Revision 3

Metal source and hydrothermal evolution of the Jiaoxi quartz vein-type tungsten deposit (Tibet): Insights from textural and compositional variations of wolframite and scheelite

YONG WANG¹,², CHUANKAI HE¹, JUXING TANG², JAN MARTEN HUIZENGA³,⁴,⁵, LIQIANG WANG², XINGHAI LANG¹

¹College of Earth Science, Chengdu University of Technology, Chengdu, 610059, China
²MNR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, CAGS, Beijing, 100037, China
³Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences, P.O. Box 5003, NO-1432, Ås, Norway
⁴EGRU (Economic Geology Research Centre), James Cook University; Townsville, Queensland 4811, Australia
⁵Department of Geology, University of Johannesburg, PO Box 524, Auckland Park, 2006, South Africa

ABSTRACT

We evaluate the controlling factors of hydrothermal wolframite and scheelite precipitation in the quartz vein-type Jiaoxi tungsten deposit situated in the western part of the Lhasa terrane (Tibet, China) using texture, major and trace element mineral geochemistry, and sulfur stable isotope geochemistry. Pyrite and chalcopyrite that are...
intergrown with Fe-enriched wolframite and siderite, have distinct in situ S isotope compositions (δ^{34}S_{V-CDT}) of −31.38 to +1.77‰, and +2.07 to +2.30‰, respectively. Major and trace element contents and in situ S isotope compositions of pyrite and chalcopyrite indicate that the hydrothermal evolution involved fluid-fluid mixing and greisenization. We report evidence for an early magmatic fluid which is characterized by the enrichment of W, Mn, Zr, Ti, Sc, and Sn and depletion of Fe. This magmatic fluid was diluted by meteoric water and interacted with biotite monzogranite porphyry to leach Fe, Mg, and Zn into the system to form wolframites with variable Fe/(Fe+Mn) ratios ranging between 0.06-0.84. The late Fe-enriched magmatic fluid released from the muscovite granite mixed with meteoric water that leached minor Fe and S from shale to form late shale-hosted wolframite with a Fe/(Fe+Mn) mass ratio of > 0.75 and coeval siderite and sulfides. This study highlights that multiple Fe sources were present in the system, including muscovite granite-released Fe through fluid exsolution, biotite monzogranite porphyry-released Fe during greisenization, and minor Fe released from the shale as a result of meteoric water leaching.

Key words: Wolframite, scheelite, trace element geochemistry, in situ S isotope, multiple Fe sources, Jiaoxi quartz vein-type W deposit

INTRODUCTION

Quartz vein-type tungsten (W) deposits represent a major class of hydrothermal deposits and typically occur as wolframite-bearing quartz veins hosted either in pelitic
rocks or in granites (Wang et al. 2010; Mao et al. 2013). Generally, tungsten is considered to be sourced from Fe-depleted highly evolved felsic magmatic rocks that are spatially associated with the deposit (Romer and Kroner 2016; Hulsbosch et al. 2016). However, formation of wolframite \([(\text{Fe, Mn})\text{WO}_4]\) does not only require W but also significant Fe and Mn in the ore-forming fluid. Therefore, tracing the source of Fe and Mn in quartz vein-type wolframite deposits has long been a subject of interest (Audétat et al. 2000; Lecumberri-Sanchez et al. 2017; Legros et al. 2019; Pan et al. 2019). However, there is no consensus on the origin of the metals because the pristine signature of the primary fluid is overprinted by multiple post-mineralization fluid events in numerous deposits (Polya et al. 2000; Harlaux et al. 2018). Recently, in situ high spatial microanalysis of W-bearing mineral phases, using multi-collector laser-ablation inductively coupled-plasma mass spectrometry (MC-LA-ICP-MS), has been used to identify multiple fluid infiltration events and the metal source (Wang et al. 2017; Hong et al. 2017; Jiang et al. 2021; Carocci et al. 2021).

Wolframite and scheelite, which can accommodate a wide range of trace elements including Ti, Sc, Zr, Hf, Nb, Ta, and REE, have been studied to constrain the hydrothermal evolution and metal sources (e.g., Kempe and Wolf 2006; Song et al. 2014; Zhu et al. 2014; Xiong et al. 2017; Sun and Chen 2017; Han et al. 2020). For example, the negative Eu anomaly of wolframite has been interpreted to be inherited from a highly evolved granite, thus indicating a magmatic source (Harlaux et al. 2018). Scheelite that precipitated from a highly evolved granite-exsolved fluid is generally Sr-depleted such that the variability of the Sr content in scheelite indicates
formation in a metamorphic environment, in which the metasedimentary or volcanic source rocks can release Sr into the hydrothermal system (Poulin et al., 2018).

Although trace element contents in wolframite and scheelite have widely been reported, comprehensive studies of both minerals in order to constrain the hydrothermal evolution and the metal sources are rare (e.g., Zhang et al., 2018).

The Jiaxi quartz vein-type W deposit is located in the western part of the Lhasa terrane (Tibet, China) (Fig. 1a) (Wang et al. 2019). Scheelite, and in particular wolframite, are the most important ore minerals in the Jiaxi deposit. Different wolframite and scheelite generations in this deposit display distinct chemical zonation. As such, they provide an ideal opportunity to trace the metal sources and constrain the hydrothermal mineralization process.

Here we present (1) textural results (optical microscopy, backscattered electron and cathodoluminescence imaging), (2) major and trace element geochemistry of wolframite and scheelite from the different mineralization stages, (3) sulphur stable isotope geochemistry of pyrite and chalcopyrite, and (4) whole-rock major and trace element geochemistry of shale that hosts the W mineralized quartz veins. This study highlights the multiple Fe sources that contributed to the hydrothermal system.

**GEOLOGICAL BACKGROUND**

**Regional geological setting**

The Lhasa terrane in southern Tibet provides evidence for the Mesozoic (accretionary orogeny) to the Cenozoic (collisional orogeny) tectonic evolution of the
Himalayan-Tibetan orogen (Yin and Harrison 2000; Ding and Lai 2003). It contains multiple post-collisional copper, gold, lead-zinc, molybdenum, and iron ore deposits (Fig. 1a; Tang et al. 2014; Hou and Cook 2009; Hou et al. 2015; Yang et al. 2016).

Zhu et al. (2011) subdivided the Lhasa terrane into a northern, central, and southern subterrane based on different basement and sedimentary cover rocks (Fig. 1a). The northern Lhasa subterrane comprises juvenile crust which is related to crustal growth associated with the southward subduction of Bangong-Nujiang ocean plate (Zhu et al. 2011, 2016). The rocks exposed in this subterrane include Middle Triassic-Cretaceous sedimentary rocks and Cretaceous volcanic rocks (Pan et al. 2012; Wang et al. 2014).


The Jiaoxi deposit is situated in the central Lhasa subterrane in the Shiquanhe River-Nam Tso Mélange zone, ~30 km northeast of Gar County (Fig. 1a). Cretaceous strata, including the Langshan and Shiquanhe Ophiolite Mélange Groups, occur in the Shiquanhe area (Fig. 1b). The locally strongly deformed Langshan Group comprises limestone and marble and unconformably overlies the Shiquanhe Ophiolite Mélange Group. The Shiquanhe Ophiolite Mélange Group comprises shale, sandstone, slate,
chert, and (ultra) basic rocks, including basalt, gabbro, serpentinitized dunite, and tuff. These rocks underwent local greenschist-facies metamorphism during the Late Cretaceous and Early Cenozoic continental collisions of the Qiangtang and Lhasa terranes, and the India and Asia continents, respectively (Fig. 1b; Yin and Harrison 2000; Kapp et al. 2003, 2005, 2007). Magmatic rocks in the Shiquanhe area are widespread and include Early Cretaceous porphyritic andesite, and Miocene biotite monzogranite, biotite monzogranite porphyry, and pegmatite veins (Fig. 1b; Wang et al. 2020). Northwest-SE and NE-SW trending fault sets have been identified (Fig. 1b).  

