



Article Characteristics of REEs and Trace Elements in Scheelite and Muscovite Ar–Ar Isotopic Dating of the Daping Tungsten Deposit

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Abstract: The recently discovered Daping tungsten deposit is located about 25 km north of Tongcheng County, Hubei Province, in the northern margin of the Sijiapu granite deposit of the Mufushan composite batholith. The ore body is produced in the northeast-oriented greisenization granite and quartz vein, and belongs to the greisen-vein-type scheelite deposit. The resources of the Daping W deposit have a value of 7935 t W and the average grade is 0.201% WO₃. Based on mineralogical and petrographic studies, scheelite is classified into two types. A study of the geochemical characteristics of rare earth elements (REEs) and trace elements indicated that some scheelite specimens showed LREE depletion. Meanwhile, the total amount of scheelite rare earth elements (REEs) is low and the ratio of LREE/HREE ranges from 0.40~2.72 in the Daping W deposit. The contents of REEs and trace elements in the two types of scheelite differ significantly. Type I scheelite has an average \sum REE content of 195.65 ppm, an LREE/HREE value of 0.5, an Eu anomaly (δ Eu) of 0.78, Mo of 366.20 ppm, Sn of 22.62 ppm, and Sr of 264.80 ppm. However, type II scheelite features an average ΣREE of 111.28 ppm, an LREE/HREE ratio of 1.43, a δEu of 1.56, Mo of 188.48 ppm, Sn of 0.15 ppm, and Sr of 829.93 ppm. The content level of Mo in the two types of scheelite is not high, indicating that this whole metallogenic environment is a reduction environment. However, this is a complex process. The presence of type I scheelite with negative Eu anomalies and relatively high Mo content indicates that the ore-forming environment in the early period of the greisen stage was relatively oxidizing. In contrast, type II scheelite contains large amounts of Sr and large positive Eu anomalies, which are likely to be released from plagioclase in the granite during greisenization. The extremely low composition of Mo in type II scheelite is closely related to the reducing environment in the later period of the greisen stage. Because Mo probably exists in its Mo⁴⁺ state, it may be difficult for it to replace W⁶⁺ in the scheelite lattice. Additionally, comparing the contents of Sn and Sr in different types of scheelite shows that the metallogenic environment changes from relative oxidation to the reduction of scheelite. The variation in trace elements and REEs in scheelite over time reflects a complex magmatic-hydrothermal mineralization environment. Additionally, the Ar-Ar system dating results for muscovite that is closely associated with scheelite in the greisenization granite vein indicate that a muscovite ⁴⁰Ar/³⁹Ar plateau age of about 133 Ma represents the time of tungsten mineralization. This muscovite ⁴⁰Ar/³⁹Ar dating result is close to the previous zircon U-Pb age data of the biotite monzogranite (ca. 140-145 Ma), which is the largest intrusion in the orefield. Meanwhile, the new age data reported here confirm that the Daping tungsten deposit represents a Mesozoic magmatic-hydrothermal mineralization event with a setting of lithospheric extension in the Mufushan composite batholith.

Keywords: Daping W deposit; tungsten mineralization environment; muscovite Ar-Ar age



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1. Introduction

The Hubei province spans the Qinling–Dabie accretionary fold belt and the Yangtze Craton's two tectonic units. It has a complex geological structure and strong magmatic activities, which are highly favorable conditions for mineralization. Several districts mineralized with Cu-Fe, W-Au-Nb-Ta, coal, P-Fe, and Ag-Ti-Pb-Zn occur in the south, the southeastern margins, the center part, and the western and southwestern margins of Hubei Province, respectively.

The Daping W deposit, a newly discovered small tungsten deposit, is located in the north of Tongcheng, southeastern Hubei Province, South China (Figure 1). With a resource of 7935 t W and a grading average of 0.201% WO₃ [1], the Daping deposit is a small greisenvein-type tungsten deposit. The Daping W deposit is one of several rare metal deposits in the southeastern part of Hubei Province, the northern area of Mufushan composite batholith, including the Huadunqiao W, Zheping Sb, Quanchong Sb, Dashimengou Au-Sb, Xiaoshui Au, Taolin Pb-Zn, and Duanfengshan Nb-Ta deposits (Figure 1).



Figure 1. Location (a) and outline map of the regional structure (b) (modified in accordance with [1,2]).

The Daping deposit has been the subject of a few studies in recent years [1,2]. These studies indicate that the mineralization of the Daping W deposit mainly occurs as veins and disseminations in greisen. Petrogeochemical studies of the granite in the Sijiapu granite deposit infer that the W mineralization is genetically related to the Sijiapu granite [1]. The Sijiapu granite, likely a branch of the Mufushan composite batholith, belongs to a product of the second intrusion of the Mufushan composite batholith in the late Yanshanian period [1,2]. Previous studies have shown that the genesis of the Daping W deposit is closely related to the Sijiapu granite. However, the metallogenic timing and the detailed mineralization conditions are still essentially unknown. This paper aims to address these problems through detailed petrographic studies, isotopic dating, and major and trace element analyses of mineralization minerals from the Daping W deposit, in order to decipher the mechanisms whereby several tungsten deposits accumulated in the northern

part of the Mufushan composite batholith. This area is significant in terms of rare-metal ore concentration in South China, and this research is important for the further study of tungsten and rare metals in this region.

Scheelite (CaWO₄) is the major ore mineral in the Daping W deposit, and it contains a wealth of important information about the mineralization environment and processes [3–5]. The crystal structure of scheelite comprises tetrahedral $[WO_4]^{2-}$ groups and irregular dodecahedral $[CaO_8]^{14-}$ groups [6]. Meanwhile, high concentrations of rare earth elements (REEs), Y, and Sr may substitute for Ca. In addition, Mo and Sn may replace W in the lattice of scheelite [7,8]. The abundance of REEs and trace elements (particularly Sr, Sn, and Mo) in scheelite can act as indicators of the mineralization environment and fluid sources, as has been discussed in many studies [6–13]. Up to now, little research has been conducted into the Daping tungsten deposit. Therefore, the formation age, the detail mineralization conditions, and the processes of tungsten mineralization remain unknown.

In this research, scheelite samples were collected from drill cores. By conducting detailed petrographic and geochronological studies and analysis of major and trace elements and REEs, we further develop our understanding of the ore-forming process. The precise muscovite 40 Ar/ 39 Ar age of the Daping W deposit is reported in order to discuss the mineralization relationship between W and rare metals in the Mufushan composite batholith. Additionally, we systematically compared the in situ REE and trace element compositions between different types of scheelite, which are used to represent the mineralization environment and processes in detail; in turn, this information is used to infer the genesis of the Daping W deposit.

2. Geological Setting

2.1. Regional Geology

The area of Daping W deposit is located at the northwestern margin of the Mufushan composite batholith. The Mufushan batholith is a giant, composite granitic massif at the junction of Hubei, Hunan, and Jiangxi Provinces. It belongs to the central segment of Jiangnan orogenic belt, which was created by the collision between the Yangtze craton and the Cathaysia blocks [14] (Figure 1a). The Jiangnan Orogenic is a part of South China and has experienced various tectonic events, such as the Neoproterozoic Jinning, the early Paleozoic Caledonian, the early Mesozoic Indosinian, the late Mesozoic Yanshanian orogenies, and so on, forming a significant number of tungsten, tin, copper, niobium-tantalum, and gold deposits, especially in the Yanshanian [15–22].

