

## Article

# Magmatic Evolution and Nb-Ta Enrichment of Early Jurassic Granitic Porphyry from the Shangxiahua Nb-Ta Deposit of the Nanling Range

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**Abstract:** The Shangxiahua Nb-Ta deposit is located in the Yongding region of Fujian Province, the south-eastern section of the Nanling Range, South China. A series of Nb-Ta deposits, associated with granitic porphyries, are present in the Yongding region. Nevertheless, the genesis of the Nb-Ta mineralisation remains practically ambiguous, and further study of the latest Nb-Ta granitic porphyries in the Nanling Range may prove beneficial in understanding the mineralisation mechanism. This paper presents a detailed analysis of the petrographic, geochemical, chronological and isotopic characteristics of the Shangxiahua granite porphyry. Shangxiahua granite porphyry is high-potassium subalkaline granite. The Rittman index ( $\delta$ ) is  $< 3.3$ , indicating a calc-alkaline signature. The aluminium saturation index ( $A/CNK$ ) is  $> 1.1$ , indicating a strong peraluminous nature. Furthermore, the rare earth elements diagram exhibits Eu-negative anomalies and an M-type “tetrad effect”, while the multi-element distribution patterns diagram shows an overall right-leaning trend. The SIMS zircon U-Pb age of the Shangxiahua granite porphyry is  $183.2 \pm 3.2$  Ma, revealing the emplacement of the granite porphyry in the Early Jurassic. The high Zr + Nb + Ce + Y content and Ga/Al ratios, along with the zircon saturation temperature  $T_{Zr}$  value of  $1033^\circ\text{C}$ , indicate that the Shangxiahua granite porphyry exhibits the characteristics of a highly differentiated A-type granite. The Sr-Nd isotope signatures indicate that the Nb-Ta-bearing magma was formed by the mixing of crust-mantle material. The evolution and mineralisation process of granite porphyry in the Shangxiahua Nb-Ta deposit can be divided into four principal stages: (1) the upwelling of Asthenosphere material due to the extensional background induced partial melting of the crust; (2) the mixing of mantle-derived magma and crustal-derived magma; (3) magmatic fractional crystallisation and (4) magma-hydrothermal interaction. Combined with the reported data of Yongding Daping niobium-tantalum mining area, it can be postulated that the enrichment of Nb-Ta ores in Shangxiahua is primarily the result of the upwelling of Asthenosphere material, which caused the partial melting of the niobium-rich Mesoproterozoic crust with high Nb-Ta value. The enrichment of Nb-Ta ore bodies in Daping is primarily attributed to the fractional crystallisation of the magma and the hydrothermal alteration, which is postulated to be associated with the presence of a crust exhibiting elevated Nb-Ta ratios in Yongding. Additionally, it is postulated that ore may be found in area with high crustal source components in the crust-mantle mixed zone. There may be high volatile-rich Nb-Ta orebodies and Sn-rich and W-rich orebodies at depth or in the surrounding area.



**Citation:** Liu, H.; Wang, J.; Chen, Q.; Huang, Y.; Li, X.; Liu, W.; Chen, B.; Xiao, F. Magmatic Evolution and Nb-Ta Enrichment of Early Jurassic Granitic Porphyry from the Shangxiahua Nb-Ta Deposit of the Nanling Range. *Minerals* **2024**, *14*, 1005. <https://doi.org/10.3390/min14101005>

Received: 27 August 2024

Revised: 27 September 2024

Accepted: 28 September 2024

Published: 3 October 2024



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**Keywords:** Nanling Range; Shangxiahua area; Nb-Ta ore body; granite porphyry; magma evolution and Nb-Ta enrichment

## 1. Introduction

Niobium and tantalum (Nb-Ta) are referred to as “strategic resources” or “key metals” and are extensively utilised in strategic and sophisticated industries (e.g., electronics, telecommunications, aerospace, and defence industries [1–3]). The Nb-Ta resources are primarily concentrated in highly fractionation granites in South China [3,4]. The Nanling Range granites, which are closely related to Nb-Ta mineralisation, have become a focal point of granite research in China, and they represent an important target for a new round of breakthroughs in mineral search [5–7]. The Nb-Ta mineralisation in the Nanling Range is mainly distributed in and around the Nanling Range ore belt. The mineralisation types are mainly divided into granite, greisen, and granite pegmatite. The granite type Nb-Ta deposits in the Nanling Range are primarily distributed in the western, central, and eastern sections of the area, with the diagenetic and metallogenic age concentrated in the Late Triassic (220~200 Ma), Late Jurassic (170~150 Ma), Early Yanshanian (170~150 Ma) and Late Yanshanian (140~125 Ma). The Early Jurassic Nb-Ta mineralisation in the Nanling Range is rarely reported. It has been demonstrated that the granites associated with Nb-Ta mineralisation in the Nanling Range are predominantly characterised by highly fractionation I/S-type granites (e.g., the Gaoling [8], the Jianfengling area of Hunan Province [9–11]). There are relatively few studies on A-type granites (e.g., Shangbao in Nanling Range [12], Daping in Fujian Province [13]), and there are still many scientific problems to be investigated. For example, rare metal deposits associated with highly fractionated granites are usually related to their late-evolutionary magmatic, hydrothermal and magma–hydrothermal interactions, but how are these rare metal elements enriched for mineralisation? Does this phenomenon also have a correlation with the source of the magma? To what extent can the mineralisation of different rare metal elements be attributed to magmatic or hydrothermal processes? In light of the aforementioned issues, this paper employs the recently identified granite porphyry in the Shangxiahu Nb-Ta deposit within the Yongding, situated in the southeastern portion of the Nanling Range, as the subject of investigation. This paper focuses on the relationship between magmatic evolution and Nb-Ta enrichment, with a particular emphasis on the types and source of granite porphyry rich in Nb-Ta deposits. In light of the reported Daping Nb-Ta deposit in the region, a prospective direction for further exploration is postulated, thereby providing a theoretical foundation for regional rare-metal prospecting.

## 2. Geological Setting

The stratigraphic sequence of the Nanling Range is based on Early Paleozoic–Early Neoproterozoic clastic and metamorphic clastic rocks, which are overlain by Late Paleozoic–Early Mesozoic carbonate rocks and interbedded clastic rocks of marl. The Nanling Range has been subject to a number of tectonic events, including the Sipo Orogeny, Caledonian Orogeny and Indo-Chinese and Yanshan movements. These have resulted in the widespread distribution of folds and faults [14–16]. The tectonics of the Nanling Range were predominantly influenced by the Tethys structural domain and the Early Jurassic Indo-Chinese Orogeny prior to the Middle Jurassic. Subsequently, the superposition of the Pacific plate tectonics and the deep inland tectonics led to the formation of the NE fault [17,18]. The period of magmatic activity in the Nanling Range is characterised by a high frequency and intensity of volcanic events, resulting in the widespread distribution of volcanic rocks. Among these, early Yanshan granites are particularly prevalent, including black mica granite, two mica granite and monzonitic granite. These granites are closely associated with the mineralisation of rare metals [5–13]. Additionally, the Nanling Range has been found to exhibit evidence of Mg-Fe-ultra-Mg-Fe magmatism, predominantly basaltic in nature. The ages of these occurrences have been determined to be  $212.3 \pm 1.7$  Ma, approximately 184 Ma, 175 Ma and 150 Ma, respectively [19–21].