**Geology of the Jiaoxi tungsten deposit**

The Jiaoxi quartz vein W deposit was discovered and explored by the Geothermal Geology Team of Bureau of Exploration of Tibet in 2015. The deposit contains 39,100 tons of WO$_3$ with a grade of 0.1-3.2% (Wang et al. 2018, 2019, 2020). The host rocks of the Jiaoxi deposit belong to the Shiquanhe Group, which comprises strongly deformed shale, sandstone, and ophiolite. Diabase dykes coeval with the ophiolite, occur in the northeast of the ore district (Fig. 2). Various granites occur in the deposit, including the 25-50 m thick biotite monzogranite porphyry (BMP) sill (Online Materials Fig. OM1a), granite porphyry (GP), and muscovite granite (MG). The BMP comprises 40-45% fine-grained phenocrysts of K-feldspar, plagioclase, quartz, and biotite in a very fine-grained matrix made with the same mineral composition. The GP comprises fine-grained phenocrysts (25-30%) of quartz, plagioclase, and minor biotite in a very fine-grained matrix with the same mineral
composition. The equigranular MG comprises quartz, K-feldspar, plagioclase, and muscovite.

Outcrops of the highly fractured BMP host numerous ore-bearing quartz veins with greisenization halos indicating hydrothermal alteration. The BMP also hosts numerous wolframite-bearing quartz veins and associated greisenization zones at depth (drill cores ZK0001 and ZK2001). The GP is exposed in the southwest of the ore district and appears as a single outcrop (< 0.1 km²). Greisenization is widely developed in the GP, but ore-bearing quartz veins are absent.

The unexposed MG is found at depth (drill core ZK2001) and hosts numerous wolframite-bearing quartz veins. A clear intrusive contact between the BMP and the MG is observed showing that the MG is younger than the BMP. The BMP, GP, and MG yield zircon U-Pb ages of 14.1±0.3, 13.82±0.22, and 13.72±0.30 Ma, respectively (Wang et al 2020). Two muscovite grains that occur in quartz veins and are intergrown with wolframite, yield ⁴⁰Ar⁻³⁹Ar ages of 13.4-13.3 Ma (Wang et al. 2018).

Geochemical analysis results show that the MG was highly evolved with high SiO₂ contents (74.4-76.3 wt.%) and low Nb/Ta (2.4-2.8), and Zr/Hf (13.5-13.9) mass ratios (Wang et al., 2020).

Hydrothermal alteration in the Jiaoxi deposit is characterized by greisenization of the BMP and MG. The ore formation is characterized by extensional quartz veins within the upper shales, the BMP, and the MG at depth (Online Materials Fig. OM1b).

More than 70 northeast trending quartz veins with a varying thickness of 5 cm to 8 m have been identified at surface (Fig. 2). The gentle and steeply dipping quartz veins
extend for more than 400 m vertically, as revealed by drill cores ZK0001 and ZK2001 (Online Materials Fig. OM1). Wolframite (dominantly present) and scheelite are the W-bearing ore minerals. The gangue minerals include pyrite, chalcopyrite, galena, sphalerite, quartz, fluorite, phengite, topaz, and beryl. Based on vein crosscutting relationships and mineral paragenesis, the Jiaoxi deposit underwent three mineralization stages: the quartz-tungstate stage, the quartz-sulfide, and the fluorite-carbonate stage (Wang et al. 2021a).

The quartz-tungstate stage is associated with the main mineralization event and is characterized by quartz, wolframite, beryl, topaz, and minor fluorite. Euhedral quartz is intergrown with sericite and eu- to subhedral wolframite (Figs. 3a and 3b). Radial sericite is commonly intergrown with euhedral topaz, and beryl. The quartz-wolframite-sericite veins are crosscut by later quartz-sulfide vein (Fig. 3c).

The sulfide stage is characterized by pyrite, chalcopyrite, galena, pyrrhotite, and sphalerite. Field observations show that early quartz-sulfide veins are crosscut by the fluorite-phengite veins (Fig. 3d).

The fluorite stage is characterized by fluorite, phengite, quartz, and minor calcite and scheelite. Fluorite-stage phengite is typically larger in size (up to 1.5 cm) than the sericite in the quartz-tungstate stage (< 0.5 cm).

**MATERIALS AND ANALYTICAL METHODS**

Three outcrop samples and 32 drill core samples (including 18 and 14 samples from drill core ZK0001 and ZK2001, respectively) of mineralized veins and greisen
were collected for this study (Fig. 2; Online Materials Fig. OM 1). Sample preparations were done at the China University of Geosciences (Beijing). Sixty-eight thick sections (30-40 µm thick) of wolframite and scheelite from the different mineralization stages were prepared for analysis.

**Electron probe microanalysis and backscattered electron imaging**

Electron probe microanalysis (EPMA) of Ca, Mg, Ti, Mn, Fe, Ni, W, Mo, Nb, and Ta was performed on wolframite and scheelite using a JXA-8100 electron microprobe equipped with a wavelength-dispersive spectrometers at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology. Natural and synthetic oxides including bustamite, rutile, hematite, molybdenite, rhodanite, olivine, pentlandite, scheelite, LiTaO₃, and LiNbO₃ were used for Ca, Ti, Fe, Mo, Mn, Mg, Ni, W, Ta, and Nb calibration, respectively. The instrument was set to operate at an accelerating voltage of 20 kV, a beam current of 10 nA, and a defocused beam of 5 µm. Counting times were 10 s for the peak and 5 s for the background for each element. The internal ZAF routine was used for data correction (Armstrong 1991).

Backscattered electron (BSE) imaging of wolframite from the different paragenetic stages was conducted at the Advanced Analytical Centre at James Cook University (Townsville, Australia) on carbon-coated polished sections using a high-resolution field emission scanning electron microscope (FE-SEM, Hitachi, SU5000). Backscattered electron images were taken using an acceleration voltage of 20 kV and an emission current of 0.19 mA.
Cathodoluminescence microscopy

Cathodoluminescence microscopy (CL) imaging of scheelite was conducted at the Advanced Analytical Centre at James Cook University (Townsville, Australia) using a FE-SEM (Hitachi, SU5000) and a Robinson CL detector and photomultiplier. The SEM-CL analysis was done at 20 kV and an emission current of 0.14 mA using a defocused beam.

Laser ablation ICP-MS trace-element analysis

In situ analysis of wolframite and scheelite of the different paragenetic stages was done by using LA-ICP-MS at the Advanced Analytical Centre at James Cook University (Townsville, Australia). Laser ablation was conducted using a Coherent Geolas Pro 193 nm ArF excimer system in helium. Ion-signal intensities were acquired by a Varian 820 quadrupole ICP-MS. Detailed instrument setup conditions are similar as described by Hammerli et al. (2013, 2014). Before analyzing, the ICP-MS was tuned to ensure robust plasma conditions (U/Th sensitivity ratio ~1%) and low oxide production (ThO⁺/Th⁺ < 0.3%) by using the NIST SRM 610 (Pettke et al. 2012). The homogeneous laser energy density was ~2 J/cm² and the repetition rate was 5 Hz. For each analysis, a 30 s background signal was collected before ablation with a duration of 30 s. Helium was used as carrier gas and argon was added as an auxiliary gas. Tungsten (determined by EPMA) was chosen as the internal standard for data reduction. The NIST SRM 610 glass was used as the external standard.
(accuracy was verified by analyzing NIST SRM 612), using the reference values of Spandler et al. (2011). GSD, GSE, and NIST SRM 612 glass were used as secondary standards for all elements. The following 45 isotopes were measured in both wolframite and scheelite: $^7$Li, $^{24}$Mg, $^{45}$Sc, $^{47}$Ti, $^{51}$V, $^{53}$Cr, $^{55}$Mn, $^{57}$Fe, $^{59}$Co, $^{60}$Ni, $^{63}$Cu, $^{66}$Zn, $^{69}$Ga, $^{72}$Ge, $^{85}$Rb, $^{88}$Sr, $^{89}$Y, $^{90}$Zr, $^{93}$Nb, $^{95}$Mo, $^{111}$Cd, $^{115}$In, $^{118}$Sn, $^{121}$Sb, $^{139}$La, $^{140}$Ce, $^{141}$Pr, $^{146}$Nd, $^{147}$Sm, $^{153}$Eu, $^{157}$Gd, $^{159}$Tb, $^{163}$Dy, $^{165}$Ho, $^{166}$Er, $^{169}$Tm, $^{172}$Yb, $^{175}$Lu, $^{178}$Hf, $^{181}$Ta, $^{182}$W, $^{208}$Pb, $^{209}$Bi, $^{232}$Th, and $^{238}$U. Data processing was performed using the Iolite software (Paton et al. 2011).