The Mufushan composite batholith was formed by polyphasic intrusion. The complex formed episodically from the late Jurassic (ca. 154 Ma) to the early Cretaceous (ca. 145 Ma), with a compositional evolution from granodiorite through biotite monzogranite and twomica monzogranite to muscovite monzogranite stocks [23,24]. Most of the granitic intrusions are Yanshanian and mostly located in the Neoproterozoic Lengjiaxi Group and a small number of Quaternary strata. Pegmatite dikes mineralized with Be, Nb-Ta, and Li-Be-Nb-Ta occur in the eastern margin, in the center part, and in the southwestern and northwestern margins of the Mufushan composite batholith, respectively [25]. Greisen-quartz veins mineralized with W occur in the northern margin of the Mufushan composite batholith. In this region, the Daping W deposit is the most typical greisen-quartz-vein-type tungsten deposit [2].

2.2. Geology of the Daping Deposit

The mineralization of the Daping deposit began in the greisenization granite veins developed in metamorphic rocks of the Neoproterozoic Xiaomuping and Dayaogu formations, which are controlled by faults and secondary fold structures, such as the Xichong Fault (NW-trending faults F1 and F2) and the Tianjiachong–Tiping Fault (SN-trending faults F3) (Figure 1). The Sijiapu and Huadunqiao bodies of granite, which are likely branches of the Mufushan composite batholith, are exposed in the south and southwest of the mining area. The lithology comprises medium-fine-grained porphyritic biotite monzogranite. The W orebodies mostly occur in the greisen-quartz veins and can be divided into six tungsten ore bodies (W1~W6) (Figure 2), among which W1 and W4 are the main ore bodies in this area (Figure 3). The dominant ore minerals include scheelite, pyrite, chalcopyrite, and molybdenite, and the gangue minerals include muscovite, fluorite, quartz, epidote, chlorite, apatite, sphene, rutile, and calcite.



Figure 2. Geological map of the Daping area (modified from [1]).



Figure 3. Prospecting line no. 15 and the location of the drill cores sampled in the Daping W deposit.

3. Petrography and Paragenesis

The tungsten ore bodies in the study area are hosted in greisenization granite and quartz veins, which are controlled by the later structural fractures. The scheelite can be divided into two types according to the samples. Type I scheelite comprises anhedral crystals less than 0.4 mm in diameter that are sporadically distributed in the incompletely altered granite veins (Figure 4a,c); Type II scheelite occurs as euhedral crystals less than 2 mm in diameter and is disseminated in greisen-quartz veins (Figure 4a,e).

The biotite in granite is altered to chlorite and epidote (Figure 4c). The medium-coarsegrained euhedral muscovite and large-grained subhedral quartz can be found around the incompletely altered granite; these substances are related by the later hydrothermal activities (Figure 4c). The quartz sulfide (mainly pyrite and chalcopyrite) veins crosscut the greisen veins in the hand samples (Figure 4b,h). Muscovite and quartz within the greisen veins are distributed on both sides of the calcite veins (Figure 4i), so the calcite veins were formed in the later stage.

Through the observation of hand samples and thin sections, the alteration and mineralization of the Daping W deposit were divided into two periods, i.e., the magmatic period (stage 1) and the metallogenic hydrothermal period (from stages 2 to 4). The magmatic and metallogenic periods can be further divided into the following stages: (1) the magmatic stage, (2) the greisen stage, (3) the hydrothermal sulfide stage, and (4) the calcite stage (Figure 5). Scheelite was scarcely formed in the transition time between stages 1 and 2 (a period that belongs to the early greisen stage), then was mainly formed in stage 2. The magmatic stage mainly represents the preparation stage of metallogenic materials, forming biotite, fine-grained quartz (Qtz1) and minor fine-grained muscovite (Ms1) (Figure 4c,d). In the transition time between stage 1 and stage 2 (the early greisen stage), the fine-grained (<0.4 mm in diameter) and euhedral-to-subhedral sporadic scheelite (Sch1) is embedded in the incompletely altered granite (Figure 4a,c), with residual biotite, minor muscovite (Ms1), and fine-grained quartz (Qtz1) (Figure 4d). The greisen stage formed euhedral scheelite (2-4 mm in diameter), muscovite (5-10 mm in diameter), quartz (6–10 mm in diameter), epidote, chlorite, fluorite, apatite, sphene, and rutile (Figure 4e). Middle-grained euhedral fluorites are distributed between the broken quartz and mica particles in the greisen, showing intergrowth features with apatite and epidote chlorite, sphene, and rutile (Figure 4d). Therefore, two kinds of scheelites can be divided, in the hand samples, according to different scheelite crystal characteristics (Figure 4a) and associated minerals (Figure 4c,e). Quartz (Qz3)-sulfide veins are a sign of the hydrothermal sulfide stage, crosscutting the greisen vein. The sulfides formed in this stage include pyrite, chalcopyrite, and molybdenite (Figure 4g,h). The last stage (the calcite stage), crosscutting other hydrothermal assemblages, is characterized by the formation of calcite veins. This constitutes the youngest hydrothermal event (Figure 4i). The mineralization periods, stages, and paragenetic sequence of the Daping tungsten mineralization are shown in Figure 5.



Figure 4. Photographs of hand samples and photomicrographs of thin sections showing the various crosscutting relationships of different types of scheelite with other minerals. (**a**) Two types of scheelite are distinguished in the hand samples. Type I scheelite is discovered in greisen with a lower degree of alteration and type II scheelite is discovered in completely altered greisen; (**b**) veinlets of pyrite and quartz (quartz 3) in greisen (quartz2); (**c**) type I scheelite sporadically distributed in the incompletely altered greisen vein, with biotite and chlorite; (**d**) some minerals (apatite, epidote muscovite, and fluorite) are generated in the greisen vein; (**e**) type II scheelite occurs as euhedral crystals disseminated in greisen veins, associating with muscovite (muscovite 2); (**f**) type II scheelite is associated with muscovite 2 and quartz 2; (**g**) a sulfide-quartz vein containing pyrite and quartz 3 crosscutting the greisen vein; (**h**) pyrite in the sulfide-quartz vein; (**i**) a calcite vein crosscutting greisen. *Sch: scheelite; Qtz: quartz; Ep: Epidote; Bi: biotite; Ms: muscovite; Chl: Chlorite; Py: pyrite; Ap: apatite; Fl: fluorite; Cal: calcite.*

Stage	Magmatic Period	Metallog	enic Hydrotherm	al Period
Mineral	Magmatic Stage	Greisen Stage	Hydrothermal Sulfide Stage	Calcite Stage
Feldspar				
Biotite	-			
Quartz	Qtz1	Qtz2	Qtz3	
Fluorite		-	-	
Muscovite	Ms1	Ms2	•	
Epidote		-		
Chlorite		-		
Scheelite	S	ch 1 Sch 2		
Pyrite				
Chalcopyrite			-	
Apatite		-		
Titanite		-	N	
Rutile		-	-	
Molybdenite			-	
Calcite				

Figure 5. Mineralization periods, stages, and paragenetic sequence of hydrothermal minerals in the Daping W deposit.

4. Samples and Analytical Methods

4.1. Samples

The newly discovered Daping W deposit is largely inaccessible, and this study is based on field mapping, the geological logging of new drill cores, and the petrography of tens of thin sections. Observations based on hand samples indicate that the scheelite is developed in the greisen dikes. The scheelite mainly takes two forms: fine-grained and medium-coarse scheelites are scattered and disseminated in greisen dikes, respectively. In this study, we collected 42 drilling samples of the Daping W deposit, and produced 100 thin sections to identify the sequence of mineral symbiosis; 26 of these thin sections were used to analyze the major and trace elements. Some representative sampling locations were located in the zk1501 and zk1502 drill cores, with hole depths of 177.8 m, 477.1 m, and 496.4 m (Figure 3).