The Yongding region is situated in the south-eastern extremity of the Nanling Range, within the southwestern Fujian-northeastern Guangdong upper Paleozoic subsidence (Yongmei subsidence), a secondary tectonic unit of the South China Fold System. It is

located at the intersection of the NW deep fault zone of Shanghang-Yunxiao and the north extension of the NE deep fault zone of Lianhuashan in Guangdong, and forms part of the eastern edge of Yongmei Mineral Settlement in the southern section of the Wuyishan metallogenic belt. The exposed stratum in the region is primarily composed of quartz glutenite, sandstone and siltstone in the sandstone section of the Lower Jurassic Xiacun Formation ( $J_1x^2$ ), dacite crystal tuff, basalt, dacite and rhyolite in the lower volcanic rock section of the Fankeng Formation ( $J_1f^1$ ) and Quaternary (Q) residual slope sediments. The fold structure in the region is not developed, mainly comprising two groups of fault zones in the NE and NNE directions, followed by the NW and EW faults. The magmatic activity in the area is frequent, mainly the early Yanshanian magmatic rocks. According to the lithological characteristics, the intrusive rocks can be divided into Early Jurassic porphyritic medium-grained biotite-bearing monzonitic granite, alkaline granite porphyry, quartz porphyry and dioritic porphyrite, Middle Jurassic fine-grained and coarse-grained granite and Late Jurassic porphyritic medium-grained biotite-bearing granite.

There are many highly fractionation granites in the Yongding region, which is a favourable place for rare polymetallic mineralisation, for example, Shangxiahu and Daping deposits [13,22]. The lithological composition of the stratum in the Shangxiahu deposit is largely consistent with that of the region. The structure in the area is dominated by faults. The NNE normal fault is developed in the central portion of the deposit. The fault structure provides an emplacement channel for the late volcanic activity, forming an alkaline granite porphyry body, and the basic gabbro-diorite veins invade later (Figure 1).

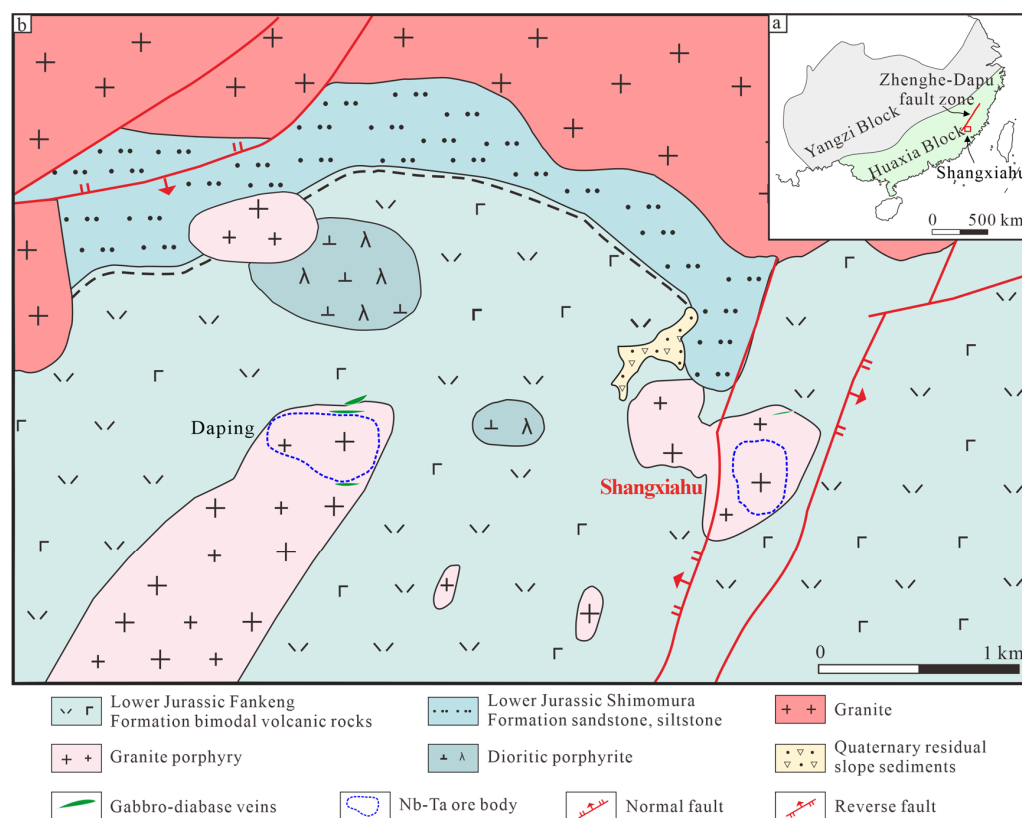


**Figure 1.** The tectonic location of the study area (a); simplified regional geological map of the Shangxiahu in Yongding region, Fujian Province, Southern China (b).

### 3. Materials and Methods

#### 3.1. Petrographic Analysis

The rock slices in this study were completed in the laboratory of The Second Geological Exploration Institute of China Metallurgical Geology Bureau (CMGB), Fuzhou, China. The

systematic identification of primary and secondary minerals, as well as unknown minerals, was conducted using a Leica DM2700P polarised light microscope.

### 3.2. Whole-Rock Geochemistry Analysis

Major-trace element analysis was conducted on whole rock samples at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (CAS) (Guiyang, China). The principal trace elements were analysed using an ARL Perform'X 4200 X-ray fluorescence spectrometer (XRF). The BHVO-2 and BCR-2 samples were used as the standard materials for calibration, with a relative error of  $\pm 1\%$  for elemental abundances  $>1.0\%$  and  $\pm 10\%$  for elemental abundances  $<1.0\%$  [23]. The samples for trace element analyses were dissolved in whole rock powder using the acid dissolution method. The analysis of trace element was conducted using an inductively coupled plasma mass spectrometer (ICP-MS) of the PlasmaQuant MS Elite type, manufactured by Jena Analytical Instruments AG, Jena, Germany.

### 3.3. Zircon U-Pb Age Analysis

In this study, zircons are separated by heavy sand elutriation and electromagnetic separation method. At the Ion Probe Centre of the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, CAS (Guangzhou, China), zircons selected under a binocular stereomicroscope were mounted in epoxy resin and polished to expose the zircon cores, thus making sample targets. Cathodoluminescence (CL) and optical microscope images were taken by using the Gatan Mono CL4 cathodoluminescence spectrometer equipped with FEI Quanta 450 FEG scanning electron microscope system to determine the homogeneous area without cracks and inclusions.

The zircon U-Pb age analysis of the samples was conducted using Cameca IMS 1280HR secondary ion mass spectrometry (SIMS) at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, CAS. The detailed process was referenced to the methodology described by Li et al. [24]. The specific parameter conditions are as follows: the intensity of the primary ion current is approximately 8 nA, and the beam spot size is  $20\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$ . The data were processed offline using the Buster 1.0 software (Gernsbach, Germany). Age calculations and concordia diagrams were generated using Isoplot 4.0 [25–27].

