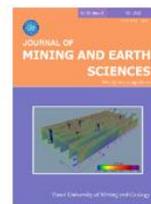




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Mineralogical and geological characteristics of the Nui Phao tungsten deposit and its resource in the Dai Tu area, northeastern Vietnam



Khang Quang Luong ¹, Hung The Khuong ^{1,*}, Dung Tien Vo ², Tuyen Danh Nguyen ³

¹ Hanoi University of Mining and Geology, Hanoi, Vietnam

² Masan High-Tech Materials, Thai Nguyen, Vietnam

³ Vinacomin - Vietbac Geology Joint Stock Company, Hanoi, Vietnam

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ABSTRACT

Typically, granitic intrusions that document the lengthy and intricate history of the magmatic-hydrothermal system are linked to tungsten deposits. Uncertainty persists about the genetic relationship between tungsten mineralization and magmatic-hydrothermal development. The primary tungsten deposit in the Dai Tu region, known as the Nui Phao deposit, has been the subject of a petrographical and microscopic examination. Tungsten mineralization in the Dai Tu area often occurs in association with the formation of skarn and greisen bodies, and it has drawn much attention from geoscientists. Based on microscopic observations, tungsten ores can be divided into three mineralization stages, namely skarnisation, greisenization, and hydrothermal stage. To examine the geochemical features of the tungsten ores, the SEM-EDS and Microscope analytical methods were performed in this study. Research results indicate that the Nui Phao tungsten deposit was formed due to different tectonic and magmatism episodes. Accordingly, the Nui Phao tungsten deposit is relatively complicated with the multi-sources of ore components. Most of the tungsten ore was accumulated in association with the metasomatism between the Ordovician-Silurian carbonate-terrigenous sedimentary rocks of the Phu Ngu formation and the Cretaceous two-mica granite of the Pia Oac complex. The research results indicate that tungsten resources obtained at levels 122 and 333 are about 227.6 thousand tons. Moreover, the hydrothermal alteration and metasomatism in the study area are influenced by at least three metasomatic episodes, including skarnisation, greisenisation, and the late hydrothermal alteration of medium to a low temperature that is genetically related to fluorite-polymetallic mineralization.

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*Corresponding author

E - mail: khuongthehung@humg.edu.vn

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1. Introduction

Tungsten has excellent electrical and thermal conductivities and high density and heat resistance. Tungsten is corrosion-resistant to a wide range of acidity and alkalinity. Tungsten electrodes are used in welding procedures, such as resistance welding, and are especially useful for welding materials like copper, bronze, or brass. Tungsten has the highest melting point of all known elements barring carbon, melting at 3.420°C and the highest specific weight of all metals, and it is known for its dimensional stability at high temperatures. Incandescent filaments and electron tubes are the most common uses for tungsten. In the vapor deposition technique, tungsten filaments or boats are employed.

The Dai Tu area has abundant mineral resource categories, a major competitive advantage in developing the metallurgical industry and mining. Geological mapping has revealed several tungsten ore deposits in the Dai Tu area. However, except for the Nui Phao region, most of these deposits are estimated to be modest

to medium in size (Ngo, 1991; Dudka, 2003; Tran et al., 2003; Nguyen et al., 2016; Khuong et al., 2020). So far, no research projects have discussed thoroughly and systematically the geological properties and tungsten mineralization in the research region, which is especially true of the lack of intensive research on ore mineralization and geological parameters of tungsten orebodies. In this paper, based on microscopic observations, geochemical data, and isotopic data presented in previous studies, we will clarify the mineralogical and geochemical characteristics of tungsten ores and their resource from the Nui Phao area, northeastern Vietnam.

2. General geological features

The lithology of the Dai Tu region is made up predominantly of coaly shale rocks interbedded with clay shale, muscovite-bearing quartzitic sandstone, chert and sandstone of which formation known as the Phu Ngu formation, is thought to have formed during the Ordovician-Silurian period (Ngo, 1991). In the northern study area, intrusive granite rocks are exposed in mass-shaped, termed Da Lien block (Figure 1B).