4.2. Muscovite Ar–Ar Dating

The muscovite sample (T16) were taken from drill core zk1502 at a depth of 496.4 m (Figure 3). The muscovite crystals were selected from the greisen vein (Figure 4e,f). The relatively straight contact surfaces between muscovite and scheelite indicate that they are closely associated (Figure 4f). The muscovite comprised euhedral aggregates with diameters of about 0.5 to 2 mm, and they were relatively fresh. Based on the field and microscopic observations, the muscovite samples related to mineralization were selected, crushed, and screened on a 60–80 mesh. The muscovite samples (purity of >99%) were carefully handpicked under a binocular microscope then cleaned ultrasonically. The muscovite separates from the T16 sample (zk1502-496.4 m) were analyzed using a method of step heating using a CO₂ laser. The mineral separates, together with the monitoring standard samples, were irradiated for 48 h in channel B4 of the Beijing 49-2 reactor at the Chinese Academy of Nuclear Energy Sciences. The biotite standard ZBH-2506 (132.7 ± 1.2 Ma) was used to monitor the neutron flux. Then, ⁴⁰Ar/³⁹Ar

stepwise heating analyses were performed at the Ar–Ar laboratory in the Institute of Geology, Chinese Academy of Geological Sciences using a HelixMC mass spectrometer. The samples were analyzed in 12 temperature steps from 700 °C to total fusion at 1400 °C. K₂SO₄ and CaF₂ crystals were analyzed to calculate Ca and K correction factors: $({}^{39}\text{Ar}/{}^{37}\text{Ar}_0)_{\text{Ca}} = 0.000806$, $({}^{36}\text{Ar}/{}^{37}\text{Ar}_0)_{\text{Ca}} = 0.0002389$, $({}^{40}\text{Ar}/{}^{39}\text{Ar})_{\text{K}} = 0.004782$. The decay constant for ${}^{40}\text{K}$ used in the calculation was 5.543 × 10⁻¹⁰ y⁻¹ [26]. The ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ spectra were constructed using Isoplot software [27]. Plateau ages are considered here when three or more consecutive steps release more than 50% of the ${}^{39}\text{Ar}$ and their respective errors overlap at the 1 σ level. More detailed information regarding these analytical methods is given by Chen et al. (2006) [28] and Zhang et al. (2006) [29].

4.3. Electron Microprobe Analysis

Some representative thin sections were selected by detailed microprobe observations and analyzed using electron microprobe analysis (EMPA). These thin sections were coated with carbon and studied using backscattered electron (BSE) imaging to characterize the crystalline form and structures of scheelite. The major elements were analyzed using a JEOL JXA8800R at the Institute of Mineral Resources, Chinese Academy of Geological Sciences. The experimental conditions were as follows: 15 kV accelerating voltage, 20 nA beam current, and 3 μ m beam diameter. All data were corrected using the standard ZAF correction procedure.

4.4. LA-ICP-MS Trace Elements Analyses of Scheelite

Analyses of the trace element compositions of scheelite were conducted on polished sections with 80 µm thickness at the National Research Center for Geoanalysis of China, using a New Wave UP 213 Nd: YAG laser and a Finnigan Element 2 high-resolution high-sensitivity double-focusing ICP-MS [30]. Helium was used as the carrier gas for the ablation cell and was mixed with argon after laser ablation. The spot size of the laser was 30 µm and the impulse frequency was 10 Hz. More details about these analytical methods are given by Zhao (2017) [31]. The NIST 612, as the external standard sample, was used as the internal standard material and determined using the average CaO concentrations of the selected samples, as measured by EMPA [32].

5. Results

5.1. Results of EMPA

Microscope observations revealed that there are two types of scheelite in the Daping W deposit. Type I scheelite comprises anhedral crystals less than 0.4 mm in diameter and is sporadically distributed in the incompletely altered granite veins (Figure 4a,c); it comprises ~10 Vol.% of the total scheelite. Type II scheelite is dominant (~80 Vol.%) and consists of euhedral crystals less than 2 mm in diameter; it is disseminated in greisenquartz veins (Figure 4a,e). The two types of scheelite have slightly different compositions (Table 1). Type I scheelite has CaO contents of 19.94–20.64 wt.% (average 20.26 wt.%), WO₃ contents of 78.58–79.25 wt.% (average 78.96 wt.%), Na₂O contents of 0.01–0.22 wt.% (average 0.11 wt.%), and Rb₂O contents of 20.18–20.74 wt.% (average 20.45 wt.%), WO₃ contents of 78.80–79.42 wt.% (average 79.08 wt.%), Na₂O contents ≤ 0.17 wt.% (average 0.05 wt.%), and Rb₂O contents of 0.02–0.15 wt.% (average 0.08 wt.%) (Table 1). The contents of other major elements are negligible.

