that the REE patterns of scheelite-II and scheelite-III were inherited from the ore-forming fluids. Given the fact that the scheelite-II and scheelite-III both crystallized from reducing fluids, the redox condition might not cause the abrupt change from negative Eu anomalies of scheelite-II to positive Eu anomalies of scheelite-III. Therefore, fluid-rock interaction is the best interpretation for explaining the positive Eu anomalies of scheelite-III. The surrounding rocks are the Jilung Neooproterozoic granodiorite which has abundant feldspar, and fluid-rock interaction could result in breakdown of feldspar and release of abundant Eu$^{2+}$, thus causing the positive Eu anomalies. This phenomenon was also recognized in the nearby Dalingshang deposit (Peng et al., 2018).

5.5. Ore genesis and implications for regional tungsten polymetallic mineralization

The Middle Jiangnan Orogenic Belt, located in the collision zone between the Yangtze and Cathaysia Blocks, has experienced multi-stage tectonic and magmatic-thermal events which resulted in large scale granitic magmatism and tungsten polymetallic mineralization (e.g., Zhou et al., 2011; Mao et al., 2013; Jiang et al., 2015; Huang et al., 2017; Mao et al., 2017; Dai et al., 2018; Song et al., 2018a; Su et al., 2018). The giant tungsten polymetallic mineralization in this region was genetically related to the Yanshanian intermediate-acid granitic magmatism, which has been subdivided into three stages at 153–137 Ma, 137–129 Ma and 129–123 Ma (e.g., Wu et al., 2012; Huang and Jiang, 2014; Mao et al., 2015; Pan et al., 2018; Su et al., 2018). The reported ore-forming ages in this region mostly range from 150 Ma to 140 Ma, indicating a close relationship with the 153–137 Ma magmatism (Mao et al., 2013; Jiang et al., 2015; Pan et al., 2017; Su et al., 2018). The U-Pb age of the ore-forming granites in the Shiweidong deposit was 144.0 ± 0.6 Ma (Huang and Jiang, 2014), which is consistent with the molybdenite Re-Os age of 140.9 ± 3.6 Ma (Peng et al., 2012), indicating that the tungsten polymetallic mineralization was triggered by the Late Jurassic-Early cre-taceous granitic magmatism. The formation of these granites was likely related to asthenospheric upwelling in an extensional setting (Huang and Jiang, 2014; Mao et al., 2015; Su and Jiang, 2017). In addition, these ore-forming granites are mainly S-type, with negative εNd(t) values of −7.78 to −7.47 and TDM ages of 1543–1568 Ma, and were sourced from the argillaceous rocks of the Neooproterozoic Shuang-qiaoshan Group (Huang and Jiang, 2012). These argillaceous rocks, enriched in W, Cu, Au and other metals, could provide enough metals for the large-scale tungsten polymetallic mineralization in this region (Zuo, 2006). The in-situ sulfides S isopes of the Shiweidong deposit, reported in this study, range from −1.73‰ to −0.31‰, consistent with that of the other deposits in the Dahutang ore field, showing that the S was sourced from a magmatic origin (e.g., Yao et al., 2016; Peng et al., 2018; Song et al., 2018b; Zhang et al., 2018). The Pb isotopic compositions of sulfides in the Shiweidong deposit also suggested a crustal source for the Pb, consistent with the source of the related ore-forming granites (Mao et al., 2013; Huang and Jiang, 2014).

The Shiweidong and other tungsten deposits in the Dahutang ore field are characterized by wolframite and scheelite mineralization, which requires abundant Mn$^{2+}$, Fe$^{2+}$ and Ca$^{2+}$ in the fluids. Fluid-rock interaction would result in the decomposition of minerals (including biotite, chlorite and muscovite), release of abundant Fe$^{2+}$, and finally precipitation of wolframite (Lecumberri-Sanchez et al., 2017). As one of the major tungsten-bearing minerals, scheelite (CaWO$_4$) requires a source rich in the Ca$^{2+}$, and the fluid-rock interaction could lead to the release of Ca via metasomatism between the fluids and surrounding rocks (Shabeer et al., 2003). The high $^{87}$Sr/$^{86}$Sr and positive Eu anomalies of scheelite-III of the Shiweidong deposit indicate an intense fluid-rock interaction, which likely resulted in not only the release of Sr and Eu but also Ca from the breakdown of plagioclase, biotite, hornblende and other minerals. Therefore, the Ca-rich minerals in the surrounding Neoproterozoic granites were likely modified by the fluids, and this process could provide enough Ca and lead to the formation of scheelite (Jiang et al., 2015). It is possible that the redox state of the fluids also plays an important role in the precipitation of wolframite and/or scheelite (Wood and Samson, 2000). Common models suggest that WO$_4^{2-}$ and HWO$_4^-$ are the main tungsten species in ore-forming fluids and precipitation of wolframite and scheelite forms via the following reactions (Wood and Samson, 2000):

$$\text{WO}_4^{2-} + \text{MCl}_n^{2-n} => \text{MWO}_4^{2-} + n\text{Cl}^- + H^+$$

whereas the $M = (\text{Fe}, \text{Mn})^{2+}$ or Ca$^{2+}$ and $n = 0–2$.

Therefore, relatively low oxygen fugacities are needed to maintain the occurrences of Mn$^{2+}$ Fe$^{2+}$, and Ca$^{2+}$, and finally result in the formation of wolframite and scheelite. We thus conclude that, the W-rich source, intense fluid-rock interaction and the relatively reducing condition are in favor of the tungsten mineralization, which result in the formation of Shiweidong tungsten deposit and other deposits in the giant Dahutang ore field.

6. Conclusions

Based on detailed geological and geochemical studies of the Shiweidong W–Cu polymetallic deposit in the Dahutang ore field, we draw conclusions as follows:

1) The S and Pb isotopes of sulfides in the Shiweidong W–Cu polymetallic deposit imply that they likely originated from a magmatic source, mainly consisting of crust components.

2) Distinct Eu anomalies and Sr isotopes between scheelite-II and scheelite-III indicate that the early stage fluids were inherited from the primary magmatic-hydrothermal fluids, whereas, that the latter stage fluids were modified by intense fluid-rock interaction and input of the meteoric fluids.

3) Mechanisms of REE substitution in scheelite were mainly of this form: $3\text{Ca}^{2+} = \square \text{Ca} + 2\text{REE}^{3+}$.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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