Laser ablation ICP-MS trace element mapping of wolframite and scheelite were conducted at the Ore Deposit and Exploration Center of Hefei University of Technology (China), following the procedure described by Wang et al. (2017). An Agilent 7900 ICP-MS equipped with a Photon Machines Analyte HE 193 nm ArF excimer was used for trace element mapping. The He carrier gas was mixed with Ar gas via a T-connector before entering the ICP. The LA ICP-MS mapping was carried out by rastering the laser beam across the sample. The sample was ablated with a beam of 15-20 μm, depending on the grain size, and a scanning speed of 15 μm/s. Ablation was performed using an energy density of 2 J/cm² and a laser pulse frequency of 8 Hz. International standard reference materials NIST SRM 610 and GSE-1 were analyzed at the start and the end of each mapping for data calibration. Data processing and images were compiled using the Geochemistry Software V4 (mapping reduction software using MATLAB, Wang et al. 2017; Xiao et al. 2018).
In situ sulfur isotope analysis

Chalcopyrite and pyrite grains intergrown with wolframite and siderite were selected for in situ sulfur isotope analysis. Sulfur stable isotope analysis was conducted at the state Key Laboratory of Geological Processes and Mineral Resources (University of Geosciences Wuhan, China) using a Thermo Scientific Neptune Plus MC-ICP-MS equipped with an NWR FemtoUC femtosecond laser system (New Wave Research, Fremont, CA, U.S.A.). The results are reported in per mil (‰) relative to the Vienna Canyon Diablo Troilite standard (δ$_{34}$S V-CDT).

Helium was used as the carrier gas and mixed with argon (make up gas) after the ablation cell. A spot size of 40 μm, a pulse frequency of 4 Hz and a laser energy density of ~2.5 J/cm$^2$ were used during single spot ablation. The Neptune Plus was equipped with nine Faraday cups fitted with $10^{11}$ Ω resistors. The sulfur isotopes ($^{32}$S, $^{33}$S, and $^{34}$S) were collected simultaneously (static mode). Details on the method are given by Fu et al. (2017). During the measurements, a pyrite standard sample (PPP-1, δ$_{34}$S$_{V-CDT}$ = 5.40 ± 0.16‰) was used as an external standard to correct the mass fractionation of S isotope for various sulfide samples. In-house references of pyrrhotite (YP136, δ$_{34}$S$_{V-CDT}$ = 1.50 ± 0.30‰) (Li et al. 2019) and chalcopyrite (JGZ-87, δ$_{34}$S$_{V-CDT}$ = 5.50 ± 0.23‰) were analyzed repeatedly as unknown samples in order to verify the accuracy of the calibration method. The accuracy is 0.01–0.15‰ for δ$_{34}$S and 0.11–0.45‰ for δ$_{33}$S. The precision is 0.16–0.40‰ (2σ) for δ$_{34}$S and 0.35–0.78‰ (2σ) for δ$_{33}$S. Data processing for LA-MC-ICP-MS analysis was conducted using the ISO-Compass software (Zhang et al. 2020).
Whole-rock major and trace elements analysis

Four fresh outcrop and drill-core shale samples were crushed (200 mesh) for whole-rock major and trace elements analysis conducted at the Beijing GeoAnalysis Co. Ltd. Major element analysis on fused glass disks of powdered samples were determined at Beijing GeoAnalysis Co. Ltd using an XRF-1800 X-ray fluorescence spectrometer. Trace elements were also analyzed at Beijing GeoAnalysis Co. Ltd using an Anglient 7500 ICP-MS system on samples that were dissolved at high pressure in Teflon bombs using an HF-HNO₃ mixture (see Wang et al. 2019 for analytical details).

TEXTURAL ASPECTS

Wolframite

Wolframite mainly developed in the quartz-tungstate stage. According to their occurrences (Fig. 4), the shale hosted quartz vein-type wolframites in the Jiaoxi deposit can be divided into four mineralization types (Table 1). Euhedral type I wolframite (WolS-I) is widely present, intimately associated with euhedral quartz and sericite aggregates, and generally larger than those in other stages (Fig. 4a). Type II wolframite (WolS-II) is subhedral and intergrown with anhedral quartz (Fig. 4b). Sericite veins are observed along the fractures in subhedral WolS-II (Fig. 4c). Type III wolframite (WolS-III) occurs as sub- to anhedral crystals in between euhedral quartz (Figs. 4d and 4e). Type IV wolframite (WolS-IV) is relatively rare compared to the
other three wolframite types and occurs as anhedral crystals intergrown with siderite
and pyrite (replaced by hematite) (Figs. 4f-4h). It should be noted that WolS-IV and
WolS-I show a distinct different colour in reflected light and that later WolS-IV typically
developed along the edge or in cracks of subhedral WolS-II (Fig. 4f). Early formed
 wolframites (especially WolS-I and WolS-II) have been altered along the grain boundary
or partly replaced by late scheelite (Fig. 4i).

Greisen-type wolframite hosted in BMP and MG can be subdivided into two
types (Fig. 5); greisen-type I (WolG-I) and type II wolframite (WolG-II). The WolG-I
develops in quartz veins within the granite and is intergrown with granular pyrite,
euhedral quartz, and radial subhedral sericite (Figs. 5a and 5b). Anhedral WolG-II is
only developed in the greisen (Figs. 5c and 5d).

The different wolframite types show a relatively homogeneous backscattered
electron response (Online Materials Figs. OM2a-2d). The WolS-IV that developed
along the early-formed euhedral WolS-I appears darker compared to the WolS-I in BSE
imaging (Online Materials Fig. OM2c).

Scheelite

Scheelite in the Jiaoxi deposit is rare and only developed in the fluorite stage at
depth. According to its occurrence, it can be subdivided into two types, i.e., type I
(SchI) and type II scheelite (SchII). Anhedral SchI (50-800 μm) replaces early
 wolframite (WolS-I and WolS-II) and occurs along the wolframite grain boundaries and
in fractures (Fig. 4i). These SchI grains show a homogeneous CL response (Online
Materials Fig. OM2e). Type II scheelite (SchII, 1-2 mm in size) is larger than SchI and occurs as sub- to euhedral crystals with concentric growth zones (Online Materials Fig. OM2f).

GEOCHEMISTRY RESULTS

Composition of wolframite and scheelite

Major elements

Major elements of wolframite and scheelite are given in Online Materials Table OM1. Structural formulae of wolframite and scheelite were calculated based on four oxygens per formula unit.

Wolframite has a variable Fe/(Fe+Mn) ratio by mass, which ranges from 0.06 to 0.84. Except for WolS-IV (0.77-0.84), vein-type wolframite is Mn-enriched (Fe/(Fe+Mn) ratio < 0.5) with compositions close to the hübnerite endmember (Fe/(Fe+Mn) ratio of 0.06 to 0.46). WolS-III has the lowest Fe concentration with a Fe/(Fe+Mn) ratio of 0.06-0.09. The Mn concentration in WolS-II ranges from 9.8 to 14.1 wt. %, which is lower than in WolS-I (14.0-15.2 wt.%) (Online Materials Fig. OM3). The highest Mn concentrations (16.5 to 17.9 wt.%) were found in WolS-III.