Table 1. EMPA analytical results of scheelite from the Daping W deposit (wt.?)	%).
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	Na ₂ O	F	$Al_2O_3\\$	SrO	MgO	Y_2O_3	K ₂ O	CaO	P_2O_5	SnO_2	WO_3	MnO	Ta_2O_5	FeO	SiO_2	TiO_2	Cr_2O_3	Au ₂ O	Cl	MoO ₃	Nb_2O_5	Rb ₂ O	Cs ² O	Total	Original Total
Type I																									
3-2-1	0.10	0.05	0.09	0.09	0.12	0.00	0.05	20.16	0.08	0.00	78.58	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.12	0.10	0.02	0.06	0.33	100.00	99.52
3-2-2	0.22	0.00	0.08	0.09	0.09	0.00	0.04	20.45	0.02	0.00	78.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.03	0.02	0.04	100.00	99.37
3-2-3	0.12	0.00	0.04	0.09	0.06	0.00	0.00	20.29	0.05	0.03	78.95	0.03	0.00	0.00	0.00	0.00	0.19	0.06	0.03	0.00	0.00	0.04	0.00	100.00	100.02
3-2-4	0.19	0.00	0.04	0.21	0.10	0.00	0.05	20.31	0.07	0.00	78.70	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.05	0.01	0.12	0.00	100.00	99.53
3-2-5	0.01	0.02	0.00	0.09	0.01	0.00	0.00	20.16	0.04	0.00	79.23	0.00	0.00	0.04	0.00	0.00	0.12	0.10	0.12	0.00	0.00	0.06	0.00	100.00	99.56
3-2-6	0.01	0.00	0.00	0.09	0.00	0.00	0.04	20.50	0.03	0.00	78.97	0.00	0.00	0.05	0.00	0.00	0.06	0.07	0.00	0.08	0.00	0.11	0.00	100.00	99.98
3-2-7	0.02	0.00	0.00	0.09	0.00	0.00	0.01	20.64	0.00	0.04	79.09	0.00	0.00	0.04	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.05	0.00	100.00	99.81
3-2-8	0.13	0.00	0.07	0.20	0.09	0.00	0.07	20.08	0.03	0.03	78.95	0.00	0.00	0.00	0.00	0.00	0.11	0.00	0.09	0.07	0.00	0.07	0.00	100.00	99.88
3-2-9	0.15	0.00	0.10	0.09	0.10	0.00	0.05	19.94	0.04	0.04	79.25	0.00	0.00	0.02	0.00	0.00	0.01	0.12	0.01	0.00	0.00	0.07	0.00	100.00	101.36
3-2-10	0.14	0.03	0.08	0.09	0.13	0.00	0.03	20.03	0.05	0.00	79.12	0.00	0.00	0.02	0.00	0.00	0.09	0.00	0.02	0.08	0.00	0.08	0.00	100.00	100.20
min	0.01	0.00	0.00	0.09	0.00	0.00	0.00	19.94	0.00	0.00	78.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00		
max	0.22	0.05	0.10	0.21	0.13	0.00	0.07	20.64	0.08	0.04	79.25	0.03	0.00	0.05	0.00	0.00	0.19	0.12	0.15	0.10	0.03	0.12	0.33		
avg	0.11	0.01	0.05	0.11	0.07	0.00	0.03	20.26	0.04	0.01	78.96	0.00	0.00	0.02	0.00	0.00	0.06	0.04	0.07	0.04	0.01	0.07	0.04		
Type II																									
15-1-1	0.12	0.04	0.00	0.09	0.00	0.00	0.00	20.35	0.07	0.00	78.96	0.00	0.00	0.02	0.00	0.00	0.14	0.03	0.00	0.07	0.00	0.12	0.00	100.00	100.79
15-1-2	0.03	0.00	0.00	0.10	0.00	0.00	0.00	20.74	0.00	0.06	78.94	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.01	0.06	0.00	100.00	100.29
15-1-3	0.03	0.00	0.00	0.09	0.02	0.00	0.00	20.59	0.02	0.02	78.92	0.01	0.00	0.13	0.00	0.00	0.05	0.00	0.00	0.03	0.00	0.10	0.00	100.00	100.76
15-1-4	0.02	0.01	0.00	0.10	0.01	0.00	0.00	20.25	0.01	0.00	79.17	0.00	0.00	0.03	0.00	0.00	0.16	0.00	0.14	0.01	0.00	0.09	0.00	100.00	99.68
15-1-5	0.00	0.00	0.00	0.09	0.03	0.00	0.02	20.58	0.04	0.00	79.03	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.04	0.00	0.07	0.00	100.00	100.44
15-1-6	0.03	0.00	0.00	0.09	0.03	0.00	0.00	20.35	0.01	0.00	78.80	0.01	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.01	0.00	0.15	0.47	100.00	100.42
15-1-7	0.06	0.00	0.00	0.09	0.01	0.00	0.01	20.38	0.02	0.01	79.33	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.05	0.00	100.00	100.44
15-1-8	0.17	0.00	0.00	0.09	0.01	0.00	0.00	20.49	0.04	0.02	78.87	0.00	0.01	0.00	0.00	0.00	0.05	0.00	0.06	0.05	0.02	0.12	0.00	100.00	99.81
15-1-9	0.05	0.00	0.00	0.09	0.00	0.00	0.00	20.18	0.08	0.00	79.42	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.00	0.04	0.00	0.04	0.00	100.00	100.85
15-1-10	0.00	0.00	0.00	0.09	0.02	0.00	0.00	20.41	0.00	0.00	79.41	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.02	0.00	100.00	100.97
15-1-11	0.03	0.00	0.00	0.09	0.00	0.00	0.00	20.60	0.04	0.00	78.92	0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.07	0.09	0.00	0.06	0.00	100.00	100.36
15-1-12	0.06	0.00	0.00	0.09	0.00	0.00	0.00	20.42	0.08	0.07	79.16	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.06	0.02	100.00	100.17
15-1-13	0.00	0.00	0.00	0.21	0.00	0.00	0.04	20.26	0.09	0.00	79.25	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.03	0.00	0.07	0.00	100.00	101.10
15-1-14	0.04	0.00	0.00	0.09	0.02	0.00	0.00	20.51	0.06	0.00	79.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.07	0.00	100.00	100.16
15-1-15	0.09	0.00	0.00	0.09	0.02	0.00	0.00	20.60	0.04	0.00	78.86	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.14	0.06	0.01	0.08	0.00	100.00	99.96
min	0.00	0.00	0.00	0.09	0.00	0.00	0.00	20.18	0.00	0.00	78.80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00		
max	0.17	0.04	0.00	0.21	0.03	0.00	0.04	20.74	0.09	0.07	79.42	0.01	0.01	0.13	0.00	0.00	0.16	0.04	0.14	0.09	0.02	0.15	0.47		
avg	0.05	0.00	0.00	0.10	0.01	0.00	0.00	20.45	0.04	0.01	79.08	0.00	0.00	0.02	0.00	0.00	0.04	0.01	0.03	0.04	0.00	0.08	0.03		

5.2. Results of LA-ICP-MS

The results of LA-ICP-MS analyses of the REEs and trace elements of 17 scheelite samples are shown in Table 2. The results of scheelite Σ REE from 61.29 to 310.90 ppm show the characteristics of lower REE levels and little variation in content in the Daping W deposit. The ratios of LREE and HREE (from 0.40 to 2.72) show partial losses in LREE. Y was positively correlated with Σ REE (Figure 6a), while Ca was not significantly correlated with Σ REE (Figure 6b).



Figure 6. (a) Ratio of Y to total rare earth element content in scheelites; (b) ratio of Na to total rare earth element content in scheelites.

Type I scheelite has Σ REE contents ranging from 117.45 to 310.90 ppm (average 195.65 ppm), an LREE/HREE (note LREE = La to Eu; HREE = Gd to Lu) ratio ranging from 0.40 to 0.65 (average 0.50), δ Eu from 0.72 to 0.90 (average 0.78), Mo from 320.40 to 475.50 ppm (average 366.20 ppm), Sr from 451.90 to 729.60 ppm (average 543.95 ppm), Li from 6.59 to 324.00 ppm (average 158.15 ppm), Be from 0.68 to 11.10 ppm (average 4.03 ppm), Nb from 11.87 to 16.10 ppm (average 13.24 ppm), Ta from 0.41 to 0.99 ppm (average 0.68 ppm), B from 0.47 to 7.34 ppm (average 3.02 ppm), Cr from 99.69 to 514.80 ppm (average 264.80 ppm), δ Ce from 0.65 to 0.81 (average 0.72), and Sn \leq 31.29 ppm (average 22.62 ppm).

Type II scheelite has Σ REE in the range of 61.29 to 258.46 ppm (average 111.28 ppm), an LREE/HREE ratio from 0.88 to 2.72 (average 1.43), δ Eu from 0.87 to 2.61 (average 1.56), Mo from 147.10 to 241.80 ppm (average 188.48 ppm), Sr from 700.70 to 1047.00 ppm (average 829.93 ppm), Li \leq 4.29 ppm (average 1.75 ppm), Be \leq 0.18 ppm (average 0.07 ppm), Nb from 2.58 to 110.50 ppm (average 14.08 ppm), Ta from 0.59 to 1.03 ppm (average 0.78 ppm), B from 0.10 to 1.55 ppm (average 0.82 ppm), Cr \leq 13.28 ppm (average 3.95 ppm), δ Ce from 1.02 to 1.40 (average 1.20), and Sn \leq 0.28 ppm (average 0.15 ppm).

The different chondrite-normalized REE (REE_N) patterns of the two types scheelite are presented in Figure 7. Type I scheelite yielded typical left-dip-type REE_N patterns, depleted in LREEs with negative Eu anomalies (Figure 7a). Meanwhile, type II scheelite with the "seagull wing" shaped REE_N patterns has positive Eu anomalies (Figure 7b). The difference between the two types of scheelite in terms of the Eu anomaly is obvious, but there is no obvious difference in relation to the Ce anomaly.



Figure 7. Chondrite-normalized REE patterns of different types of scheelite from the Daping W deposit (**a**) type I, (**b**) type II. The chondrite values are taken from Sun and McDonough (1989) [33].

The Eu anomalies can be represented by a correlation diagram between the Eu_N and Eu_N^* (Figure 8a). Most data for the type I scheelites are plotted below the 1:1 line, which shows the negative Eu anomaly; the data of type II scheelites, which are plotted above the 1:1 line, show the positive Eu anomaly. (Figure 8a).

In summary, type I scheelite has relatively high Mo and Sn contents, low Sr content, and negative Eu. Type II scheelite has low Mo and Sn contents, slightly higher Sr content, and positive Eu (Figure 8).