### 3.4. Sr-Nd Isotope Analysis

The whole rock Sr-Nd isotope Analysis was completed using a Thermo Fisher Scientific Neptune Plus multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, CAS (Guiyang, China). The precision of the instrument was evaluated using international standard samples NBS SRM 987 ( $200\text{ }\mu\text{g/L}$ ) and JNdi-1 ( $200\text{ }\mu\text{g/L}$ ). The detailed experimental procedures and analytical methods are presented in Lin et al. [28].

## 4. Results

### 4.1. Petrography

The ore-bearing rock mass of the Shangxiahua Nb-Ta deposit is a medium-grained K-feldspar granite porphyry (Figure 2), which is light grey to flesh pink in colour (Figure 2a,c), with a light red weathering surface, porphyritic structure and massive structure. The content of phenocrysts in minerals is higher, accounting for about 40%–45%. It typically exhibits a size range of 1 to 3.5 mm and is primarily composed of alkali feldspar, quartz and muscovite. The matrix exhibits a microcrystalline texture and is compositionally similar to the porphyry, comprising primarily alkali feldspar, quartz and muscovite. Accessory minerals include zircon, columbite, thorite, monazite and others.

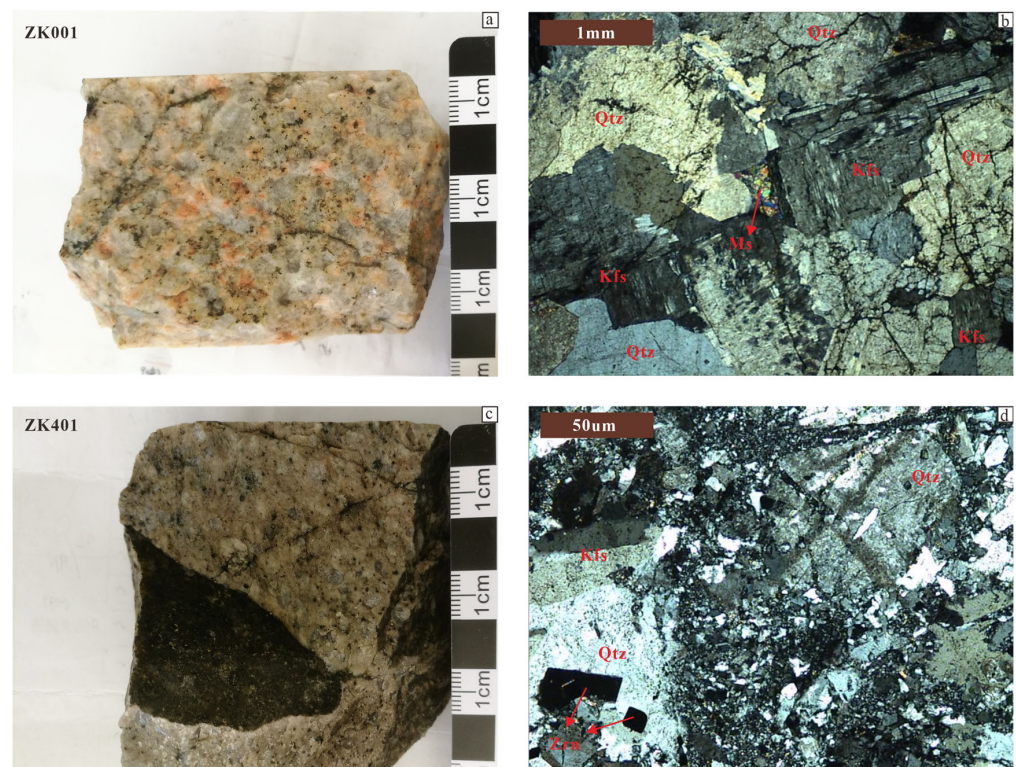


**Figure 2.** Photographs of hand specimens (a,c) and microscopic features (b,d) of granite porphyry from the Shangxiahuh Nb-Ta deposit. The mineral abbreviations are as follows: Kfs (potassium feldspar), Qtz (quartz), Ms (muscovite) and Zrn (zircon).

#### 4.2. Whole-Rock Geochemistry

The Shangxiahuh granite porphyry, as a whole, exhibits high silica ( $\text{SiO}_2 = 71.19 \text{ wt}\% \sim 75.49 \text{ wt}\%$ ), sub-alkaline ( $\text{ALK} (\text{K}_2\text{O} + \text{Na}_2\text{O}) = 7.12 \text{ wt}\% \sim 8.96 \text{ wt}\%$ ) and potassium-rich ( $\text{K}_2\text{O} = 2.99 \text{ wt}\% \sim 4.57 \text{ wt}\%$ ) characteristics (Table 1). The rock is a subalkaline granite (Figure 3a), with a Rittman index ( $\delta$ ) of 1.80–2.60,  $\delta < 3.3$ , belonging to the calc-alkaline suite. Most of the sample data fall within the peraluminous range on the A/NK-A/CNK diagram (Figure 3b), with A/CNK ( $\text{Al}_2\text{O}_3 / (\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}) = 0.98 \sim 1.14$ , most  $> 1.1$ , which is a weakly peraluminous rock. Furthermore, the Shangxiahuh granite porphyry exhibits low MnO (0.07 wt%–0.26 wt%), MgO (0.17 wt%–0.49 wt%), CaO (0.11 wt%–1.14 wt%),  $\text{TiO}_2$  (0.04 wt%–0.51 wt%) and  $\text{P}_2\text{O}_5$  (0.04 wt%–0.13 wt%). The aforementioned characteristics indicate that the Shangxiahuh granitic porphyry is silica-rich and sub-alkaline, and Mg-, Ca-, Ti- and P-poor, which is similar to what is reported for the Daping granitic porphyry [13].

**Table 1.** Major and trace element compositions of granite porphyry from the Shangxiahuh Nb-Ta deposit.

| Sample No.                     | SXH001-1 | SXH001-3 | SXH002-1 | SXH401-1 | SXH401-2 | SXH402-2 | SXH402-3 |
|--------------------------------|----------|----------|----------|----------|----------|----------|----------|
| $\text{SiO}_2$ (wt%)           | 73.43    | 74.68    | 75.49    | 72.89    | 72.37    | 74.12    | 71.19    |
| $\text{Al}_2\text{O}_3$ (wt%)  | 13.79    | 13.29    | 12.33    | 13.90    | 12.53    | 12.54    | 12.17    |
| $\text{TFe}_2\text{O}_3$ (wt%) | 2.05     | 1.41     | 2.26     | 2.06     | 3.84     | 2.03     | 4.88     |
| CaO (wt%)                      | 0.11     | 0.31     | 0.12     | 0.13     | 1.14     | 1.09     | 1.14     |
| MgO (wt%)                      | 0.37     | 0.17     | 0.27     | 0.33     | 0.28     | 0.25     | 0.49     |
| $\text{K}_2\text{O}$ (wt%)     | 4.57     | 3.32     | 4.09     | 2.99     | 3.16     | 3.35     | 3.95     |
| $\text{Na}_2\text{O}$ (wt%)    | 4.33     | 5.64     | 3.74     | 5.83     | 4.17     | 4.39     | 3.17     |
| $\text{TiO}_2$ (wt%)           | 0.05     | 0.04     | 0.25     | 0.19     | 0.51     | 0.16     | 0.29     |
| MnO (wt%)                      | 0.07     | 0.09     | 0.13     | 0.07     | 0.16     | 0.15     | 0.26     |
| $\text{P}_2\text{O}_5$ (wt%)   | 0.04     | 0.04     | 0.04     | 0.04     | 0.13     | 0.05     | 0.07     |
| LOI (wt%)                      | 0.56     | 0.24     | 0.45     | 0.62     | 1.09     | 1.38     | 1.89     |
| Total                          | 99.37    | 99.22    | 99.17    | 99.05    | 99.38    | 99.51    | 99.50    |