For the greisen type wolframites, WolG-I and WolG-II have distinct different Fe and Mn contents. The Fe content in WolG-II (11.31-15.54 wt. %) is significantly higher than in WolG-I (2.51-5.29 wt. %). The WolG-II Fe/(Mn+Fe) ratio ranges from 0.47 to 0.78, indicating ferberitic wolframite whereas hübneritic WolG-I has a Fe/(Fe+Mn) ratio of 0.10-0.23 (Online Materials Fig. OM3). A positive linear trend can be
observed for Fe/(Mn+Fe) versus W (a.p.f.u.) (Online Materials Fig. OM3). Most wolframite grains, except for the WolS-IV, have a homogenous Fe-Mn content, which is consistent with the homogenous BSE image (Online Materials Fig. OM2). However, some WolS-I and WolS-II grains that are replaced by WolS-IV show Fe-Mn zonation (Fig. 6). The two different scheelite types show similar major element compositions with WO$_3$ and CaO contents of 78.7-79.2 and 19.8-20.2 wt. %, respectively.

Trace elements

Trace elements for wolframite and scheelite are given in Online Materials Table OM2. Fe, Mn and Ca were analyzed by EPMA and also by LA-ICP-MS for data quality verification. The results show that LA-ICP-MS data are in good agreement with the EMPA data (Online Materials Fig. OM4), confirming the reliability of the LA-ICP-MS analysis.

Trace element concentrations for different wolframite types are summarized in Online Materials Figure OM5. Wolframite in the Jiaoxi deposit is generally enriched in Mg, Sc, Ti, Cr, Nb, Zr, Sn, and Ta (Online Materials Fig. OM5). WolS-II and WolG-II have Mg concentrations of 124-506 ppm and 134-493 ppm, respectively, which are higher than in the other wolframite types (WolS-I: 57-100 ppm, WolS-III: 23-43 ppm, WolS-IV: 37-54 ppm, WolG-I: 37-54 ppm, WolG-I: 7-27 ppm) (Online Materials Fig. OM5a). The Sc and Sn contents of WolS-I, WolS-III, WolS-IV, and WolG-I (Sc: 5-119 ppm, Sn: 1-118 ppm) are higher than in WolS-II (Sc: 2-16 ppm, Sn: < 1-4 ppm) and WolG-II (Sc: 2-30 ppm, Sn: 1-2 ppm) (Online Materials Fig. OM5b and 5h). BMP hosted greisen-type wolframite have higher Ho, Y, Nb, and Ta contents than the shale-hosted wolframite (Online
All wolframite types show positive trends for Y vs. \( \Sigma \text{REE} \), Zr vs. Hf, Ti vs. Sn, and Sc vs Ti (Figs. 7a-7d). WolS-II and WolG-II show higher Mg, Zn, Cr and lower Ti, Sn, Sc, Zr contents than the other wolframite types (Online Materials Fig. OM5). All wolframite types show two distinct trends for Mg vs. Sc, and Zn vs. Sn (Figs. 7e and 7f).

Wolframite in the Jiaoxi deposit has variable \( \Sigma \text{REE} \) concentrations (< 8715 ppm). Shale-hosted wolframite (5-9 ppm) has relatively lower \( \Sigma \text{REE} \) concentrations than the granite-hosted wolframites (5-8715 ppm). The average \( \Sigma \text{REE} \) concentration of shale-hosted wolframite decreases from 5 (WolS-I) to < 1 ppm (WolS-IV). The \( \Sigma \text{REE} \) concentration of WolG-I (5-13 ppm) is lower than that of WolG-II (9-8715 ppm). All wolframite types, except for WolG-II, show HREE enrichment (< 1-19 ppm) compared to LREE (< 1-4 ppm, the LREE content is below the detection limit for most shale-hosted wolframite samples, see Online Materials Table OM2). It is noteworthy that WolG-II shows a highly variable LREE (1-8650 ppm) content whereas the HREE content (8-65 ppm) is relatively consistent.

The REE patterns for all wolframites show a positive Eu anomaly and LREE-HREE fractionating (Figs. 8a-8e). The HREE contents of the greisen-type wolframite (WolG-II and WolG-I) are higher than in the MG (Figs. 8b and 8d).

Scheelite is enriched in Fe, Mn, Cr, Nb, Sr, Y, and Ta (Online Materials Fig. OM6). Type I scheelite (SchI), which replaces wolframite, shows a much higher Fe (870-3800 ppm) and Mn (511-1700 ppm) content than the eu- to subhedral type II scheelite (SchII, Fe: 141-870 ppm, Mn: 18-411 ppm). Type I scheelite (SchI) has a
higher La (average value of 83 ppm) and Eu (average value of 27 ppm) content than SchII (La: 33 ppm, Eu: 10 ppm) (Online Materials Fig. OM6). SchI and SchII show similar Sr (98-779 ppm), Y (22-148 ppm), Na (6-55 ppm), Mg (21-273 ppm), and Nb (9-25 ppm) contents (Online Materials Table OM2).

Compared to wolframite, scheelite has a higher $\Sigma$REE content (167-1233 ppm). The SchI $\Sigma$REE content (170-1233 ppm) is higher than that of SchII (167-636 ppm). Both SchI and SchII show LREE enrichment (59-1080 ppm) relative to HREE (26-153 ppm), and a positive Eu anomaly (Fig. 8f).

**Minor and trace element maps**

Two wolframite grains (ZK2001-200.94 and ZK2001-331.34) showing Fe-Mn zonation were selected for LA-ICP-MS trace element mapping (Fig. 6). Wolframite ZK2001-200.94 shows the textural features typical of WolS-IV (Figs. 9b and 9c). The rim composition has higher Fe, Nb, and Ta contents (typical for WolS-IV) than the core. The core has a higher Mn content than the rim and shows Nb growth zonation similar to WolS-I (Fig. 9h). The core and rim are separated from each other by a geochemical transitional zone (Figs. 6b and 10i).

Wolframite crystal ZK2001-331.34 exhibits three zones (Online Materials Fig. OM7). The core has higher Mn and Ti contents and shows Nb, Ta, and Sc zonation typical for WolS-I (Online Materials Fig. OM7). The core is surrounded by a mantle that shows higher Fe concentrations than the core but is still a Mn-enriched hübnerite, which is typical for WolS-II. The rim of the crystal has the highest Fe content and higher Sc and Ti but lower Nb and Ta contents than the mantle, which is typical for
One SchII grain that shows CL zoning (Online Materials Fig. OM2f) was selected for LA-ICP-MS mapping, demonstrating Mg, Li, Sr, Nd, Y, and \( \Sigma \)REE zonation (Fig. 10). The Mg and Sr contents decrease whereas the Li, REE, Nd, and Y contents increase from the core to the rim (Fig. 10).

**Whole-rock chemistry of shale**

Shale whole-rock major and trace element data are presented in Online Materials Table OM3. The shale has higher SiO\(_2\) contents (52.3-60.5 wt.%) and similar Al\(_2\)O\(_3\), MgO, and total Fe\(_2\)O\(_3\) contents compared to other shales in Tibet (Xie et al., 2014). The shale has similar REE contents with PAAS and show a negative Eu anomaly on the chondrite-normalized REE patterns (Fig. 8) (Taylor and McLennan, 1985).