Figure 8. (a) Plot of Eu_N (chondrite-normalized Eu concentration) versus Eu*_N [= $(Sm_N \times Gd_N)^{1/2}$] for different types of scheelite from the Daping W deposit; (b) δ Eu versus Mo diagram of different types of scheelite; (c) δ Eu versus Sn diagram of different types of scheelite; (d) δ Eu versus Sr diagram of different types of scheelite.

Minerals 2023, 13, 317

1.75

avg

0.07

14.08

0.78

0.82 3.95

829.93 188.48 0.15

4.09

17.94

3.73

23.72

9.78

5.63

13.58

2.25

13.83

2.90

7.64

0.94

4.63

0.61

50.27

111.28 1.43

1.56

1.20

								2						ч 1					1 0	1								
	Li	Be	Nb	Ta	В	Cr	Sr	Мо	Sn	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	ΣREE	L/H	δEu	δCe
Type I																												
3-6	6.59	0.68	16.10	0.99	0.96	99.69	729.60	475.50	0.00	0.81	8.60	3.80	41.43	29.40	11.26	68.59	10.53	69.89	13.97	36.18	3.25	11.58	1.61	198.70	310.90	0.44	0.74	0.65
3-5	175.90	2.24	12.22	0.69	0.47	514.80	460.50	320.40	25.28	0.97	5.46	1.89	25.62	17.15	6.67	40.10	6.61	42.72	10.64	28.02	2.43	12.04	1.29	125.50	201.61	0.40	0.75	0.74
3-2	126.10	2.10	11.87	0.65	3.33	163.30	533.80	336.00	31.29	0.64	5.45	1.84	23.20	14.68	5.01	29.58	5.10	31.68	6.50	18.90	1.68	7.54	0.84	93.58	152.63	0.50	0.72	0.81
3-13	324.00	11.10	12.78	0.41	7.34	281.40	451.90	332.90	11.28	1.63	5.94	2.06	20.64	12.11	3.95	14.80	3.32	26.86	6.31	12.29	1.31	5.39	0.85	70.27	117.45	0.65	0.90	0.68
avg	158.15	4.03	13.24	0.68	3.02	264.80	543.95	366.20	22.62	1.01	6.36	2.40	27.72	18.34	6.72	38.27	6.39	42.79	9.35	23.85	2.17	9.14	1.15	122.01	195.65	0.50	0.78	0.72
Type II																												
15-6	0.03	0.03	7.90	0.79	1.55	3.86	813.30	161.40	0.01	3.83	16.70	2.82	13.63	4.50	4.29	5.64	1.15	8.16	1.63	5.00	0.69	4.26	0.52	41.41	72.82	1.69	2.61	1.25
15-7	2.00	0.00	4.14	0.68	1.09	0.28	795.20	156.20	0.00	2.45	12.86	2.54	18.18	7.88	4.92	8.95	1.88	12.26	2.48	6.52	1.02	4.46	0.68	44.81	87.08	1.28	1.79	1.26
15-10	0.26	0.00	3.56	0.87	1.25	3.66	883.60	159.90	0.28	12.49	41.20	7.86	41.94	11.39	7.07	12.67	1.91	12.52	2.48	7.12	0.98	6.58	0.65	60.41	166.84	2.72	1.80	1.02
15-8	0.00	0.00	110.50	1.03	0.86	2.01	1047.00	209.10	0.00	14.37	55.16	11.26	61.73	28.25	15.78	32.53	4.60	19.84	3.12	6.58	0.66	4.07	0.52	29.75	258.46	2.59	1.59	1.06
15-9	0.95	0.06	7.89	0.80	1.07	13.28	703.30	209.80	0.09	1.68	9.69	2.77	20.60	9.52	3.98	13.70	2.17	13.82	2.55	5.81	0.74	4.42	0.38	55.96	91.84	1.11	1.07	1.10
15-3	0.00	0.01	5.82	0.72	0.74	0.04	700.70	183.00	0.23	0.85	7.23	1.88	13.59	6.54	5.24	10.79	1.78	12.95	2.55	6.82	0.97	3.90	0.56	29.26	75.65	0.88	1.91	1.40
15-1	0.00	0.11	7.27	0.75	0.61	7.15	734.00	174.90	0.07	1.67	9.57	2.49	16.95	6.07	4.10	12.37	2.07	12.53	2.82	8.13	0.74	3.60	0.45	40.63	83.55	0.96	1.45	1.15
15-2	3.34	0.06	3.61	0.82	0.56	6.65	910.20	176.20	0.00	2.16	16.78	4.19	32.42	17.59	9.29	26.18	4.61	26.95	5.58	13.20	1.47	7.47	0.88	99.42	168.76	0.95	1.32	1.37
15-4	0.00	0.00	17.03	0.79	0.70	0.00	947.30	147.10	0.25	4.79	17.96	2.98	11.70	3.83	2.85	4.34	0.72	4.74	1.04	3.22	0.57	2.15	0.40	27.89	61.29	2.57	2.13	1.17
15-11	0.66	0.00	5.85	0.59	0.10	0.98	788.80	216.00	0.24	1.49	7.35	1.63	15.23	6.00	2.87	10.82	1.78	10.92	2.78	6.88	0.66	2.90	0.30	47.73	71.61	0.93	1.09	1.16
15-12	2.39	0.00	2.87	0.90	0.64	4.11	859.20	234.60	0.16	1.79	11.33	2.46	19.25	7.25	4.78	15.33	2.09	13.68	3.84	10.38	1.31	5.25	0.75	55.04	99.48	0.89	1.39	1.32
15-13	1.79	0.18	2.58	0.80	0.90	0.00	740.80	241.80	0.02	1.99	9.49	1.87	12.73	4.73	1.60	6.61	1.48	9.28	2.09	7.41	1.03	4.66	0.86	54.87	65.82	0.97	0.87	1.20
15-14	4.29	0.00	4.00	0.62	0.66	1.42	865.70	180.20	0.14	3.64	17.86	3.71	30.44	13.61	6.37	16.66	2.99	22.19	4.79	12.31	1.46	6.49	0.96	66.30	143.49	1.11	1.29	1.19

Table 2. LA-ICP-MS analytical results of REE and trace elements (ppm) of scheelite from the Daping W deposit.

5.3. Ar–Ar Dating of the Muscovite

There were performed 12 heating steps for sample T16 (zk1502-496.4). The plateau and inverse isochron ages are listed in Table 3 and shown in Figure 9. The middle 6 steps yielded a well-defined plateau age of 133.45 \pm 1.34 Ma (Figure 9a) with about 83.2% of the ³⁹Ar for the sample T16 (zk1502-496.4). Accordingly, isochrons yielded ages of 132.71 \pm 1.59 Ma (MSWD = 2.32) for the sample T16 (zk1502-496.4) (Figure 9b). The initial ⁴⁰Ar/³⁶Ar ratios from the inverse isochron plots are 325.4 \pm 37.0, more than the atmospheric value of 295.5 \pm 5.0. However, the ratio of ³⁹Ar/³⁶Ar is strongly correlated with the ratio of ⁴⁰Ar/³⁶Ar, which is strictly distributed on a straight line (Figure 9b). Additionally, the isochronal age is consistent with the plateau age, suggesting that the muscovite dating age for the T16 (zk1502-496.4) is reliable.

Table 3. ⁴⁰Ar/³⁹Ar analytical data for muscovite from the Daping W deposit.