Table 1. Cont.

| Sample No.                        | SXH001-1 | SXH001-3 | SXH002-1 | SXH401-1 | SXH401-2 | SXH402-2 | SXH402-3 |
|-----------------------------------|----------|----------|----------|----------|----------|----------|----------|
| DI (%)                            | 93.81    | 95.97    | 93.51    | 94.43    | 87.30    | 90.93    | 84.38    |
| A/NK                              | 1.14     | 1.03     | 1.16     | 1.08     | 1.22     | 1.15     | 1.28     |
| A/CNK                             | 1.12     | 0.99     | 1.14     | 1.06     | 1.01     | 0.98     | 1.05     |
| Rb (ppm)                          | 397      | 285      | 116.3    | 256      | 178.52   | 120.3    | 156      |
| Sr (ppm)                          | 9.68     | 9.87     | 32       | 74       | 56.65    | 59       | 64       |
| Ba (ppm)                          | 42       | 74.1     | 158      | 51.6     | 56.7     | 76.1     | 99.4     |
| Th (ppm)                          | 20.1     | 23.6     | 50.2     | 79.2     | 45.7     | 133      | 104      |
| U (ppm)                           | 36.9     | 20.8     | 13.2     | 17.8     | 32.2     | 21       | 22.7     |
| Nb (ppm)                          | 425      | 334      | 253      | 303      | 542      | 305      | 361      |
| Ta (ppm)                          | 55.7     | 57.1     | 39.4     | 21.2     | 45.56    | 36.2     | 29.4     |
| Zr (ppm)                          | 993      | 1510     | 197      | 1570     | 1380     | 746      | 705      |
| Hf (ppm)                          | 100      | 139      | 19.5     | 136      | 127      | 69.5     | 61.9     |
| Li (ppm)                          | 10.5     | 4.51     | 10.3     | 9.67     | 3.36     | 6.57     | 14.4     |
| Cs (ppm)                          | 1.65     | 1.51     | 1.64     | 1.17     | 1.54     | 2.33     | 2.39     |
| Be (ppm)                          | 8.3      | 5.07     | 8.08     | 6.33     | 5.05     | 6.17     | 6.96     |
| Ga (ppm)                          | 45       | 45.7     | 40.9     | 50.9     | 59.6     | 45.8     | 47.2     |
| Y (ppm)                           | 33.9     | 4.28     | 39.4     | 28.9     | 23.4     | 78.4     | 76.7     |
| La (ppm)                          | 12       | 7.07     | 31.5     | 18.7     | 15.21    | 33.9     | 25.3     |
| Ce (ppm)                          | 20.7     | 15.6     | 63.1     | 39.6     | 32.1     | 67.5     | 53       |
| Pr (ppm)                          | 2.48     | 1.61     | 6.76     | 3.78     | 3.65     | 7.18     | 5.47     |
| Nd (ppm)                          | 7.16     | 4.36     | 21.2     | 9.11     | 51.5     | 21.9     | 17.4     |
| Sm (ppm)                          | 1.76     | 0.779    | 4.76     | 1.87     | 11.2     | 5.03     | 4.28     |
| Eu (ppm)                          | 0.085    | 0.0767   | 0.0248   | 0.0526   | 0.0454   | 0.301    | 0.391    |
| Gd (ppm)                          | 1.84     | 0.488    | 4.01     | 1.67     | 1.54     | 5.04     | 4.79     |
| Tb (ppm)                          | 0.494    | 0.0872   | 0.742    | 0.462    | 0.564    | 1.18     | 1.12     |
| Dy (ppm)                          | 4.02     | 0.603    | 6.03     | 3.89     | 4.65     | 8.86     | 8.5      |
| Ho (ppm)                          | 1.01     | 0.158    | 1.55     | 1.03     | 1.23     | 2.16     | 2.05     |
| Er (ppm)                          | 4.15     | 0.802    | 5.32     | 4.7      | 5.64     | 8.37     | 7.95     |
| Tm (ppm)                          | 1.07     | 0.271    | 0.845    | 1.34     | 0.98     | 1.99     | 1.91     |
| Yb (ppm)                          | 9.75     | 3.17     | 8.72     | 12.9     | 12.3     | 17.5     | 17.1     |
| Lu (ppm)                          | 1.7      | 0.665    | 1.34     | 2.26     | 1.56     | 2.92     | 2.95     |
| ΣREE (ppm)                        | 68.22    | 35.74    | 155.90   | 101.36   | 142.17   | 183.83   | 152.21   |
| LREE (ppm)                        | 44.19    | 29.50    | 127.34   | 73.11    | 113.71   | 135.81   | 105.84   |
| HREE (ppm)                        | 24.03    | 6.24     | 28.56    | 28.25    | 28.46    | 48.02    | 46.37    |
| LREE/HREE                         | 1.84     | 4.72     | 4.46     | 2.59     | 3.99     | 2.83     | 2.28     |
| (La/Yb) <sub>N</sub> <sup>1</sup> | 0.88     | 1.60     | 2.59     | 1.04     | 0.89     | 1.39     | 1.06     |
| (La/Sm) <sub>N</sub> <sup>1</sup> | 4.40     | 5.86     | 4.27     | 6.46     | 0.88     | 4.35     | 3.82     |
| δEu                               | 0.143    | 0.354    | 0.017    | 0.089    | 0.019    | 0.181    | 0.263    |
| δCe                               | 0.882    | 1.090    | 1.010    | 1.090    | 1.022    | 1.009    | 1.054    |
| TE <sub>1,3</sub>                 | 1.1      | 1.1      | 1.0      | 1.2      | 0.8      | 1.1      | 1.1      |
| Tzr (°C)                          | 984      | 1020     | 819      | 1033     | 1012     | 935      | 936      |

<sup>1</sup> The normalisation values from Sun and McDonough, 1989 [31].

The total rare earth elements (ΣREE) of the Shangxiahui granite porphyry range from 35.74 to 183.83 ppm, and (La/Yb)<sub>N</sub> = 0.88~2.59, indicating that the light and heavy rare earth elements of the rock body are not obviously differentiated (Table 1). The normalised rare earth elements distribution curves (Figure 4) have obvious ‘V’ type Eu negative anomaly, δEu = 0.017~0.354, no obvious Ce anomaly, δCe = 0.882~1.090, showing an obvious M type ‘tetrad effect’, and the overall performance is the enrichment of light rare earth and heavy rare earth relative to medium rare earth. The multi-element distribution patterns of the Shangxiahui granite porphyry show an overall right-dipping trend (Figure 4), characterised by a relative enrichment of high field strength elements (Th, U, Ta, Nb, Hf, etc.), relative deficit of large ionic lithophile elements (Ba, Sr) and relative enrichment of Rb, with notable Ti and P deficits. The Rb/Sr ratios (2.04~41.01), Y/Ho ratios (19.02~37.41), Zr/Hf ratios (9.93~11.54) and Nb/Ta ratios (5.85~14.29) of the Shangxiahui granite porphyry are elevated.