**Sulfur isotopic compositions**

Sulfur isotope compositions of pyrite and chalcopyrite grains are given in Online Materials Table OM4. Chalcopyrite intergrown with siderite (Fig. 11a) shows uniform \( \delta^{34}S_{V-CDT} \) values ranging between +2.07 and +2.30‰ (Figs. 11b and 11c). Pyrite that is intergrown with siderite and chalcopyrite, on the other hand, shows a wide \( \delta^{34}S_{V-CDT} \) range (Fig. 11d) (−31.4 to −2.4‰). Anhedral pyrite that is either intergrown with WolS-IV or occurs in between euhedral quartz has \( \delta^{34}S_{V-CDT} \) values ranging from −11.7 to +1.8‰, with most of the \( \delta^{34}S_{V-CDT} \) values ranging between +1.0 and +1.8‰ (Figs. 11e and 11f).
DISCUSSION

Controls on trace element variations in wolframite and scheelite

The chemical compositions of wolframite and scheelite are controlled by the chemical composition of the ore-forming fluid and the crystallochemical effect (Xiong et al. 2017; Harlaux et al. 2018). For example, wolframite HREE enrichment is considered to be controlled by the similar ionic radii of the HREE (Dy$^{3+}$: 1.07 Å; Lu$^{3+}$: 0.98 Å), and Fe$^{2+}$ (0.78 Å) and Mn$^{2+}$ (0.83 Å). For scheelite, LREE enrichment is controlled by the similar ionic radii of the LREE (La$^{3+}$: 1.03 Å; Nd$^{3+}$: 0.98 Å) and Ca$^{2+}$ (1.0 Å) (ionic radii data are from Shannon, 1976).

The very high LREE contents determined in WolG-II (three analyses; 8715 ppm, 2630 and 176 ppm) (Online Material Table OM2) can be explained by fractures in the wolframite as revealed by BSE imaging. These very high LREE values are not considered in the discussion below.

The wolframite and scheelite in the Jiaoxi deposit are characterized by HREE and LREE enrichment, respectively (Fig. 8). It is noteworthy that almost wolframite (except for WolS-Ⅲ and WolS-Ⅳ) and all scheelite types show a large positive Eu anomaly (Eu/Eu* ratios of 0.95-30, Fig. 8), which is different from wolframite and scheelite that are genetically related to highly evolved Eu-depleted granite (Harlaux et al. 2018 and references therein; Zhang et al. 2018; Xiong et al. 2017; Yang et al. 2019a). The large positive Eu anomaly of wolframite and scheelite can be explained...
by: (1) the presence of Eu$^{3+}$ in an oxidized mineralizing fluid due to the similar ionic
radius of Eu$^{3+}$ (0.95 Å) and Mn$^{2+}$ (0.83 Å), Fe$^{2+}$ (0.78 Å), and Ca$^{2+}$ (1.0 Å) (Shannon
1976; Goldman et al. 2013), or (2) the addition of Eu to the hydrothermal system (Sun
and Chen et al. 2017; Li et al. 2018).

The scheelite chondrite-normalized Eu concentrations (Eu$_N$) do not show a
correlation with the calculated chondrite-normalized Eu values (Eu$_N^*$, Online
Materials Fig. OM8), which indicates a reduced Eu$^{3+}$-dominated fluid from which
scheelite precipitated (Song et al. 2014; Sun and Chen 2017; Li et al. 2018). Reducing
conditions are also implied by (1) Raman analysis of primary fluid inclusions hosted
in quartz coexisting with wolframite revealed the presence of CH$_4$ in the mineralizing
fluid (Wang et al. 2021a), and (2) the widespread presence of pyrrhotite (Fig. 3d)
(Shen et al. 2010; Cao et al. 2014; Sun and Chen 2017). Therefore, the positive Eu
anomaly of wolframite and scheelite cannot be explained by an oxidized mineralizing
fluid, suggesting that Eu was added. The breakdown of plagioclase during
greisenization was a likely source for Eu.

Zirconium and Hf are considered to be geochemical twins, i.e. Zr/Hf mass ratios
are relatively constant (35-40) in most geological systems (Hoskin and Schaltegger
2003). In the Jiaoxi deposit, the greisen type wolframites show a lower Zr/Hf mass
ratio (20-27) than the Zr/Hf mass ratio in the shale-hosted wolframite (WolS-I: 39-50,
F-B-enriched fluid mobilizes Zr relative to Hf thereby fractionating the element pair
(Rubin et al. 1993; Jiang et al. 2005; Cheng et al. 2019). Therefore, the relatively
lower Zr/Hf ratio of the greisen type wolframites compared to shale-hosted
wolframite indicates that the ore-forming fluid in the greisen stage was enriched in F,
which is supported by the presence of abundant fluorite in the greisen ores (Fig. 5b).
With regards to the other major and trace elements (e.g., Fe, Mn, Ti, Sc, Mg, Sn,
Zr, Nb, and Ta), the different wolframite types have a distinct chemistry. For example,
WolG-II and WolS-II show different Mg, Sc, Sn, and Zn contents compared to WolG-I,
WolS-I, WolS-III, and WolS-IV (Figs. 7e and 7f). These elements are insensitive to redox
conditions (except for Sn), so the variable composition cannot be explained by redox
changes. In addition, fluid inclusion and stable isotope studies revealed that
wolframite precipitation in the Jiaoxi deposit occurred within a limited temperature
range (330-380°C; Wang et al. 2021a). Thus, the chemical variability can also not be
explained by temperature changes. Therefore, the variable wolframite chemistry is
best explained by the variable chemical composition of the fluid from which
wolframite precipitated (Harlaux et al. 2018; Yang et al. 2019a; Xiong et al. 2017).

**Wolframite and scheelite chemistry as a monitor of fluid evolution**

**Fluid-fluid mixing.** All wolframite types show a linear trend for Y vs. ΣREE, Zr
vs. Hf, Ti vs. Sn, and Sc vs. Ti (Figs. 7a-7d), which is evidence for (1) a continuous
hydrothermal evolution during which these elements were progressively removed
from a single fluid phase during mineralization (Korges et al. 2018; Cheng et al.
2019), or (2) fluid-fluid mixing (Harlaux et al. 2020; Carocci et al. 2021).

The replacement of early Mn-enriched wolframite by late Fe-enriched
wolframite (Fig. 4f) indicates that the Fe/(Fe+Mn) ratio increased in the ore-forming fluid (Fig. 6). Trace element mapping shows chemical zoning of wolframite, i.e. the rim has higher HREE, Nb, and Ta contents compared to the core (Fig. 9 and Online Materials Fig. OM7). Therefore, the possibility of a single fluid differentiation model can be excluded as in that scenario the contents of these elements would progressively decrease, which is not the case. Therefore, the chemical variability of wolframite is best explained by a fluid-fluid mixing model.

We propose a fluid-fluid mixing model involving a magma-exsolved fluid and a meteoric water. The Nb, Ta, Ti, Sc, Sn, Y, Zr, Hf, Ho, Y, and ∑REE-enriched fluid endmember has the chemical characteristics of a highly evolved granite-derived fluid (Hulsbosch et al. 2016). Mixing of this magmatic fluid with meteoric water induced dilution, which is supported by the linear correlations of Y vs ∑REE, Zr vs. Hf, and Ti vs. Sn (Figs. 7a-7c). The large variation of δ34S_V-CDT values of pyrite (−31.4 to +1.8‰) intergrown with wolframite and siderite (Fig. 11) is also consistent with mixing of a magmatic fluid with meteoric water (Li et al. 2021). The negative δ34S_V-CDT values of pyrite implies that S was derived from shale-hosted pyrite suggesting that the meteoric water leached the shale-hosted pyrite during fluid migration (Kohn et al. 1998; Lin et al. 2016). This hypothesis is supported by the stable oxygen isotope data of quartz and wolframite, and fluid inclusion data (Wang et al. 2021a).