Т	(40 • (39 •)	(37 • (39 •)	(36 A (39 A)	(38 • (39 •)	⁴⁰ Ar(r)	³⁹ Ar(k)	Age	Error±2
(°C)	- (**Ar/**Ar) m	$(3^{\prime} Ar/3^{\prime} Ar)_{m}$	$({}^{30}Ar/{}^{37}Ar)_{m}$	$({}^{30}Ar/{}^{37}Ar)_{m}$	(%)	(%)	(Ma)	(Ma)
700	161.64826	0.27965	0.35589	0.09183	34.96	0.60	115.34	4.84
780	100.03745	0.03006	0.12051	0.03601	64.40	1.46	130.92	2.03
850	88.62859	0.02928	0.08112	0.03161	72.95	3.12	131.37	1.02
900	86.98936	0.00291	0.07505	0.02786	74.51	6.91	131.67	0.86
940	69.10440	0.00082	0.01160	0.01587	95.04	15.52	133.36	0.47
980	67.63268	0.00000	0.00694	0.01490	96.97	21.43	133.18	0.46
1020	68.37243	0.00000	0.00975	0.01550	95.78	21.49	132.99	0.48
1060	70.10919	0.00633	0.01440	0.01620	93.93	12.23	133.71	0.50
1100	71.14390	0.00487	0.01675	0.01693	93.04	7.48	134.37	0.59
1140	72.77204	0.03099	0.02388	0.01944	90.30	5.07	133.44	0.77
1200	76.29759	0.00000	0.03062	0.01924	88.14	2.60	136.44	1.41
1400	83.27316	0.08206	0.05877	0.02415	79.15	2.08	133.83	2.36



Figure 9. ⁴⁰Ar/³⁹Ar spectrum (a) and isochron ages (b) of muscovite from the Daping W deposit.

6. Discussion

6.1. Characteristics and Geological Significance of REEs and Trace Elements

Previous research indicates that the REEs and trace elements characteristic of scheelite can be used to determine the types of deposits [8–10,12–14]. The greatly contrasting Mo content in different scheelite samples is an effective index for distinguishing different types of deposits (Figure 10) [34]. The generally low concentrations of Mo in the Daping scheelite reflect that the Daping W deposit constitutes a vein-greisen-type deposit (Figure 10). In addition, the ratio of Sr to Mo is an important geochemical indicator for estimating the mineralization conditions of scheelite [35,36]. In a magmatic hydrothermal environment, scheelite is generated from ore-forming fluids of the highly differentiated felsic magma. The Sr is generally depleted in felsic magma, and the ratio of Sr to Mo in scheelite is low in a magmatic hydrothermal environment [35]. In contrast, the Sr is easily enriched in a

metamorphic environment, and can be released by mineral metamorphism. Therefore, the ratio of Sr to Mo is much higher in the metamorphic environment than in the magmatic environment [36,37]. Scheelite samples from the Daping W deposit have low values of Sr/Mo. All data were plotted in the scope of magmatic–hydrothermal scheelite in the Sr/Mo– δ Eu diagram (Figure 11), indicating that the tungsten mineralization was related to regional magmatic hydrothermal activities. Therefore, the element composition of scheelite can reflect the composition of hydrothermal fluids and mineralization conditions [34,38–40].



Figure 10. A comparison of MoO₃ contents (%) in different types of scheelite from the Daping deposit with those from various types of tungsten deposits around the world, with data from various sources [41–49].

The REE composition of scheelite is generally influenced by the crystal structure and the charge balance, especially for a site the size of the Ca site [10,34]. Many studies have explored the substitution mechanisms of trivalent REEs for divalent Ca in scheelite [10,13,34,40]. These mechanisms are commonly recognized to solve the charge balance problem, such as:

$$2Ca^{2+} = REE^{3+} + Na^+$$
 (1)

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

$$3Ca^{2+} = 2REE^{3+} + Ca$$
 (3)

Ca: Ca²⁺ ion vacancy

The results for the REEs and trace elements of scheelite in the Daping W deposit show a poor correlation of REEs and Na (Figure 6b), and the concentration of Na is very low. Meanwhile, the correlation between Nb + Σ REE and Ca + W was poor, with a Pearson correlation coefficient of negative 0.005. The above relationships indicate that the first two substitution mechanisms ((1) and (2)) are not applicable to the Daping W

deposit. Meanwhile, the third may be the predominant mechanism of REE substitution in scheelite. Therefore, scheelite primarily inherits the REE pattern from the ore-forming fluid [7–9,32,34].

In summary, the differences in the distribution of REEs and trace elements in different types of scheelite can be an important indicator of the mineralization process of the Daping W deposit, providing information related to ore-forming sources and the mineralization environment and process. This paper focuses on the redox environment in the process of mineralization.



Figure 11. Plot of Sr/Mo versus δ Eu for scheelite samples from the Daping W deposit (after Poulin et al., 2018 [35]).

6.1.1. Distribution of Rare Earth Elements in Scheelite

The distribution of rare earth elements in scheelite can be used as an indicator to distinguish the source of ore-forming materials and the environment, providing a basis for the prospecting and evaluation of ore deposits [8]. The total content of rare earth elements ($\Sigma REE + Y$) in the scheelite of the Daping deposit ranges from 89.18 to 509.60 ppm, which is slightly higher than the $\Sigma REE + Y$ contents in scheelite (ranging from 40.50 to 123.60 ppm) of the Woxi vein-type Au-Sb-W deposit [41] and the $\Sigma REE + Y$ in scheelite (from 40.50 to 123.60 ppm) of the Houchangchuan vein-type W deposit (from 311.80 to 321.91 ppm) [50]. However, this value is far lower than that of the $\Sigma REE + Y$ in scheelite (from 4413 to 9584 ppm) of the Xingluokeng porphyry-type W deposit and slightly lower than the $\Sigma REE + Y$ in scheelite (from 4413 to 9584 ppm) [51] of the Dongyuan porphyrytype W deposit (from 553.05 to 2095.40 ppm) [52]. Previous studies of the vein (greisen)type and porphyry (skarn)-type tungsten deposits in South China have shown that the content of REEs in two types of tungsten mineral deposits (scheelite or wolframite) differs significantly. According to ΣRE_2O_3 , the porphyritic (skarn)-type tungsten deposit generally ranges from 1049.70 to 3034.59 ppm (with an average of 1884.36 ppm); meanwhile, the vein (greisen)-type generally ranges from 66.57 to 445.38 ppm (with an average of 334.88 ppm). The content of REEs in the vein (greisen)-type tungsten minerals is lower than that in the porphyritic (skarn)-type tungsten minerals [9]. Therefore, the Daping W deposit constitutes a vein (greisen)-type tungsten deposit.

According to the distribution of rare earth element chondrites in the Daping scheelite (Figure 7), we can distinguish two types of scheelite. The ratio of $(La/Nb)_N$ in type I scheelite is less than 10, and there are weak negative Eu anomalies (δ Eu from 0.26 to 0.90, average 0.78) in this type of scheelite, reflecting the deficiency of LREE in this type of scheelite. The type II scheelite rare earth element chondrites are in the shape of a seagull, and the positive Eu anomalies (δ Eu from 0.87 to 2.61, average 1.56) reflect the inconspicuous differentiation of LREE and HREE. Previous studies of the vein (greisen)-type and porphyry

(skarn)-type tungsten deposits in South China have shown that the distribution of REEs clearly differs between the two types of tungsten mineral deposits (scheelite or wolframite). Moreover, the pattern curves of scheelite and wolframite in the same type have essentially the same shape. The scheelite REE pattern curves of porphyry (skarn)-type tungsten deposits are consistently inclined to the right by 25–30°, while those of vein (greisen)-type tungsten deposits are sharply inclined to the left, with the heavy REE being larger than the light REE or nearly equal to the light REE.

The significant difference in REE patterns between type I and type II scheelite reflects the fact that there are small negative Eu anomalies and large positive Eu anomalies in the early stage of greisen and the middle stage of greisen, respectively. From type I to type II scheelite, the total content of rare earth elements gradually decreases. The characteristics of REE content and patterns indicate that the ore-forming materials are mainly derived from crust granites, namely biotite or two-mica granites. Meanwhile, the results of REEs and trace elements also can be attributed to variation in mineralization conditions and processes, which are reflected by Eu anomalies, and Sn, Mo, and Sr contents.