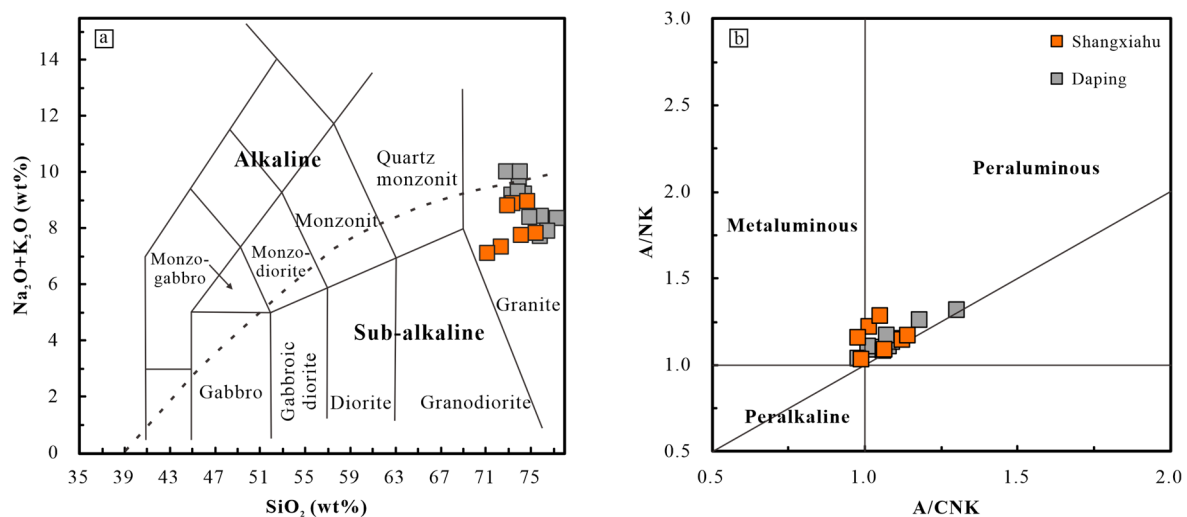


**Figure 3.**  $\text{Na}_2\text{O} + \text{K}_2\text{O}$ - $\text{SiO}_2$  (a) (after Peccerillo and Taylor, 1976 [29]) and  $\text{A/NK}$ - $\text{A/CNK}$  (b) (after Maniar and Piccoli, 1989 [30]) diagrams of granite porphyry from the Shangxiahua Nb-Ta deposit. The data of granite porphyry in the Daping Nb-Ta deposit are obtained from Wang et al., 2020 [13] and are the same below.

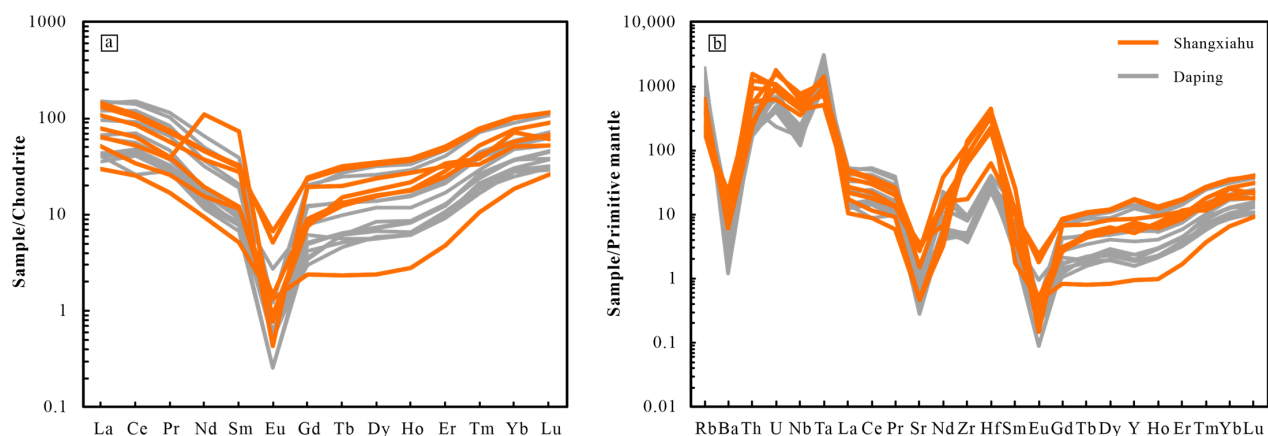


**Figure 4.** Normalised rare earth elements (a) and multi-element distribution patterns (b) of granite porphyry from the Shangxiahua Nb-Ta deposit (normalisation values after Sun and McDonough, 1989 [31]).

#### 4.3. Zircon U-Pb Age

The zircon CL images of the Shangxiahua granite porphyry (Figure 5a,c) demonstrate a comprehensive crystal form with a notable degree of authomorphism, exhibiting a transition from authomorphic to semi-authomorphic, predominantly columnar and elongate. The granitic porphyry samples SXH402-2 and SXH402-3 zircons are characterised by a high concentration of Th and U, with a relatively low Pb content of 3.35 ppm (Table 2). The Th/U ratios intervals of the two groups of zircons were 0.42–0.92 (mean: 0.61) and 0.16–1.26 (mean: 0.66), respectively. Furthermore, the two groups of zircons CL images exhibit pronounced oscillatory zones, indicating that the selected zircons are predominantly magmatic orogenic zircons [32]. A total of 21 zircon points were analysed for the sample SXH402-2. Two occurrences with measurements significantly deviating from the harmonic curve were excluded from the subsequent analysis and are not included in the table. The remaining 19 occurrences were distributed near the harmonic curve, with a test age of  $183.2 \pm 2.2$  Ma (MSWD = 1.13) (Figure 5). A total of 19 zircon points were analysed for sample SXH402-3. Four points with measurements that deviated significantly from the harmonic curve, potentially representing a loss of Pb or U, were excluded from the table.

The remaining 15 points were distributed near the harmonic curve, with a test age of  $183.2 \pm 3.2$  Ma (MSWD = 0.98) (Figure 5). The similarity of the test ages of the two sets of samples provides evidence that the dating results are reliable.