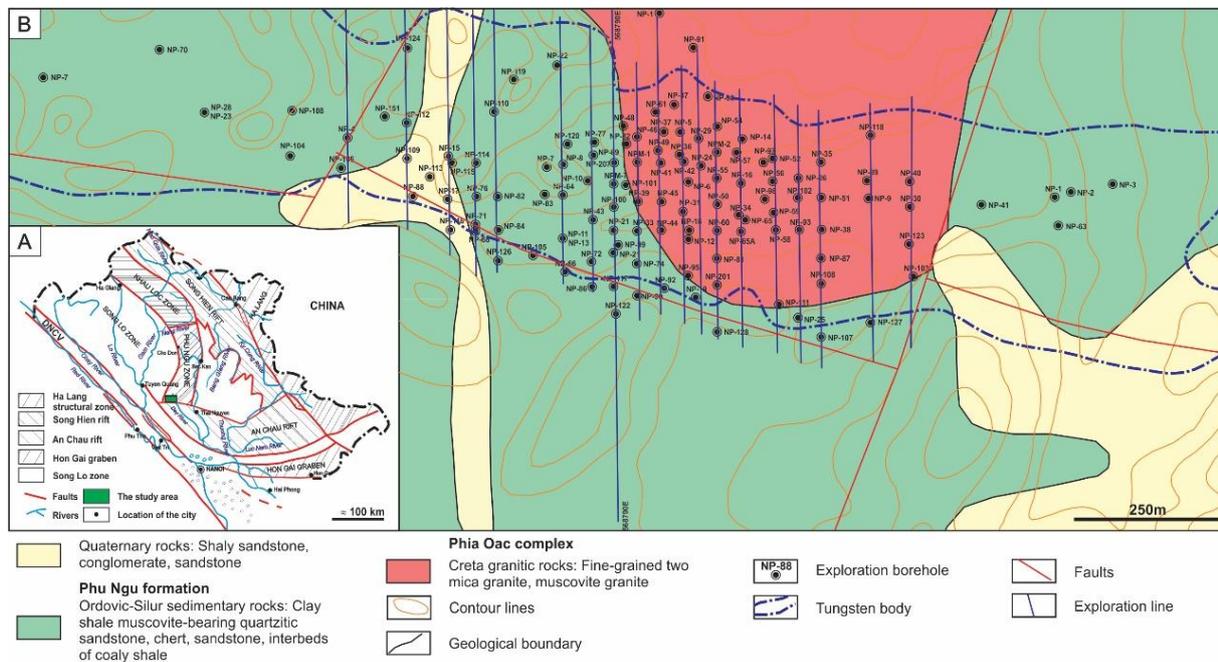


Figure 1. A-Tectonic sket map of northeastern Vietnam, showing the study area (Dovijkov, 1965); B-Simplified geological map of the Nui Phao tungsten deposit, Dai Tu area (modified from Dudka, 2003; Tran et al., 2003).

Quaternary sediment distributes along the river and valley.

In the Dai Tu area, three fault systems have also been identified (Dudka, 2003; Tran et al., 2003; Vo, 2017). They are northwest-southeast, northeast-southwest, and near a west-east trending system of which the northwest-southeast fault system has been supported as the major fault and controlled the main structure of the Dai Tu area. Most of the tungsten orebodies discovered in the Nui Phao deposit are related to this fault system and the Da Lien and Nui Phao granitic massive (Phan, 2003; Tran et al., 2003; Nguyen et al., 2016).

3. Methods

The authors have applied field investigation, analytical and mineral resource estimation methods to evaluate tungsten mineralization characteristics in the Nui Phao deposit based on the combination of geological data collected, synthesized, and processed from previous documents.

3.1. Field investigation

The method applied is to use the geological mapping in the Nui Phao deposit for the descriptive outcrops, distribution, and characteristics of geological orebodies, namely strike-dip formats, thickness, host rocks relation, and physical parameters. The observed, thin, and thick samples were also taken to evaluate structural, textural ore, and host rocks.

3.2. Analytical methods

Thirty samples were collected from Nui Phao deposits (i.e., in outcrops and drill cores), and ore types in the study area to examine the ore mineralogy and geochemistry (major and minor elements). Thin and polished sections were prepared from rock chips at Hanoi University of Mining and Geology. Microscope (Carl Zeiss – Axio Scop. A1) and Scanning electron microscope (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) (Quanta 450, FEI Company, Hillsboro, OR, USA) were initially applied to determine and estimate mineral modes qualitatively.

3.3. Mineral resource estimation

A technical and economic stage, as well as a socioeconomic stage, are usually included in the mineral resource appraisal process. From analytical data generated in sample tests, technical evaluation leads to the calculation of tonnage (quantity) and mineral or metal content (quality), either worldwide or for portions of the deposit. The estimate is made using either traditional or geostatistical approaches. The selection of the specific classical method can be modified based on the type and form of the material contained (Pogrebiski, 1973). Based on the tungsten bodies' geological, distributed features, and strike-dip formats, the tungsten reserves/resources of the Nui Phao deposit are calculated following the geological block method (Pogrebiski, 1973; Kazdan, 1997).

The formula determines the ore reserves/resources of each block.

$$Q_i = S_i \times m_i \times D \quad (1)$$

The ore reserves/resources of the orebody.

$$Q = \sum Q_i \quad (2)$$

In which: Q - total ore reserves/resources of the orebody (ton); Q_i - ore reserves/resources of the i -th ore block (ton); D - bulk density of tungsten ore (ton/m³); S_i - area distribution of tungsten orebody (m²); m_i - average thickness of tungsten body (m).

4. Results and Discussion

4.1. Features of tungsten orebody

4.1.1. The major tungsten orebody characteristics

The Tiberon Minerals Company is exploring and developing the main orebody, a potential orebody in the Nui Phao deposit, which has numerous tungsten orebodies. The examined area's mineralization exhibits the following characteristics.