6.1.2. Indication of Eu Anomalies and Trace Element Characteristics

The Eu anomalies are an important indicator of the degree of magma differentiation and metallogenic redox environments [9]. The crystal of scheelite (CaWO₄) has a tetrahedral structure and the ionic radius of Ca is 1.12 Å. Eu (both Eu²⁺ and Eu³⁺) can substitute Ca in scheelite through entering the lattice of scheelite crystal. The ionic radii of Eu²⁺ and Eu³⁺ are 1.25 Å and 1.066 Å in scheelite, respectively [53–55]. Based on the charge balance, Eu²⁺ can easily replace the Ca²⁺ in reducing conditions, which can produce positive Eu anomalies in scheelite. Meanwhile, the Eu³⁺ can substitute Ca²⁺ by entering the lattice of scheelite, reflecting that the metallogenic environment is in relatively oxidative conditions and resulting in negative Eu anomalies. The two types of scheelite have Eu anomalies that are clearly different, as shown in Figures 7 and 8a. The data for type I are plotted below the 1:1 line (Figure 8a), representing a negative Eu anomaly. Meanwhile, most of the data of type II are plotted above the 1:1 line, representing a positive Eu anomaly. Therefore, the changes in the Eu anomalies indicate that the solution environments of type I and type II scheelite precipitation in the Daping deposit are constantly changing (from an oxidizing to a reducing environment).

In addition, Mo, Sn, and Sr are always enriched in the high-temperature gasification hydrothermal stage formed in the late stage of magma crystallization differentiation. Since these elements are similar to W^{6+} in terms of ionic radius, ionic potential, or electronegativity, they can be enriched in tungsten minerals (scheelite and wolframite) by the isomorphic substitution of W. The characteristics of trace elements also have certain indicative significance to the changes in the ore-forming fluid environment and the sources of ore-forming materials. Mo^{6+} and Mo^{4+} are two different valence states of Mo. Mo^{6+} mostly appears in oxidizing conditions, whereas Mo^{4+} mostly appears in reducing conditions [54]. Due to them having same ionic radius, W^{6+} (0.62 Å) can be easily substituted by Mo^{6+} (0.62 Å), forming a complete solid solution powellite (CaMoO₄) [55]. However, Mo^{4+} has difficulty replacing W^{6+} . Therefore, the concentration of Mo in scheelite is much higher in an oxidizing environment but lower in a reducing environment. The diagram of (Mo-Eu)/Eu* shows that the content of Mo in type I scheelite is higher than that in type II, indicating that scheelite mineralization changes from an oxidizing to reducing environment during the early-to-late greisen stage.

Similarly, there are two different valence states of Sn: Sn⁴⁺ and Sn²⁺. Sn⁴⁺ mostly occurs in relatively oxidative environment and Sn²⁺ often appears in reduction environments [55]. Due to its ionic radius being similar to Sn⁴⁺ (0.77 Å) and W⁶⁺ (0.68 Å) in scheelite, Sn⁴⁺ can easily substitute for W⁶⁺, whereas Sn²⁺ (1.30 Å) can hardly enter scheelite lattices due to its large ionic radius, and therefore has difficulty substituting for W⁶⁺. Meanwhile, Sn mainly reflects incompatibility during magmatic evolution in reducing environments. The diagram of Sn-Eu/Eu^{*} shows that the content of Sn in type I is higher than

in type II scheelite in the Daping W deposit. The Sn content characteristics indicate that the scheelite mineralization in the Daping W deposit changes from an oxidation environment to a reduction metallogenic environment between the early and late periods of the greisen stage. In addition, Sn is more likely to be enriched in type I scheelite (early greisen stage), as it is mainly affected by the late magmatic–hydrothermal solution. Meanwhile, type II scheelite is generated in the middle of greisen stage, which is mainly affected by primary mineral decomposition and is generally accompanied by some formation water.

In the process of granite greisenization, the content of Sr in ore-forming fluids is continuously enriched by Sr released from the alteration of plagioclase. Then, the content of Sr in type I scheelite is lower than that in type II scheelite. Therefore, the precipitation sequences of the two different types of scheelite were also verified by the content characteristics of the trace elements in scheelite.

According to the characteristics of Eu anomaly, Sn and Sr contents in the Daping scheelite, it is inferred that ore-forming fluids are mainly derived from crust granite (such as biotite and two-mica granite). Based on the comparation of δ Eu, Mo and Sn in different types scheelite, it is found the precipitation environment of scheelite is from oxidation to reduction environment in the Daping W deposit.

6.2. Timing of Tungsten Mineralization

The method of muscovite Ar–Ar dating is widely used to date hydrothermal ore deposits e.g., [56–60]. As described above, the muscovite sample was formed in the second (greisen) stage. The results of the muscovite age-spectrum plateau data and its isochronal age date are 133.5 ± 1.3 Ma and 132.7 ± 1.6 Ma, respectively, implying that the 40 Ar/ 39 Ar ages of the muscovite were not affected by the later thermal disturbance. The muscovite 40 Ar/ 39 Ar age refers to the timing of the original muscovite crystallization, which can represent the greisen stage. Thus, the muscovite 40 Ar/ 39 Ar age of 133.5 ± 1.3 Ma could represent the timing of tungsten mineralization at 133 Ma.

Ages of mineralization represent an important clue to understanding ore deposits, both from an academic perspective and an exploration point of view [61]. Previous studies have shown that Late Jurassic and Early Cretaceous granite are widely distributed and constitute the main body of the Mufushan composite batholith, which can be roughly divided into four periods: (1) the first stage (154~145 Ma) in the Early Yanshanian period, which mainly comprises granodiorite and coarse- and medium-grained porphyritic biotite monzogranite; (2) the second stage (145~140 Ma) in the late Yanshanian period, which mainly comprises gneissic biotite monzogranite; (3)the third stage (140~130 Ma) in the Late Yanshanian period, which mainly comprises two-mica monzogranite; (4) the fourth stage (117~98 Ma) in the Late Yanshanian period, which mainly comprises fine-grained muscovite monzogranite [2,15,62].

The Daping W deposit has a close spatial relationship with the Sijiapu biotite monzogranite outcropping in the south of the mining area, which is located in the north of the Mufushan composite batholith. The Sijiapu granite body is a grayish white medium-finegrained porphyritic biotite monzogranite, which is the product of the second intrusion of the Mufushan composite batholith in the Late Yanshanian period. The Daping W deposit is 1.4 km away from the Sijiapu granite body. The muscovite ⁴⁰Ar/³⁹Ar age is likely much closer to the age of two-mica monzogranite; however, considering the error rates of different mineral dating methods [24], we think that the metallogenic parent rock of the Daping W deposit is the biotite monzogranite; previous studies that are based on field observation also concluded that the Sijiapu granite body (biotite monzogranite) is the metallogenic parent rock of the Daping W deposit [1]. Next, we will systematically study the source of the ore-forming materials of this deposit.

6.3. Tungsten Mineralization and Diagenesis

The metallogenic age of the Daping W deposit obtained in this work (133.5 ± 1.3 Ma) is consistent with the zircon U-Pb ages ($140.2 \sim 145$ Ma) of biotite monzogranite obtained in the

previous studies within the error range [62–65], and is also consistent with the zircon U-Pb ages (131.9~139.3 Ma) of two-mica monzogranite samples from the Mufushan composite batholith, within the error range [62–64,66]. In contrast, the metallogenic age of the Daping W deposit may be much closer to the diagenesis age of two-mica monzogranite in the Mufushan batholith.