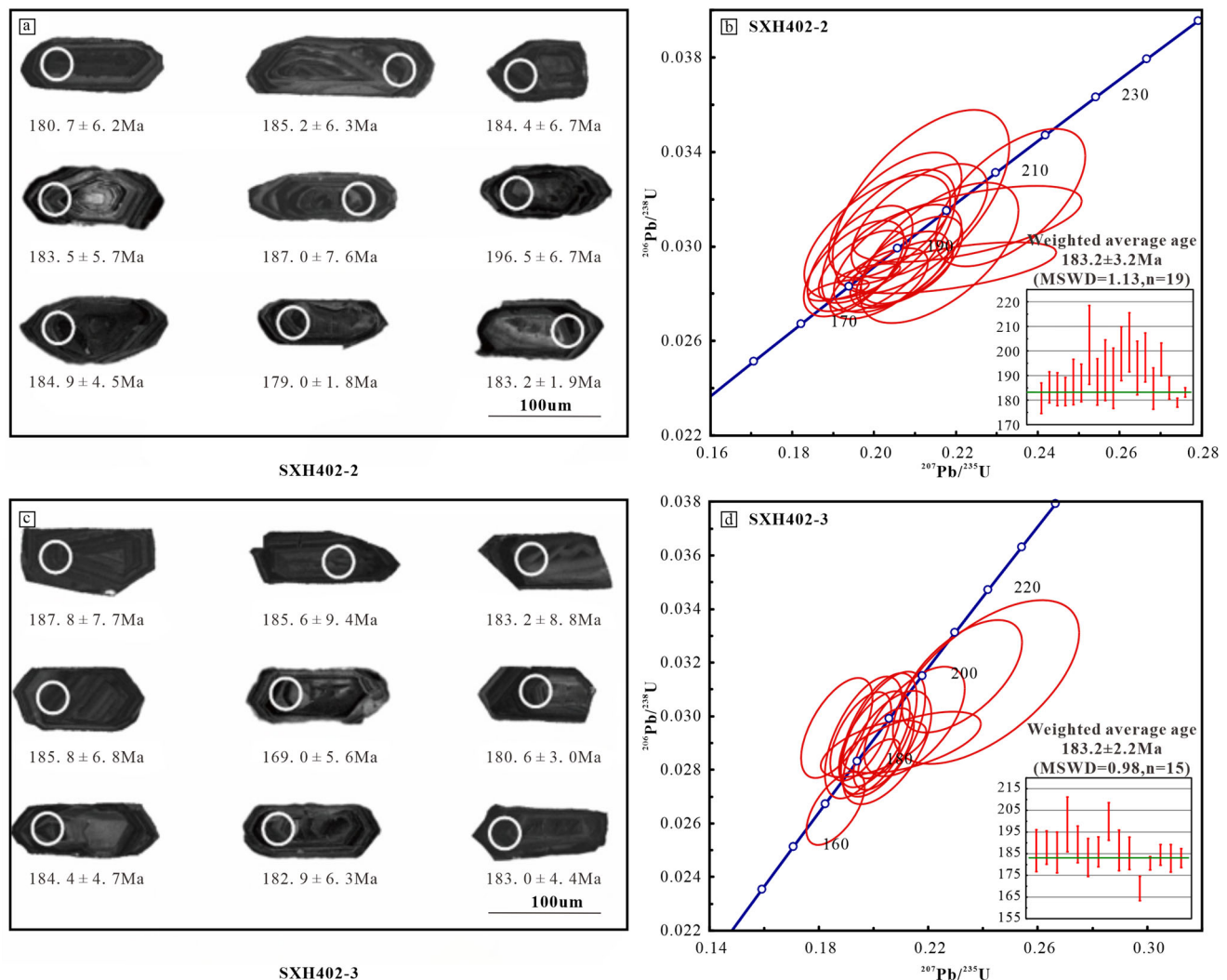


**Figure 5.** Zircon CL images (a,c) and U-Pb concordia diagrams (b,d) of granite porphyry from the Shangxiahui Nb-Ta deposit.

**Table 2.** SIMS zircon U-Pb data of granite porphyry from the Shangxiahui Nb-Ta deposit.

| Sample No. | Pb    | Th    | U     | Th/U | $^{207}\text{Pb}/^{235}\text{U}$ | $^{207}\text{Pb}/^{235}\text{U}$ | $^{206}\text{Pb}/^{238}\text{U}$ | $^{206}\text{Pb}/^{238}\text{U}$ | $^{207}\text{Pb}/^{235}\text{U}$ | $^{207}\text{Pb}/^{235}\text{U}$ | $^{206}\text{Pb}/^{238}\text{U}$ |
|------------|-------|-------|-------|------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| SXH402-2   | (ppm) | (ppm) | (ppm) |      | Ratio                            | 1 $\sigma$                       | Ratio                            | 1 $\sigma$                       | Age (Ma)                         | 1 $\sigma$                       | Age (Ma)                         |
| 1          | 52    | 700   | 1374  | 0.51 | 0.20121                          | 0.00789                          | 0.02843                          | 0.00099                          | 186.1                            | 6.7                              | 180.7                            |
| 2          | 92    | 1452  | 2304  | 0.63 | 0.19724                          | 0.00711                          | 0.02915                          | 0.00101                          | 182.8                            | 6.0                              | 185.2                            |
| 3          | 63    | 970   | 1628  | 0.60 | 0.20624                          | 0.00795                          | 0.02902                          | 0.00107                          | 190.4                            | 6.7                              | 184.4                            |
| 4          | 62    | 804   | 1580  | 0.51 | 0.20744                          | 0.00782                          | 0.02887                          | 0.00091                          | 191.4                            | 6.6                              | 183.5                            |
| 5          | 79    | 1177  | 2236  | 0.53 | 0.19658                          | 0.00849                          | 0.02949                          | 0.00148                          | 182.2                            | 7.2                              | 187.4                            |
| 6          | 60    | 802   | 1580  | 0.51 | 0.20922                          | 0.00818                          | 0.02943                          | 0.00122                          | 192.9                            | 6.9                              | 187.0                            |
| 7          | 69    | 1064  | 1813  | 0.59 | 0.21146                          | 0.01425                          | 0.03190                          | 0.00256                          | 194.8                            | 11.9                             | 202.5                            |
| 8          | 104   | 1273  | 3002  | 0.42 | 0.20577                          | 0.01029                          | 0.02950                          | 0.00151                          | 190.0                            | 8.7                              | 187.4                            |
| 9          | 74    | 1245  | 1973  | 0.63 | 0.20353                          | 0.01077                          | 0.03026                          | 0.00198                          | 188.1                            | 9.1                              | 192.2                            |
| 10         | 104   | 1707  | 2936  | 0.58 | 0.21592                          | 0.01278                          | 0.02973                          | 0.00196                          | 198.5                            | 10.7                             | 188.9                            |
| 11         | 68    | 851   | 1780  | 0.48 | 0.20516                          | 0.01071                          | 0.03133                          | 0.00175                          | 189.5                            | 9.0                              | 198.9                            |
| 12         | 119   | 2324  | 2969  | 0.78 | 0.23334                          | 0.01206                          | 0.03207                          | 0.00192                          | 213.0                            | 9.9                              | 203.5                            |
| 13         | 91    | 1482  | 2462  | 0.60 | 0.20079                          | 0.01178                          | 0.03040                          | 0.00174                          | 185.8                            | 10.0                             | 193.1                            |
| 14         | 68    | 1061  | 1791  | 0.59 | 0.21108                          | 0.01098                          | 0.03109                          | 0.00159                          | 194.5                            | 9.2                              | 197.3                            |
| 15         | 91    | 1571  | 2411  | 0.65 | 0.19505                          | 0.00807                          | 0.02907                          | 0.00134                          | 180.9                            | 6.9                              | 184.7                            |
| 16         | 7     | 138   | 150   | 0.92 | 0.22286                          | 0.01842                          | 0.03096                          | 0.00106                          | 204.3                            | 15.3                             | 196.5                            |
| 17         | 7     | 137   | 166   | 0.82 | 0.21924                          | 0.01671                          | 0.02910                          | 0.00071                          | 201.3                            | 13.9                             | 184.9                            |

Table 2. Cont.