The main tungsten orebody is located where the Phu Ngu Formation's Ordovician-Silurian sediments and the steeply sloping Cretaceous Da Lien granite come into internal and external contact (Tran et al., 2003; Figure 2). This orebody is extended about 2 km in east-west trending, around 200÷400 m in width. This orebody's

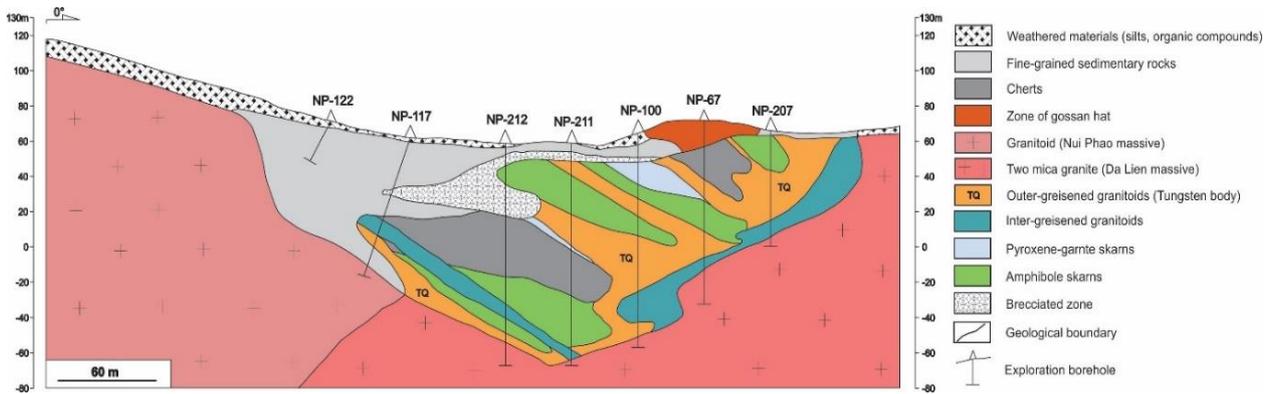


Figure 2. Geological cross-section along No. 568790E line of the Nui Phao tungsten deposit (modified from Dudka, 2003; Tran et al., 2003).

thickness can range from 43 m in the west to 159 m in the east. The "granite blade," the highest point of the Da Lien granite massif, functions as a critical point of the main orebody. To the east of the granite massif is where the main tungsten orebody is found. It has to do with a granite rock metamorphic zone that is up to 50 m thick (mainly internal greisenized granitoids).

Strong oxidation has caused the upper portion of the main tungsten body to produce a gossan zone that is rich in quartz and iron. In the northwestern Da Lien massif, the tungsten orebody is exposed on the surface as the polymetallic skarn/greisen zone. The orebody is exposed in an area of 850 m × 200 m × 10 m (length × width × depth).

The mineralized zone is made up of the interchanged byproducts of the hornfels thermal metamorphism of dike and granite, as well as skarnification, albitization, and greisenization. The granite massifs of Nui Phao and Da Lien encircle the mineralized zone, which is covered by a weathered layer that ranges in thickness from 20 to 40 m. The skarn and greisen zones are where the majority of the tungsten orebody is released. The metasomatic rocks consist of pyroxene, garnet, amphibole-biotite-(danalite), calcite, and magnetite-(danalite). Granitic dikes intrude on the Phu Ngu sedimentary rocks and are also metasomatized. Albite fluorite greisenization accompanied by biotite and pyrrhotite that overprints the skarn alteration around the Da Lien granite contact, and quartz veins are also present. Polymetallic mineralization is mainly developed in greisenized rocks and consists of fluorite, scheelite, native

gold, native bismuth, and chalcopryrite. Allantite, cassiterite, uncommon molybdenite, and Pb-Zn sulfides are further minor minerals.

4.1.2. Quality of tungsten orebody

The veinlet-disseminated type tungsten ores account for 90% of all type ores. Their bodies were hosted in the contact zones of two-mica granitoid and the pyroxene-garnet skarn zones. Most of the bodies in the Phu Ngu formation are classed as outer contact zones but the minor bodies formed in the greisenized granite are classed as the inter-contact zone. Quartz-scheelite ore is the primary ore type, and it is mostly dispersed in feldspar metamorphic skarn rocks and overlaying greisen metamorphic rocks, but to a less extent than in greisenized granite.

* Composition of ore minerals

The metallic minerals account for about 1% to 2% of the main orebody and are composed of magnetite, scheelite, wolframite, chalcopryrite, molybdenite, and pyrite. The gangue minerals account for about 98% to 99% of the orebody including quartz, feldspar, biotite, and clay minerals (Figure 3).

Magnetite: Magnetite in tungsten ores of the veinlet-disseminated type ore is 0.20÷0.80 mm in grain size, sometimes reaching ≈2 mm; they are distributed in ore bunch, band-shaped, disseminated, and scattered in skarn rocks (Figure 4a-b, e). Magnetite occurred closely with pyrite I and chalcopryrite I, forming mineral assemblages (Figure 4c-d).