The study of REE partitioning in the Daping scheelites shows that heavy REEs are larger than light REEs and are nearly equal to the light REEs in the type I and type II scheelite. In other words, scheelite REE pattern curves are left-inclined and have a "Seagull" shape in the Daping deposit, and therefore constitute a vein(greisen)-type tungsten deposit. Additionally, the ore-forming materials are mainly derived from crust granites of the vein (greisen)-type tungsten deposit [8], such as biotite monzogranite. Based on our research, the Daping W deposit is a vein (greisen)-type deposit that is genetically related to the biotite monzogranite in the Mufushan composite batholith.

6.4. Metallogenic Background of the Daping W Deposit

South China is an important strategic mineral resource base. The late Mesozoic magmatic evolution of the South China Block has long been debated. Two distinct competing models have been proposed: a subduction model [67] and a lithospheric extension model [68]. The subduction model is, so far, the most popular model accounting for the origin and evolution of the Jurassic–Cretaceous magmatism in SE China [69]. The subduction model emphasizes the low-angle subduction of a Paleo–Pacific Plate in the Early-Middle Jurassic, subsequent roll-back in the Cretaceous, and the consequential formation of late Mesozoic magmatic belt of 600 km in width, with the migration of Jurassic–Cretaceous magmatic activity oceanward towards the coast of southeast China [70,71].

A large number of Mesozoic continental crust remelting granitoids have developed in South China, and are closely related to the largescale mineralization of W, Sn, Li, Be, Nb, Ta, REE, U, and other metals. Highly differentiated granites and regional tectonic control are the keys to rare metal (W-Sn-Nb-Ta-Be) mineralization in this area. There are lots of metallogenic types, such as the granite-type, pegmatite-type, vein-type, skarn-type, and ribbon rock-type [72]. The main metallogenic epochs of the rare metal deposits in South China are represented by the following seven periods: the Silurian (424~420 Ma), Early Triassic (248~244 Ma), Late Triassic (220~214 Ma), Later Jurassic (160~150 Ma), Late Jurassic-Early Cretaceous (150~140 Ma), Early Cretaceous (135~125 Ma), and Early Cretaceous–Late Cretaceous (105~90 Ma). Among these periods, the Early Cretaceous (135~125 Ma) is the most important period for large-scale rare metal mineralization in South China; it not only has the highest intensity of mineralization, but also includes various types of mineralization, representing the peak period of the large-scale thinning or disintegration of the continental lithosphere in the Mesozoic in South China [25,72–77].

It is clear that the partial melting of crustal materials, continuous energy supply, and large-scale extension are favorable for magma differentiation and evolution; these are the key ingredients for the formation of large-scale deposits of rare metals (such as W-Sn-Nb-Ta-Li-Be). The endogenetic deposits in South China are characterized by horizontal zoning around intermediate acid intrusive rocks. The contact zone between the rock mass and wall rock is the site of hydrothermal activity, which is superimposed by multistage tectonic activity and becomes a favorable metallogenic space for hydrothermal migration and precipitation. There is also some non-ferrous metal mineralization in the rare metal deposits in South China, such as the Songshugang (Nb-Ta-W-Sn) ore deposit in Jiangxi Province, the Limu W-Sn-Nb-Ta ore deposit in Guangxi Province, and the Xianghualin W-Sn-Nb-Ta-Pb-Zn ore deposit in Hunan Province. The Daping W deposit is located in the northwest of the Mufushan composite batholith. There are several rare metal deposits near the Daping tungsten deposit (133 Ma), such as the Huadunqiao tungsten deposit, the Duanfengshan (Nb-Ta) rare metal deposit (128~130 Ma) [25], the Zheping Pb-Zn deposit, the Renli (Li-Be-Nb-Ta) rare metal deposit (125~133 Ma), and so on (Table 4 and Figure 12), which are distributed from the north to the south of the Mufushan composite batholith. Meanwhile, the Daping W deposit is adjacent to the large Xianglushan W deposit in Jiangxi Province, which has a similar metallogenic background. Therefore, the study area constitutes a good prospecting site for W-(Sn)-Nb-Ta polymetallic ore.

Timing	Late Jurassic-Early (150~125)	v Cretaceous Ma)
Deposit	150~135 Ma	135~125 Ma
W		I
Nb(Ta)		
Li		
Be		

Figure 12. Diagram of the Metallogenetic epoch sequence in the Mufushan composite batholith, with data from various sources [15,25,62,78].

Table 4. Metallogenic age of the Mufushan composite batholith.

Deposit	Sampling Location	Lithology	Analytical Methods	Age (Ma)	References
W deposit	Daping (the north of the batholith)	Greisen	Muscovite Ar-Ar dating	133.5	This paper
Nb-Ta deposit	Duanfengshan (the northwest of the batholith)	Col-pegmatite	Muscovite Ar-Ar dating	127.7	[25]
Nb-Ta deposit	Renli (the south of the batholith)	Col-pegmatite	lepidolite Ar-Ar dating	125.7	[14]
Li deposit	Chuanziyuan (NO. 106 dike) (the south of the batholith)	Spd-pegmatite	Muscovite Ar-Ar dating	130.8	[78]
Li deposit	Chuanziyuan (NO. 206 dike) (the south of the batholith)	Spd-pegmatite	Muscovite Ar-Ar dating	135.4	[53]
Be deposit	Daxing (the center of the batholith	Brl-pegmatite	Muscovite Ar-Ar dating	130.5	[25]

7. Conclusions

- (1) Based on the petrographic observations, the alteration and ore-forming process of the Daping W deposit can be divided into the magmatic period (stage 1) and the metallogenic hydrothermal period (from stages 2 to 4). Meanwhile, the metallogenic period includes four stages: (1) the magmatic stage, (2) the greisen stage, (3) the hydrothermal sulfide stage, and (4) the calcite stage. There are two main types of scheelite in the Daping W deposit: type I in the early greisen stage and type II in the middle greisen stage.
- (2) The characteristics of the REEs and trace elements of the two types scheelite are obviously different. Type I scheelite has left-dip-type REE patterns, negative Eu anomalies, relatively high contents of Mo and Sn, and low contents of Sr. However, type II scheelite has "seagull wing"-shaped REE patterns, positive Eu anomalies, low concentrations of Mo and Sn, and intermediate-to-high Sr content.
- (3) The content of W in the greisen veins in the study is proportional to the intensity of greisenization and muscovite, which are closely associated to the scheelite. Therefore, the muscovite 40Ar/39Ar age of 133.5 ± 1.3 Ma may represent the timing of tungsten

mineralization at 133 Ma. The Daping W deposit was formed in the Late Yanshanian period, between the first Mufushan intrusion of biotite monzonite granite (zircon U-Pb age 140.2–145 Ma) and the second intrusion of medium-fine-grained mica monzonite granite (zircon U-Pb age 131.9–137 Ma). Based on the error rates of different mineral-dating methods and previous studies [24], it is inferred that biotite monzogranite is more likely to be the metallogenic parent rock of the Daping W deposit. Further research on the genetic connections of tungsten-forming minerals is needed.

(4) The Daping deposit is located in the Toncheng–Jiugongshan W-Sn-Au-Ag and rare metal IV metallogenic belt of Yanshanian Au-Ag-Pb-Zn-W, and the rare metal metallogenic belt in the eastern section of the Jiangnan Orogenic belt. Two km to the west of the study area is the large granite-pegmatite Nb-Ta deposit in the Duanfengshan area. On the south side is the Mufushan composite batholith, in which several Li-Be-Nb-Ta pegmatite veins are exposed. This area is characterized by many hydrothermal activities. The study area is located near the contact zone between the granite body and the wall rock. Several structures are developed, with good hydrothermal ascending channels and ore control conditions. To sum up, the Daping area has good ore storage space and is a favorable area for prospecting W-(Sn)-Nb-Ta polymetallic ores.

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