| Sample No. | Pb    | Th    | U     | Th/U | <sup>207</sup> Pb/ <sup>235</sup> U | <sup>207</sup> Pb/ <sup>235</sup> U | <sup>206</sup> Pb/ <sup>238</sup> U | <sup>206</sup> Pb/ <sup>238</sup> U | <sup>207</sup> Pb/ <sup>235</sup> U | <sup>207</sup> Pb/ <sup>235</sup> U | <sup>206</sup> Pb/ <sup>238</sup> U |
|------------|-------|-------|-------|------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| SXH402-2   | (ppm) | (ppm) | (ppm) |      | Ratio                               | 1σ                                  | Ratio                               | 1σ                                  | Age (Ma)                            | 1σ                                  | Age (Ma)                            |
| 18         | 96    | 1778  | 2394  | 0.74 | 0.19135                             | 0.00491                             | 0.02815                             | 0.00029                             | 177.8                               | 4.2                                 | 179.0                               |
| 19         | 84    | 1098  | 2112  | 0.52 | 0.19875                             | 0.00506                             | 0.02882                             | 0.00030                             | 184.1                               | 4.3                                 | 183.2                               |
| Sample No. | Pb    | Th    | U     | Th/U | <sup>207</sup> Pb/ <sup>235</sup> U | <sup>207</sup> Pb/ <sup>235</sup> U | <sup>206</sup> Pb/ <sup>238</sup> U | <sup>206</sup> Pb/ <sup>238</sup> U | <sup>207</sup> Pb/ <sup>235</sup> U | <sup>207</sup> Pb/ <sup>235</sup> U | <sup>206</sup> Pb/ <sup>238</sup> U |
| SXH402-3   | (ppm) | (ppm) | (ppm) |      | Ratio                               | 1σ                                  | Ratio                               | 1σ                                  | Age (Ma)                            | 1σ                                  | Age (Ma)                            |
| 1          | 58    | 809   | 1558  | 0.52 | 0.20344                             | 0.01018                             | 0.02933                             | 0.00154                             | 188.0                               | 8.6                                 | 186.4                               |
| 2          | 26    | 285   | 740   | 0.39 | 0.18651                             | 0.00863                             | 0.02956                             | 0.00123                             | 173.6                               | 7.4                                 | 187.8                               |
| 3          | 84    | 1386  | 2312  | 0.60 | 0.19627                             | 0.00933                             | 0.02921                             | 0.00150                             | 182.0                               | 7.9                                 | 185.6                               |
| 4          | 3     | 56    | 79    | 0.72 | 0.24107                             | 0.02248                             | 0.03128                             | 0.00202                             | 219.3                               | 18.4                                | 198.5                               |
| 5          | 18    | 470   | 374   | 1.26 | 0.21489                             | 0.01215                             | 0.02981                             | 0.00135                             | 197.6                               | 10.2                                | 189.3                               |
| 6          | 71    | 1144  | 1934  | 0.59 | 0.20495                             | 0.01065                             | 0.02883                             | 0.00140                             | 189.3                               | 9.0                                 | 183.2                               |
| 7          | 60    | 736   | 1643  | 0.45 | 0.19524                             | 0.00736                             | 0.02925                             | 0.00109                             | 181.1                               | 6.3                                 | 185.8                               |
| 8          | 10    | 204   | 220   | 0.93 | 0.23231                             | 0.01448                             | 0.03149                             | 0.00139                             | 212.1                               | 11.9                                | 199.9                               |
| 9          | 61    | 890   | 1763  | 0.50 | 0.20172                             | 0.00926                             | 0.02935                             | 0.00149                             | 186.6                               | 7.8                                 | 186.5                               |
| 10         | 93    | 1694  | 2445  | 0.69 | 0.20026                             | 0.00858                             | 0.02914                             | 0.00118                             | 185.3                               | 7.3                                 | 185.2                               |
| 11         | 43    | 687   | 1215  | 0.56 | 0.18603                             | 0.00704                             | 0.02656                             | 0.00090                             | 173.2                               | 6.0                                 | 169.0                               |
| 12         | 120   | 620   | 3771  | 0.16 | 0.20194                             | 0.00502                             | 0.02841                             | 0.00049                             | 186.8                               | 4.2                                 | 180.6                               |
| 13         | 6     | 119   | 149   | 0.80 | 0.21400                             | 0.01663                             | 0.02903                             | 0.00076                             | 196.9                               | 13.9                                | 184.4                               |
| 14         | 116   | 2079  | 2946  | 0.71 | 0.20364                             | 0.00730                             | 0.02878                             | 0.00101                             | 188.2                               | 6.2                                 | 182.9                               |
| 15         | 7     | 171   | 173   | 0.99 | 0.19994                             | 0.01275                             | 0.02879                             | 0.00070                             | 185.1                               | 10.8                                | 183.0                               |

#### 4.4. Sr-Nd Isotope

The results of the Sr-Nd isotope analyses of the Shangxiahu granite porphyry are presented in Table 3. After correcting the isotope values for the age of 183.2 Ma obtained from zircon U-Pb dating, it can be observed that the (<sup>87</sup>Sr/<sup>86</sup>Sr)<sub>i</sub> values of Shangxiahu granite porphyry are relatively low, with variations in the range of 0.379801~0.707960. Additionally, the values of ε<sub>Nd</sub>(t) falls within the range of −7.0~−5.7.

Table 3. Major and trace element compositions of granite porphyry from the Shangxiahu Nb-Ta deposit.

| Sample No.                                           | SXH002-1 | SXH401-1 | SXH401-2 | SXH402-2 | SXH402-3 |
|------------------------------------------------------|----------|----------|----------|----------|----------|
| Age (Ma)                                             | 183.2    | 183.2    | 183.2    | 183.2    | 183.2    |
| Sm (ppm)                                             | 4.76     | 1.87     | 11.2     | 5.03     | 4.28     |
| Nd (ppm)                                             | 21.2     | 9.11     | 51.5     | 21.9     | 17.4     |
| <sup>147</sup> Sm/ <sup>144</sup> Nd                 | 0.13567  | 0.12403  | 0.13141  | 0.13879  | 0.14863  |
| <sup>143</sup> Nd/ <sup>144</sup> Nd                 | 0.512272 | 0.512265 | 0.512269 | 0.512279 | 0.512221 |
| 2σ                                                   | 0.000005 | 0.000007 | 0.000004 | 0.000005 | 0.000006 |
| ( <sup>143</sup> Nd/ <sup>144</sup> Nd) <sub>i</sub> | 0.512109 | 0.512116 | 0.512111 | 0.512113 | 0.512043 |
| εNd(t)                                               | −5.7     | −5.6     | −5.7     | −5.7     | −7.0     |
| T <sub>DM</sub> (Ma)                                 | 1715     | 1505     | 1632     | 1772     | 2173     |
| T <sub>2DM</sub> (Ma)                                | 1433     | 1422     | 1430     | 1428     | 1538     |
| <sup>87</sup> Sr/ <sup>86</sup> Sr                   | 0.699945 | 0.631044 | 0.713149 | 0.7075   | 0.702    |
| <sup>87</sup> Rb/ <sup>86</sup> Sr                   | 1.26910  | 1.16335  | 1.22395  | 1.33847  | 0.97463  |
| 2σ                                                   | 0.000005 | 0.000006 | 0.000004 | 0.000004 | 0.000006 |
| ( <sup>87</sup> Sr/ <sup>86</sup> Sr) <sub>i</sub>   | 0.579284 | 0.379801 | 0.707960 | 0.652316 | 0.634529 |
| Mantle component (%)                                 | 53%      | 54%      | 53%      | 53%      | 47%      |