Scheelite: Scheelite in the veinlet-disseminated type ore is 0.05÷0.50 mm in grain

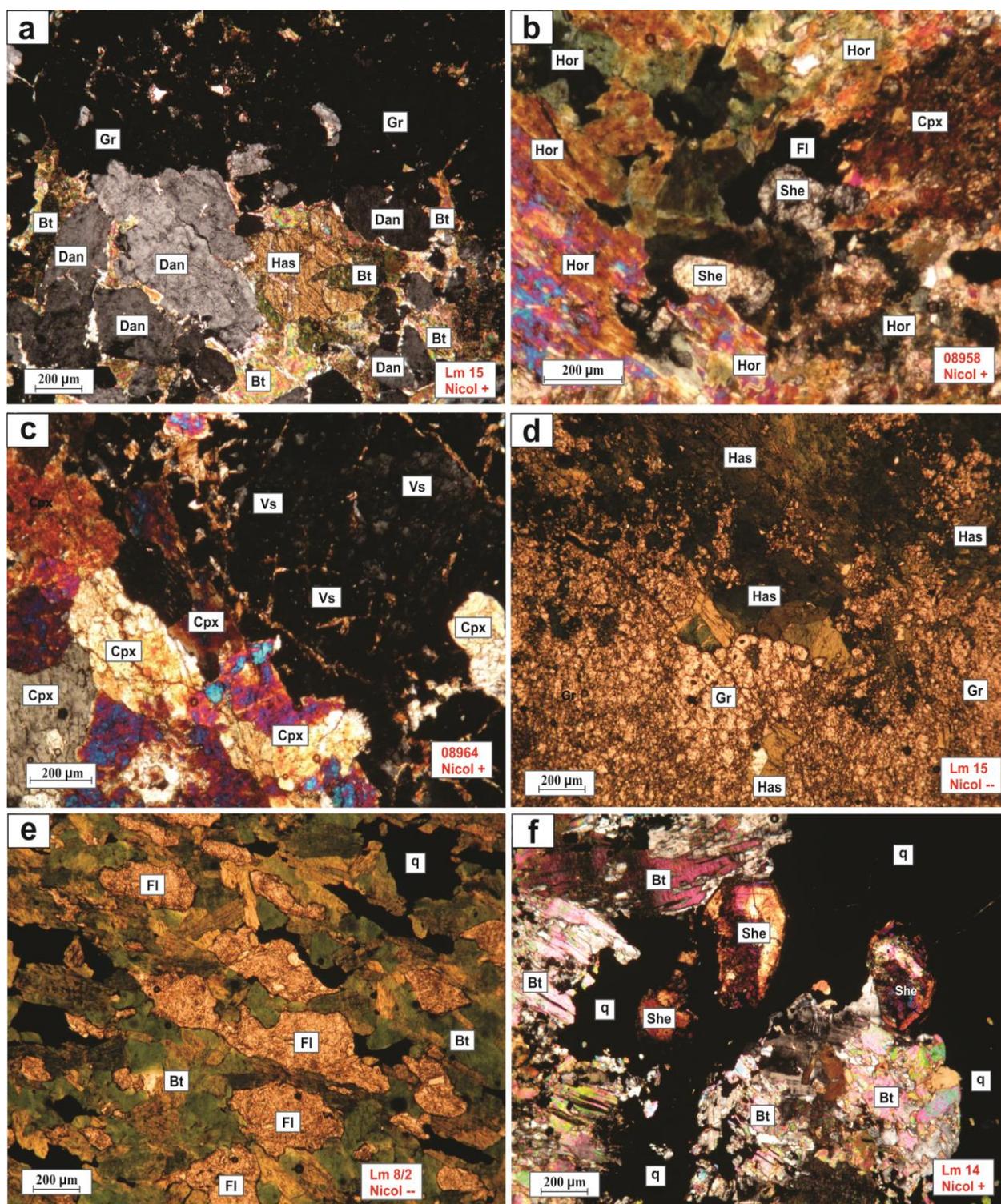


Figure 3. The gangue minerals of Nui Phao tungsten deposit; Hastingsite is replaced by biotite, and danburite (a) and is corroded by scheelite, fluorite, and ore minerals (b); Pyroxene (hedenbergite)-Vesuvian mineral assemblage (c). Garnet minerals are replaced by hastingsite (d); The greisenization process produces the mineral biotite along with other minerals (e), and ore minerals (f) (Photo from Vo, 2017). Vs-Vesuvian, Cpx-Clinopyroxene, Gr-Garnet, Has-Hastingsite, Hor-Hornblende, Bt-Biotite, Dan-Danburite, She-Scheelite, Fl-Fluorite, q-Ore minerals.