Leaching metals from coeval granites during the greisenization

Vein-type and greisen-type wolframite show two trends defined by their Mg, Zn, Cr, Ti, and Sn concentrations. The Wol_S-Ⅰ, Wol_S-Ⅲ, Wol_S-Ⅳ and Wol_G-Ⅰ are Sn-Ti-
Sc-enriched and Mg-Zn-depleted, and WolS-II and WolG-II are Sn-Ti-Zr-Sc-enriched (Figs. 7e and 7f). Enrichment of Sn, Ti, and Sc in wolframite has been reported for numerous quartz vein-type W deposits (Kempe and Wolf 2006; Zhu et al. 2014; Harlaux et al. 2018) which can be explained through coupled substitution (Tindle and Webb 1989):

\[ 2(\text{Fe, Mn})^{2+} + \text{W}^{6+} \leftrightarrow 2\text{Sc}^{3+} + (\text{Ti, Sn})^{4+} \]  

The positive correlations of Sc vs Ti of wolframite (Fig. 7d) in the Jiaoxi deposit confirm this interpretation. Tin enrichment is generally considered to be inherited from a highly evolved magma through fluid exsolution (Heinrich 1990). As discussed above, the Ti-Sc-enriched fluid represents the magma-exsolved fluid. The lower content of Ti, Sc, and Sn in WolS-II and WolG-II, compared to other wolframite types, may have been caused by a fluid-fluid mixing induced dilution.

Breakdown of plagioclase, K-feldspar, and biotite during greisenization would result in an increase of the pH of the ore-forming fluid causing subsequent wolframite precipitation (Wood and Samson 2000; Hulsbosch et al. 2016; Yang et al. 2019a; Wang et al. 2021a). During greisenization, biotite breakdown would enrich the ore-forming fluid in Mg, Zn, and Fe (Carocci et al. 2021). Due to their similar ionic radii (Shannon 1976), Mg\(^{2+}\) (0.72 Å) and Zn\(^{2+}\) (0.74 Å) can readily substitute for Fe\(^{2+}\) (0.78 Å) and Mn\(^{2+}\) (0.83 Å) in wolframite by simple substitution, thus causing the precipitation of Fe-Mg-enriched wolframites (Goldman et al. 2013). This conclusion is supported by the positive correlation of Mg vs. Fe/(Fe+Mn) and Zn vs. Fe/(Fe+Mn) for wolframite (Figs. 12a and 12b). Leaching Fe from biotite during greisenization has
also been proposed for the Shimenshi and Xihuashan W deposits (Zhang et al. 2018; Yang et al. 2019a). The breakdown of plagioclase resulted in Eu-enrichment of the fluid, which is reflected in the positive Eu-anomaly of scheelite as discussed previously. Plagioclase breakdown would also release significant Ca into the system, which, in the presence of increasing fluid F content, was removed by the precipitation of fluorite in the greisen (Wang et al., 2021b).

Both CL imaging and the element maps show primary oscillatory zoning of SchII (Fig. 10), which is common for magmatic-related scheelite that precipitated from a hydrothermal fluid with a variable trace element composition (Poulin et al. 2018). The SchII core has higher Sr and Mg and lower REE, Y, Li, and Nd contents compared to the rim (Fig. 10). Poulin et al. (2018) proposed that the relative enrichment or depletion of Sr in the scheelite may be related to the nature of the ore-forming fluid and that the W-bearing fluid exsolved from a highly fractionated magma is commonly Sr-depleted. Considering that decomposition of biotite, plagioclase, and K-feldspar during greisenization would release Sr, Ca, and Mg into the hydrothermal fluid, we propose that the SchII core precipitated from a BMP modified-fluid. In conclusion, the decomposition of plagioclase and biotite during the greisenization not only buffered the pH of the magma-exsolved fluid but also released Fe, Zn, Mg Ca, and Eu into the hydrothermal fluid.
Source and nature of Fe in the wolframite. Numerous sources have been proposed for Fe, including Fe sourced from (1) a highly evolved granite through fluid exsolution (Korges et al., 2018; Harlaux et al. 2018; Yang et al. 2019b), or (2) biotite-bearing granites or metamorphic rocks through fluid-rock interaction (Lecumberri-Sanchez et al. 2017; Zhang et al. 2018). Our data suggest that the Jiaoxi deposit has multiple Fe sources, including the highly evolved MG, the BMP (i.e., Fe released during greisenization), and the shale. The main arguments for this are given below.

Michaud and Pichavant (2019) proposed that the Fe/(Fe+Mn) ratio of wolframite can be used as a tracer for the wolframite deposition environment and that Mn-enriched wolframites (hübnerite) mainly precipitate from a Mn-enriched fluid that exsolved from a highly evolved granite. In the Jiaoxi deposit, these early-formed Mn-enriched wolframites (including Wol S-I and Wol S-III) also indicate that the early ore-forming fluid that exsolved from the highly evolved MG is Mn-enriched. The Mg vs. Fe/(Fe+Mn) and Zn vs. Fe/(Fe+Mn) for wolframite show a positive and a vertical trend (Fig. 12). The positive trend (Wol S-II, Wol G-I, and Wol G-II) indicates that Fe can be leached into the hydrothermal system during greisenization as discussed previously. The vertical trend, on the other hand, shows that a part of Fe (Wol S-IV) is unrelated to greisenization and may be added into the system through other process.

Compared to the Mn-enriched cores, the Fe-enriched rim of two wolframite grains shows higher Nb (51-130 ppm), Ta (1-3 ppm), and Ti (70-440 ppm) but lower \( \Sigma \)REE (< 1 ppm), Y (< 1 ppm), and Ho (< 1 ppm) contents (Figs. 6 and 9, and Online...
Materials Fig. OM7), indicating that the late WolS-IV precipitated from a Fe-Nb-Ta-Ti-enriched and ΣREE-Ho-depleted hydrothermal fluid. As discussed above, the low Ho, Y, and ΣREE contents in the fluid are interpreted to result from fluid-fluid mixing induced dilution. In other words, the late WolS-IV formed in an open hydrothermal system, in which the meteoric water and the magmatic fluid both have the possibility to carry Fe for the WolS-IV. If Fe in the late hydrothermal fluid was carried by the magmatic fluid, it may either have been directly sourced from the highly evolved MG and/or leached from the shale during the fluid-rock interaction.

Lecumberri-Sanchez et al. (2017) proposed that the wolframite precipitated when an Fe-poor W-bearing fluid interacted with sedimentary rocks and leached Fe from the Fe-enriched shale during muscovitization and tourmalinization. In the Jiaoxi deposit, tourmalinization and muscovitization are absent in the contact zone between quartz veins and shale (Fig. 3c), indicating that the Fe extracted from the shale through fluid-rock interaction was probably limited during the precipitation of the quartz vein-hosted wolframites. In addition, the shale has a high ΣREE (150-180 ppm) and relatively low FeO (< 5 wt.%) content (Online Materials Table OM3), and shows a relatively smooth HREE pattern that is different from WolS-IV (Fig. 8c). This also indicates that the contribution of shale-released material into the hydrothermal system is minor (Harlaux et al. 2018). An alternative explanation is that the meteoric water leached Fe from the shales. The extremely negative δ34S_V-CDT values of pyrite (−31.8 to −11.7‰) that is intergrown with wolframite and siderite suggest that sedimentary sulfur derived from shale-hosted pyrite was added to the system (Li et al. 2021). This
implies that Fe was leached into the system as a result of the breakdown of shale-hosted pyrite. However, as discussed above, most of the pyrite and chalcopyrite have uniform positive $\delta^{34}\text{S}_{\text{V-CDT}}$ values and the $\delta^{34}\text{S}_{\text{V-CDT}}$ values increased from $-31.4$ to $-2.4\%$ in a small area in the pyrite grain ($< 200 \ \mu\text{m}$) that is intergrown with chalcopyrite and siderite (Fig. 11d). This observation, together with previous published uniform S isotopic data of galena, sphalerite, pyrrhotite, pyrite, and chalcopyrite in the sulfide stage ($\pm 2.6$ to $+3.7\%$, Wang et al. 2021a), suggest that S in the Jiaoxi deposit is dominantly magmatic (i.e., the amount of shale-released S was limited). The precipitation of pyrite, chalcopyrite, galena, pyrrhotite, and sphalerite (Figs. 4g and 11) in the sulfide stage requires a significant amount of Fe. The uniform positive sulfur isotope compositions of these minerals, as discussed above, indicates that the highly evolved MG had the potential to provide sufficient Fe for the quartz vein-type deposit.