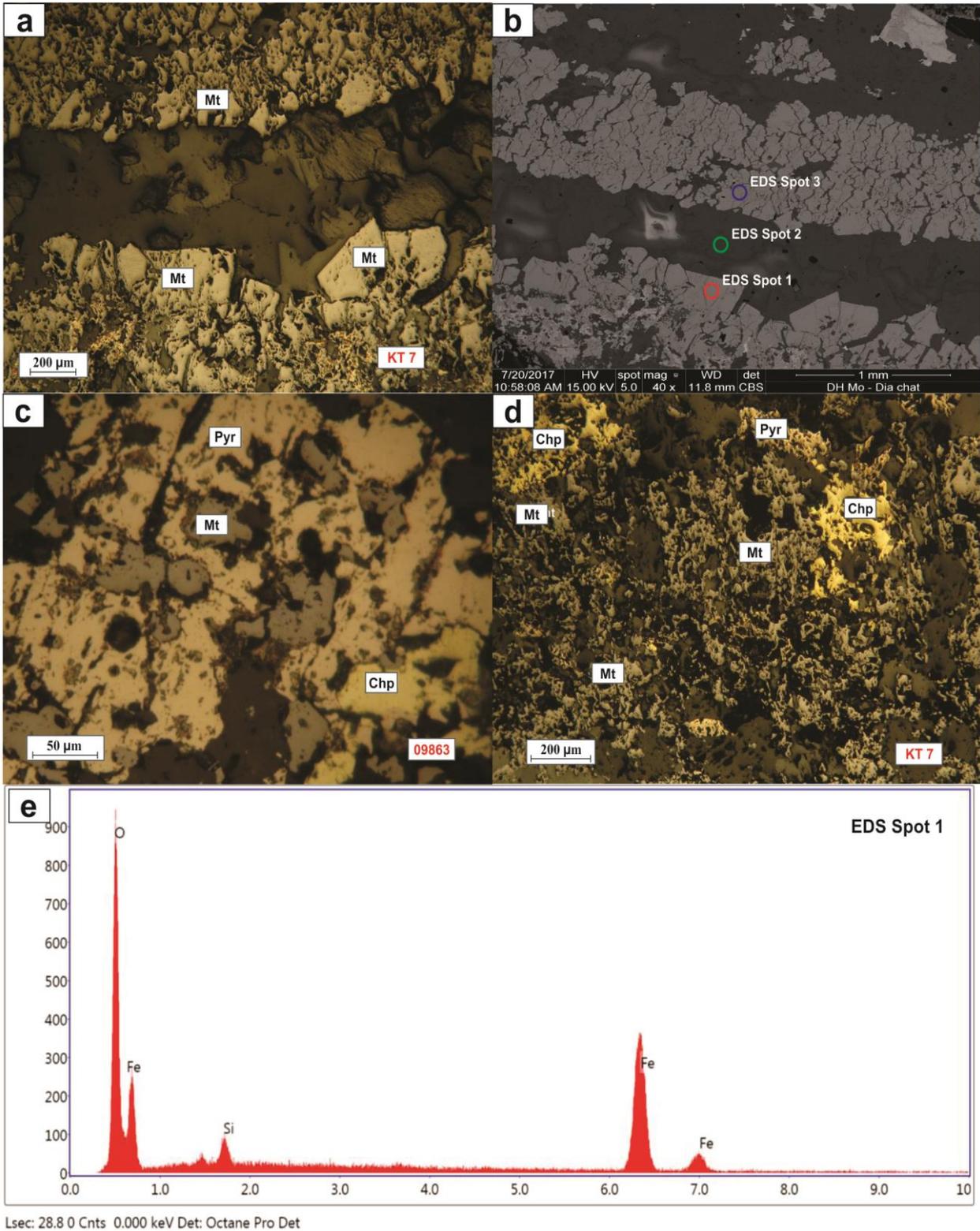


Figure 4. Band-shaped xenomorphic magnetite is found in the skarn rocks (a- A picture of an ore sample is taken using reflection contrast microscopy, b, e- Magnetite is captured under scanning electron microscope-SEM); Along with pyrrhotite I and chalcopyrite I, magnetite formed a group of minerals (c, d). Mt-Magnetite, Pyr-Pyrrhotite, Chp-Chalcopyrite.

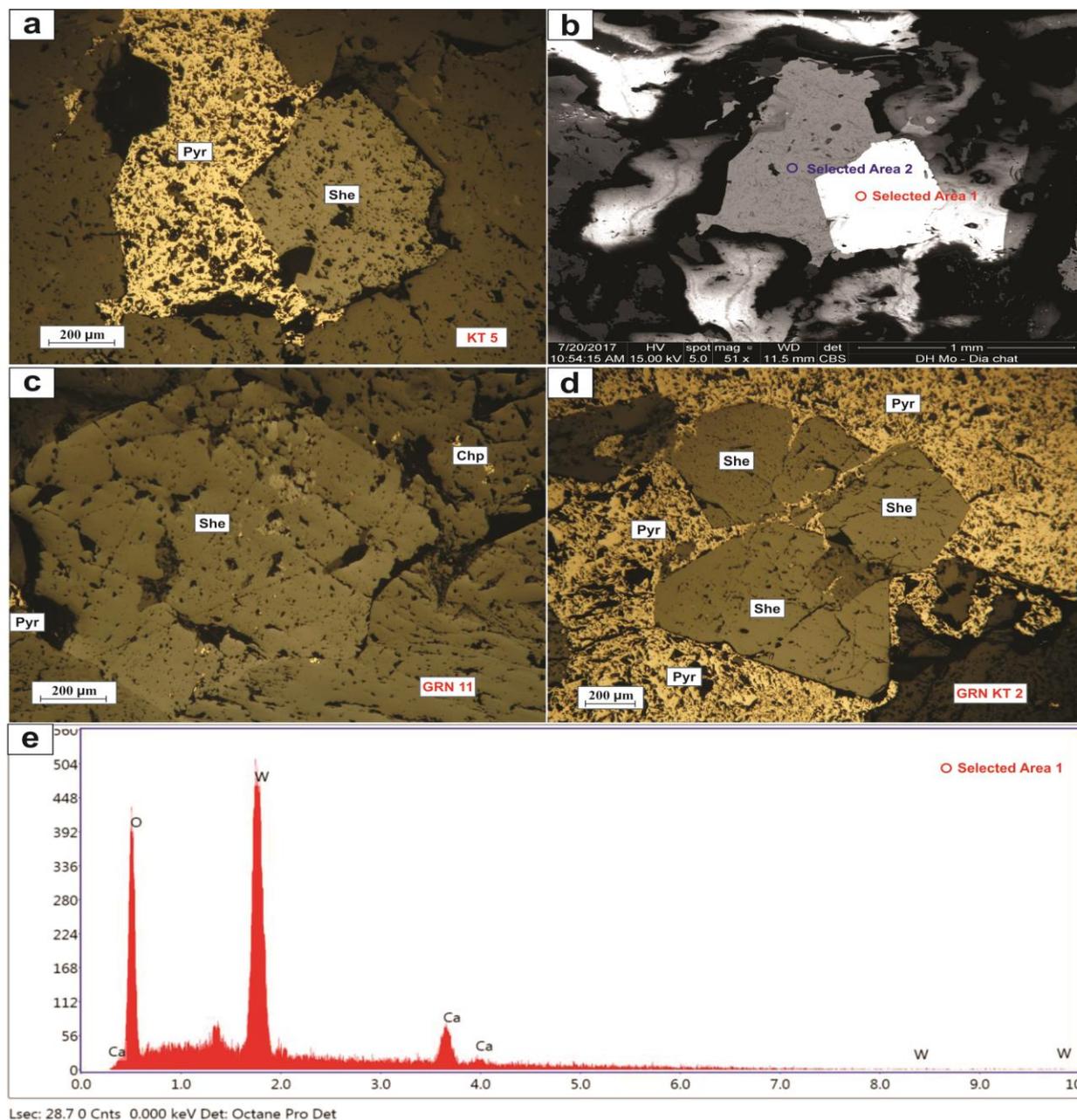


Figure 5. With evaluated points of mineral components, SEM and reflection contrast microscopy images of scheelite I are shown in (a, b, e). Within and outside of the greisenized zone, scheelite II is found (c, d). She-Scheelite, Pyr-Pyrrhotine, Chp-Chalcopyrite.

size, sometimes ≈ 1 mm, and primarily produced in anhedral granular crystals. Two generations of scheelite have been recognized based on distribution, shape, size, ore mineral relationships, and mineral paragenesis features. A paragenetic link exists between scheelite I (idiomorphic crystal) and pyrite I, chalcopyrite I, and other minerals (Figures 5a-b).

Semi-idiomorphic and allotriomorphic Scheelite II is granular, with grain sizes varying from 0.2 to 1.5 mm, occasionally exceeding 2 mm. Scheelite II is found in close association with quartz I and fluorite, where it forms veins and fissures. It is also found in greisenised granite (internal greisen) of the Da Lien massif. Fluorite,

quartz I, and scheelite II combine to generate a mineral paragenesis (Figures 5c-d).

+ Wolframite: Wolframites in tungsten ores of the veinlet-disseminated type ore are 0.01÷0.074 mm in grain size and are mostly produced in anhedral granular crystals. Wolframite minerals were scattered between the gangue minerals and the sparsely disseminated or dense disseminated zone. (Figure 6).

+ Chalcopyrite: Chalcopyrites are the dominant copper ore of the veinlet-disseminated type ore. Chalcopyrites are 0.20÷0.50 mm in grain size and are mostly produced in anhedral granular crystals. Those crystals were scattered between the gangue minerals and the sparsely disseminated or dense disseminated zone. Based on ore textures and mineral paragenesis, two

chalcopyrite generations have been distinguished. Chalcopyrite I accounts for about 5% total of chalcopyrite in the mine. It is often accompanied by pyrrhotine I and magnetite, forming a mineral paragenesis (Figure 4c). Chalcopyrite II is one of the most abundant sulfide minerals in the mine, which accounts for approximately 95% total of chalcopyrite in the Nui Phao mine. Chalcopyrite II has a paragenetic relationship with pyrrhotine II and bismutite, forming a mineral paragenesis (Figures 4d, 5c).