Implications for ore genesis

The hydrothermal evolution and related ore genesis can be summarized as follows (Fig. 13). During the late crystallization stage of the highly evolved MG, the initial mineralizing fluid was exsolved. High concentrations of F+Cl in the evolving magma lowered the solidus temperature to 400-600°C. Continuous accumulation of hydrothermal fluid induced extensive hydraulic fracturing (Breiter et al. 2017), during which the hydrothermal fluid, enriched in W, Nb, Ta, Mn, and REE, moved up and mixed with meteoric water to form the Mn-enriched WolS-I (Figs. 13a and 13b). The
residual fluid moved further upward and leached Mg, Zn, Sr, Ca, and Fe from the BMP through the breakdown of biotite, plagioclase, and K-feldspar. The increasing pH values of ore-forming fluid caused local precipitation of Fe-enriched (Fe/(Mn+Fe) > 0.5), greisen-type wolframite (Fig. 13c). Subsequently, this fluid moved upward and mixed with the meteoric water to form WolS-II, WolS-III with relative high Mg and Zn contents. The late Fe-enriched fluid exsolved from the MG moved up and mixed with meteoric water that that carried Fe and S leached from the surrounding shale, to form the Fe-enriched WolS-IV, siderite, pyrite, and minor chalcopyrite. This Fe-enriched fluid also partly replaced previously wolframite grains along the fractures and edges to form wolframite grains with Fe and Mn zoning (Fig. 13b). As temperature decreased and the hydrothermal fluids became depleted in Fe, Mn and F (Wood and Samson 2000; Liu et al. 2021), BMP-derived, Ca-enriched fluid interacted with early-formed wolframite to form SchI and the core of SchII. Finally, the late MG-exsolved REE-Y-enriched fluid moved upward and mixed with the meteoric water to form the SchII rim with high ∑REE and Y contents (Fig. 13d).

These results suggest that the initial ore-forming fluid exsolved from the highly evolved magma of the quartz vein-type tungsten deposit is W- and Mn-enriched. During the fluid evolution, metals such as Fe, Sr, Mg, Zn, and Ca from the surrounding granite and metamorphic rocks were added into the hydrothermal fluid when the system became open. Compared with other quartz vein-type tungsten deposit around the world, such as the Xihuashan in south China, the Nyakabingo, and Bugarama deposits in central Rwanda, and the Argemela mineralized district in
Portugal, several generations of wolframite were observed (Goldmann et al., 2013; Zhang et al., 2018; Michaud and Pichavant, 2019). These different wolframite generations in a deposit commonly show a large variation of Fe/(Mn+Fe) ratios and Mg, Zn, Nb, and Sn contents, which also indicates a dynamic ore-forming environment transitioning with time from a closed to an open hydrothermal system. This study demonstrates that the textural and compositional variations of wolframite and scheelite can be utilized as an optimal proxy to reconstruct the dynamic hydrothermal process of a tungsten deposit.

**ACKNOWLEDGMENTS AND FUNDING**

This study was financially supported by a grant from the National Key Research & Development Program of China (2021YFC2900100), the Opening Foundation of MNR Key Laboratory of Metallogeny and Mineral Assessment (grant number: ZS2101), the Sichuan Science and Technology Program (2020JDJQ0042), and the Scientific Research Fund of the China Central Non-Commercial Institute (SYSCR2019-03). We would like to thank Mr. Danzhen Wangxiu and Lishen for their assistance in the field, Ms. Liu Mu, Ms. Chen Hongfang, and Dr. Hu Yi for analytical assistance, and Prof. Huang Huiqing for his assistance in data processing. This manuscript greatly benefitted from constructive reviews by Julie Michaud and Iuliu Bobos. Finally, we would like to thank the associate editor Paul Tomascak for his detailed editorial comments.
REFERENCES CITED


Goldmann, S., Melcher, F., Gäbler, H.-E., Dewaele, S., De Clercq, F., and Muchez, P.


An example from an iron oxide–copper–gold (IOCG) deposit in southern Peru.

Chemical Geology, 575. 120230.


Geochemical evolution of halogen-enriched granite magmas and mineralizing fluids of the Zinnwald tin-tungsten mining district, Erzgebirge, Germany.


Generation of post-collisional porphyry copper deposits in southern Tibet triggered by subduction of the Indian continental plate. Economic Geology, 19, 279-300.


Figure captions

FIGURE 1. (a) Tectonic framework of the northern, southern and central Lhasa subterraneas (after Liu et al. 2014), showing the location of Miocene (ultra)potassic rocks and ore deposits including the Jiaoxi deposit in the central Lhasa subterrane. (b) Geological sketch map of the Jiaoxi deposit showing the outcrops of the magmatic rocks and stratigraphic units (after Wang et al. 2020). Abbreviations: BNS = Bangong-Nujiang Suture; SNMZ = Shiquan River-Nam Tso Mélangé zone; LMF = Luobadui-Milashan fault; KF = Karakorum fault; IYZS = Indus-Yarlung Zangbo Suture. Data from Liu et al. (2014), Yang et al., (2016), and references therein.

FIGURE 2. Geological map of the Jiaoxi deposit, showing the occurrence of lodes and their relationships with the surrounding rocks (after Wang 2019). The sections A-A’ and B-B’ can be found on Online materials Figure 1.

FIGURE 3. Photographs showing representative mineral assemblages and vein crosscutting relationships. (a-b) Euhedral wolframite crystals intergrown with quartz and sericite. (c) Early quartz-wolframite-sericite vein crosscut by a later quartz-pyrite vein. (d) A quartz-pyrrhotite-pyrite vein crosscut by a later fluorite-phengite vein. Abbreviations: Wol = wolframite, Fl = fluorite, Qz = quartz, Ph = phengite, Py = pyrite, Po = pyrrhotite, Ser = sericite.
FIGURE 4. Reflected light photomicrographs showing the occurrence of different shale-hosted wolframite types. (a) Early euhedral WolS-I intergrown with quartz and sericite assemblages. (b-c) Subhedral WolS-II intergrown with quartz and crosscut by sericite veins. (d-e) Anhedral WolS-II crystal filling the gaps between euhedral quartz crystals. (f) Anhedral WolS-II grain replaced by WolS-IV along the edge and cracks; (g) Anhedral WolS-IV intergrown with pyrite. (h) Anhedral WolS-IV and siderite filling space among euhedral quartz crystals and replaced by late hematite. (i) Early euhedral WolS-I crystals replaced by late scheelte along the edge. Abbreviations: Wol = wolframite, Qz = quartz, Ph = phengite, Py = pyrite, Po = pyrrhotite, Ser = sericite. Hem = hematite, Sch = scheelite, Sd = siderite.

FIGURE 5. Photomicrographs showing the greisen type wolframites. (a and b) Occurrence of WolG-I intergrown with pyrite, sericite, and quartz (b: cross-polarized light); (c) Occurrence of WolG-II; (d) Anhedral WolG-II intergrown with sericite and quartz (cross-polarized light).

FIGURE 6. EPMA traverses of wolframite grains showing contents from cores to rims along (a) Reflected light image of WolS-II. (b) Fe and Mn contents from the A (core) to B (rim) in WolS-II. (c) Backscattered electron image of wolframite crystal ZK2001-200.94. (d) Fe and Mn contents from C (rim) to D (rim) in wolframite crystal ZK2001-200.94.
FIGURE 7. Plots of (a) Y vs. ΣREE, (b) Zr vs. Hf, (c) Ti vs. Sn, (d) Sc vs. Ti, (e) Mg vs. Sc, and (f) Sn vs. Zn for different wolframite types. Positive linear trends can be observed in (a), (b), (c), and (d). WolS-II and WolG-II samples have higher Mg and Zn but lower Sc and Sn contents than the other wolframite types (grey domains in (e) and (f)).