+ Molybdenite: Molybdenites are 0.05-0.20mm in grain size and are primarily produced in foliated or scaly aggregation. Molybdenites occur in a quartz vein with disseminated or fine veinlet or modular structure, and it is closely related to magnetite, and pyrrhotine (Figure 7).

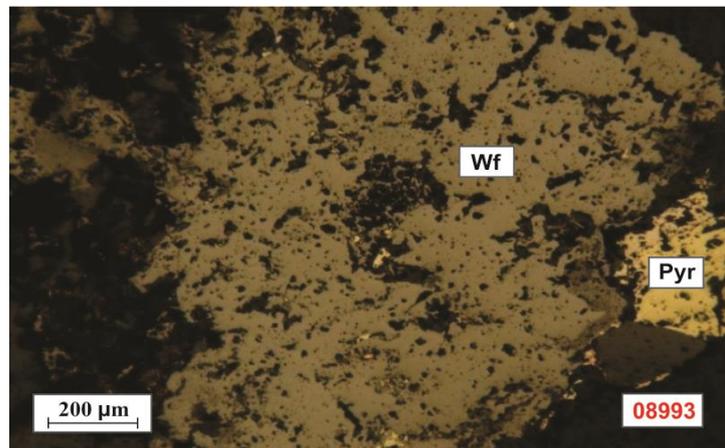


Figure 6. Wolframite (Wf) is disseminated in granite rocks corroded by pyrrhotine (Pyr).

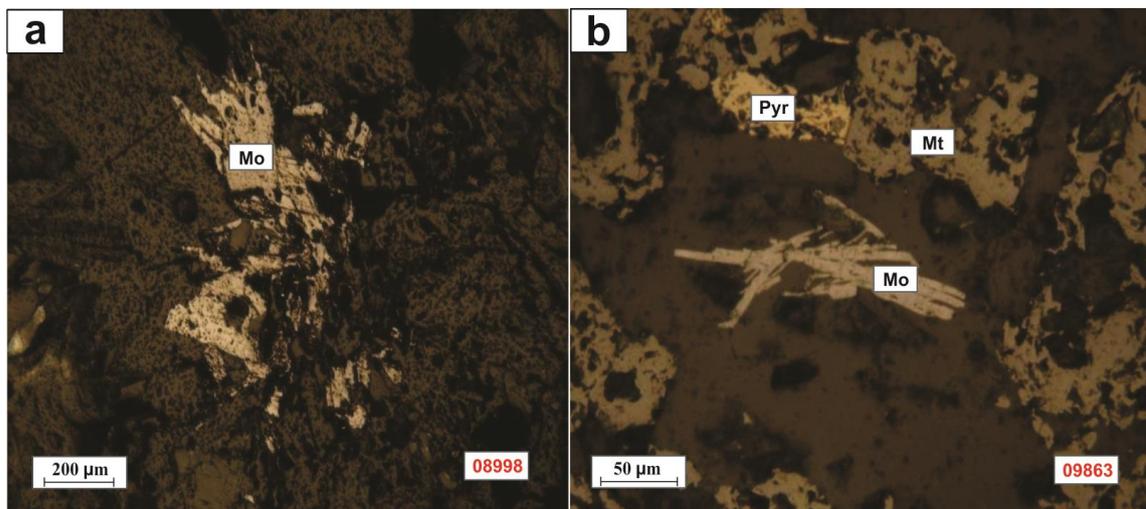


Figure 7. In greisenized rocks, molybdenite is lamella-shaped and foliated (a), and quartz veins cut skarn rocks (b). Mo-Molybdenite, Pyr-Pyrrhotine, Mt-Magnetite.

* Textures of ores

Scheelites mainly have xenomorphic granular textures, wolframites are idiomorphic-hypidiomorphic tabular or columnar textures, chalcopyrites are anhedral granular textures, and molybdenites are foliated or scaly aggregation textures.

* Structures of ores

Ore structures include brecciated structures, vein structures, and massive systems. Apart from the independent structure types mentioned above, it frequently generates compound structures with many configurations, such as disseminated-banded, disseminated-net vein, disseminated-vein, and disseminated-banded-net vein-fine vein structures. As mineralization has increased, metal minerals have a dispersed structure that has evolved into a dense disseminated structure, banded structure, or a mixture of two or more complicated geological patterns. Vein structure is frequently created and filled in tectonic fractures, and brecciated and enormous structures are frequently encountered between fault fracture zones and between strata.

* Ore chemical components

The beneficial component of ores in this mine are mainly tungsten and copper. Tungsten (W) in scheelite and wolframite accounts for 97.36÷98.66%, and tungsten in tungstite accounts for only 1.34-3.29%. Copper (Cu) occurs mainly in copper sulfides such as chalcopyrite, bornite, and tetrahedrite, accounting for 86.15÷94.73%.