FIGURE 8. Chondrite-normalized REE patterns of different wolframite and scheelite types in the Jiaoxi deposit. Chondrite REE values are from Boynton (1984). REE contents of muscovite granite (MG) are from Wang et al. (2020).

FIGURE 9. BSE image and LA-ICP-MS trace element mapping for wolframite crystal ZK2001-200.94 (same as in Fig. 6c). (a) Homogeneous BSE image. (b-h) Trace element mapping show Fe-Mn-HREE-Sc-Sn-Ti-Nb zonation for wolframite. (i) Schematic diagram for the growth zonation of WolS-I and the chemical zonation of WolS-I and WolS-IV.

FIGURE 10. Cathodoluminescence image and LA-ICP-MS trace element mapping for a scheelite crystal (SchII). (a) Cathodoluminescence image showing oscillatory zoning. (b-g) Trace element mapping showing primary oscillatory Mg, Li, Nd, Sr, Y, ΣREE zonation f. (h) Schematic diagram showing the chemical zonation of scheelite.
Figure 11. In situ sulfur isotope compositions ($\delta^{34}$S$_{V-CDT}$ values in per mil) for pyrite and chalcopyrite intergrown with the Fe-enriched Wol$_{S-IV}$ and siderite. (a) Chalcopyrite and pyrite intergrown with siderite developed in between euhedral quartz crystals. (b) Sulfur isotope compositions of pyrite showing a large variation in a small area. (c and d) Chalcopyrite showing uniform positive sulfur isotope compositions. (e and f) Pyrite intergrown with wolframite showing a highly variable sulfur isotope compositions.

Figure 12. Binary plots of (a) Mg vs. Fe/(Fe+Mn), (b) Zn vs. Fe/(Fe+Mn) showing positive and vertical trends (grey arrows). The positive trend indicate that a part of Fe was added into the hydrothermal system with Zn, Mg and Eu during the greisenization. The vertical trend implies Fe enrichment in the Wol$_{S-IV}$ that is unrelated to the greisenization process.

Figure 13. (a) Schematic representation (not to scale) of hydrothermal evolution and migration of metals in the Jiaoxi deposit. The brown-red arrows indicate the MG exsolved fluid comprising the elements W, Mn, Fe, REE, F, S, Nb, Ta, Sn, and Sc. The green arrows show the MG exsolved fluid leaching Fe, Mg, Zn, Eu, Ca, and Sr from the BMP. The blue arrows illustrate meteoric water leaching Fe and S from the shale by. See text for a further discussion of hydrothermal evolution process. (b) Sketch showing the textural and compositional variations of Wol$_{S-1}$ and Wol$_{S-IV}$. (c) Sketch showing the location of greisen-type wolframite and their high Fe/(Mn+Fe) ratios (>
49. (d) Sketch showing the textural and compositional variations of scheelite.

Abbreviations: GP-granite porphyry, MG-muscovite granite, BMP-biotite monzogranite porphyry.
Online Materials Figure OM1
Simplified geologic cross sections of the Jiaoxi deposit (after Wang et al. 2018). See Fig. 2 for the locations of the cross sections A-A’ and B-B’.

Online Materials Figure OM2
High-contrast BSE and CL images of different wolframite and scheelite types. (a-d) BSE images showing homogeneous textures of different wolframite types. (e) SEM-CL images show anhedral Sch_I crystals with homogeneous textures along the WolS-I. (f) SEM-CL image showing a subhedral SchII crystal with growth zoning.

Online Materials Figure OM3
Compositional variations of different wolframite types in the Jiaoxi deposit determined by EPMA represented in a W vs. Fe/(Fe+Mn) diagram.

Online Materials Figure OM4
Compositions of Fe and Mn of wolframite in the Jiaoxi deposit determined by EPMA and LA-ICP-MS.

Online Materials Figure OM5
Box-whisker plots for the chemical compositions of different wolframite types. All elemental concentrations are in ppm. The top and bottom of the boxes represent the 25th and 75th percentile of the data and the horizontal lines at the end of the whisker...
represent the end of the 1.5 times the interquartile range. The black box represents the mean value.

Online Materials Figure OM6

Box-whisker plots for concentrations (in ppm) of two scheelite types.

Online Materials Figure OM7

Backscattered electron image and LA-ICP-MS trace element mapping for wolframite crystal ZK2001-331.34. (a) Backscattered electron image showing a relatively homogeneous texture. (b-k) Trace element mapping demonstrating wolframite Fe, Mn, Mg, Ti, Ta, Sc, Mg/Sc, Ti/Cr, Mn/Fe, and Nb zonation. (l) Schematic diagram for the chemical zones in crystal ZK2001-331.34.

Online Materials Figure OM8

Chondrite-normalized Eu concentrations (EuN) vs. calculated EuCN* values for scheelites. EuN* = (SmN × GdN)½. The dashed line represents EuN/EuN* = 1
<table>
<thead>
<tr>
<th>Wolframite type</th>
<th>Textural relations and crystal shape</th>
<th>Mineral Chemistry</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shale-hosted wolframite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WOlS-I</td>
<td>Widely developed; Associated with euhedral quartz and sericite; Euhedral crystal.</td>
<td>0.20 &lt; Fe/(Fe+Mn) &lt; 0.24; Ti: 418 - 1360 ppm; Sn: 28 - 118 ppm; Mg: 57-100 ppm.</td>
<td>Fig. 4a</td>
</tr>
<tr>
<td>WOlS-II</td>
<td>Intergrown with anhedral quartz; Cross cut by sericite veins; Subhedral crystal.</td>
<td>0.1 &lt; Fe/(Fe+Mn) &lt; 0.4; Ti: 2 - 485 ppm; Sn: 0.5 - 4 ppm; Mg: 124 - 506 ppm.</td>
<td>Fig. 4b-c</td>
</tr>
<tr>
<td>WOlS-III</td>
<td>Sub- to anhedral crystals; Filling in gaps between quartz crystal.</td>
<td>0.06 &lt; Fe/(Fe+Mn) &lt; 0.09; Ti: 6 - 376 ppm; Sn: 0.8 - 37 ppm; Mg: 23 - 43 ppm.</td>
<td>Fig. 4d-e</td>
</tr>
<tr>
<td>WOlS-IV</td>
<td>Relatively rare; Replace the early formed wolframite crystal Anhedral crystal.</td>
<td>0.75 &lt; Fe/(Fe+Mn) &lt; 0.83; Ti: 7 - 376 ppm; Sn: 1.6 - 19 ppm; Mg: 37 - 54 ppm.</td>
<td>Fig. 4f-h</td>
</tr>
<tr>
<td>Greisen-hosted wolframite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WOlG-I</td>
<td>Develops in quartz veins within the granite; Intergrown with granular pyrite, euhedral quartz, and sericite; Subhedral crystal.</td>
<td>0.1 &lt; Fe/(Fe+Mn) &lt; 0.2; Ti: 14 - 36 ppm; Sn: 2 - 12 ppm; Mg: 7 - 27 ppm.</td>
<td>Fig. 5a-b</td>
</tr>
<tr>
<td>WOlG-II</td>
<td>Only develops in the greisen; Anhedral crystal; Grain size &lt;500 μm.</td>
<td>0.47 &lt; Fe/(Fe+Mn) &lt; 0.78; Ti: 22 - 219 ppm; Sn: 1.3 - 2.4 ppm; Mg: 134 - 493 ppm.</td>
<td>Fig. 5c-d</td>
</tr>
</tbody>
</table>
Figure 1
Figure 7