4.2. Mineral Paragenesis and Ore-Forming Processes

Based on analysis results of the mineral components, structural and textural ores, mineral paragenesis, and hydrothermal processes of host rocks, the Nui Phao tungsten deposit can be divided into stages and periods of ore-forming processes as follows (Figure 8):

* Metasomatic skarn stage

The metasomatic process between the Da Lien granite massive and limestone, claystone rocks of the Phu Ngu formation formed skarn rocks during three stages:

Early skarn stage: forming skarn rocks and a mineral assemblage characterizes it as andradite

+ hedenbergite +/- scapolite +/-vesuvianite+/- wollastonite.

Middle skarn stage: forming skarn rocks, characterized by hastingsite magnetite-scheelite I-pyrrhotine I, chalcopyrite I mineral assemblage.

Post skarn stage: forming skarn rocks, characterized by biotite+/-danalite+/-datolite+/-danalite+/-danburite mineral assemblage.

* Ore forming stage

This stage is started forming ore production, and the first step is the metasomatic process between felspar and greisenization, corresponding mineral assemblages as follows.

Greisenisation stage: The post-magmatic solution causes greisenization of skarn rocks to form metamorphic rocks as the external greisen, and greisenization of the two-mica granite Da Lien massif to form internal greisen. This stage is formed product ores with the characteristics of the quartz I - scheelite II - fluorite mineral assemblage in both external and internal greisen.

Early hydrothermal stage: This stage causes quartzization, sericitization, chloritization, and epidotization of host rocks, forming tungsten ores with the typical mineral assemblage as quartz II - pyrrhotine II - chalcopyrite II - Bi. They are distributed in the external and internal greisen, and also in skarn rocks are not greisenized.

* Post ore forming stage

This stage has only one period and is considered a post-hydrothermal type. The ore-forming process in the Nui Phao deposit is ended and characterized by quartz III - calcite mineral assemblage.

4.3. Tungsten resource estimation

Based on the formulas (1, 2), the tungsten resources of the Nui Phao deposit are established in Table 1.

The calculated results show that the total tungsten reserves/resources of the Nui Phao deposit are obtained 227,584 tons of levels 122 and 333; 168,096 tons of level 122, and 59,488 tons of level 333, respectively.

5. Conclusion

The main results of this work can be summarized as follows:

Ore forming stage	Skarn			Ore		Post-ore
Mineralization stage	Early	Middle	Late	Greisen	Early hydrothermal	Late hydrothermal
Mineral association	And-Hed-Sca-Ves-Wol	Has-She I-Pyr I-Chp I	Bio-Dana-Dat-Danb	Qua-She II-Fluo	Qua-Pyr II-Chp II-Bi	Quartz-Calcite
Minerals						
Quartz	-----	-----	-----	-----	-----	-----
Calcite	-----	-----	-----	-----	-----	-----
Andradite	=====					
Hedenbergite	=====					
Scapolite	-----					
Vesuvianite	-----					
Wollastonite	-----					
Hastingsite		=====				
Danalite			=====			
Datolite			=====			
Danburite			=====			
Microline				=====		
Albite				=====		
Muscovite				=====		
Biotite			=====	=====		
Beryl				-----		
Fluorite				=====		
Topaz				-----		
Sericite					=====	
Chlorite					=====	
Epidote					=====	
Sheelite		-----		=====		
Pyrrhotine		-----			=====	
Pyrite					=====	
Chalcopyrite		-----			=====	
Native Bismuth					=====	
Bismuthine					-----	
Sphalerite					-----	
Molybdenite				-----		
Wolframite				-----		
Magnetite		=====				

----- Locally occurring ===== Minor ===== Main

Figure 8. Mineral paragenesis of the Nui Phao deposit, Dai Tu area.

Table 1. Tungsten resources of the Nui Phao deposit, Dai Tu area.

Nº	Reserve/resource levels	Ore reserve/resource (10 ³ tons)	Tungsten content (%)	Tungsten resource (ton)
1	122	83,220	0.21	168,096
2	333	27,040	0.22	59,488
	122+333	110,260		227,584

The tungsten mineralization in the Nui Phao deposit can be divided into three mineralization stages, namely skarnisation, greisenization, and hydrothermal stage, and the late hydrothermal alteration medium to a low temperature that is genetically modified related to the fluorite-polymetallic mineralization.

Most of the tungsten ore was accumulated in association with the metasomatism between the Ordovician - Silurian carbonate - terrigenous sedimentary rocks of the Phu Ngu formation and Cretaceous two-mica granite of the Pia Oac complex. The calculated results indicate that tungsten resources obtained at levels 122 and 333 are about 227.6 thousand tons.

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Contribution of authors

Khang Quang Luong designed ideas and finalized the checking manuscript. Hung Khuong wrote the article draft and discussed research problems, Dung Tien Vo analyzed samples, and Tuyen Danh Nguyen prepared the pictures and database.

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