## 5. Discussion

### 5.1. Age of Granite Porphyry

The Nb-Ta deposits in the Yongding region are primarily concentrated in the Daping and Shangxiahu area. Previous studies have indicated that the period of rock formation and Nb-Ta mineralisation in this region is the Early Jurassic. Xu et al. [33] obtained zircon U-Pb ages of (189 ± 6)~(195 ± 2) Ma and 184 ± 2 Ma for the volcanic rocks of the Fankeng Formation in Xiaba Village and Wuhu Village in the Yongding region, respectively. Wang et al. [13] used SIMS and LA-ICP-MS in situ analyses of granitic porphyry zircons from the Daping Nb-Ta deposit and obtained zircon U-Pb ages of 186.7 ± 1.2 Ma and 190.7 ± 1.1 Ma, respectively. Wang et al. [21] obtained a plagioclase zircon U-Pb age of 184.0 ± 6.5 Ma for gabbro veins in the Daping Nb-Ta deposit. It can be concluded that the

igneous rocks of the Yongding region were formed by an eruption that occurred during the Early Jurassic period. Furthermore, the U-Pb age of Nb-Ta ores by Wang et al. [34] is approximately 183 Ma, which is consistent with the age of igneous rocks within the error range. This evidence suggests the occurrence of an Early Jurassic granitic porphyry type Nb-Ta mineralisation in South China. The results of this study demonstrate that the zircon U-Pb age of the Shangxiahuh granite porphyry is  $183.2 \pm 3.2$  Ma (Figure 5), which is slightly later than the reported crystallisation age ( $186.7 \pm 1.2$  Ma– $190.7 \pm 1.1$  Ma) of the granite porphyry in the Daping Nb-Ta deposit in Yongding region.

## 5.2. Magma Types and Source of Granitic Porphyries

### 5.2.1. Magma Types

Granites can typically be classified into four genetic categories: I-Type, S-Type, M-Type and A-Type [35–37].

Compared with I-type, S-type and M-type granites, the Shangxiahuh granite porphyry samples have higher HFSE content ( $Zr + Nb + Ce + Y = 552.5\text{--}1977.5$  ppm, Figure 6a), Ga/Al ratios ( $10,000 \times Ga/Al = 6.2\text{--}9.0$ , Figure 6b), total alkali metal content ( $Na_2O + K_2O = 7.12\text{wt}\%\text{--}8.96\text{wt}\%$ , Figure 6a) and FeO<sub>t</sub>/MgO ratios (4.99–12.34), which are the characteristics of A-type granite [35,38] and fall within the discrimination range of A-type granite (Figure 6a). In general, A-type granites are characterised by relatively high HFSE content, such as the Beitou, Wengong and Suzhou rocks [39,40]. However, due to the strong fractional crystallisation of A-type granite, highly fractionation granites can be formed, and the high  $10,000 \times Ga/Al$  ratios of highly fractionation granites correspond to the low Al and high Ga characteristics of A-type granite. Therefore, A-type granite and highly fractionated granite are not easy to distinguish [41–49].

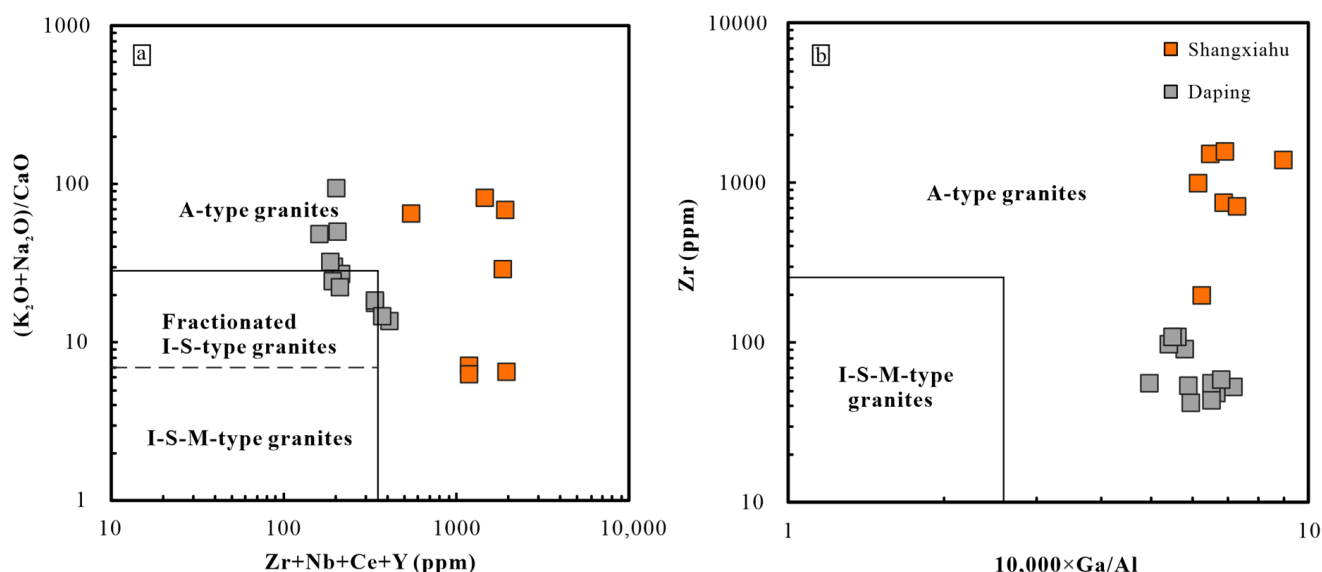


**Figure 6.**  $(K_2O + Na_2O)/CaO$ - $Zr + Nb + Ce + Y$  (a) and  $Zr$ - $10,000 \times Ga/Al$  (b) diagrams of granite porphyry from the Shangxiahuh Nb-Ta deposit.

In response to this problem, we have identified by the following characteristics. First, A-Type granites are best characterised by high temperatures. In contrast to water-rich and low-temperature I-Type, S-Type and highly evolved granites and pegmatites, A-Type granites are generally considered to have formed from relatively anhydrous and high-temperature magma [50,51]. The Shangxiahuh granite porphyry has a high  $SiO_2$  content (71.19 wt%–75.49 wt%), and the average of differentiation index (DI) is 91.47%, indicating that it is a highly fractionation granite. The calculation results of the zircon-saturation temperature ( $T_{Zr}$ ) values show that it is between 819 °C and 1033 °C (Table 1), which may not represent the temperature of the initial magma in the source area [52,53]. However,

no inherited zircons are found in the samples, indicating that the zircons in the melt are not saturated, and the  $T_{Zr}$  values may represent the minimum temperature of the initial magma in the source area. Therefore, the initial magma temperature of the Shangxiahua granite porphyry may have been higher than 819 °C, which is significantly higher than the formation temperatures of the I-type granites (unfractionated: 781 °C, fractionated: 764 °C) and the S-type granites (<800 °C), and consistent with the high temperature characteristics of the A-type granites (>800 °C) [36,37,52]. In addition, the characteristic minerals of type I and S granites (e.g., hornblende, cordierite, muscovite, garnet, etc.) have not been found under the microscope [54–56]. Therefore, comprehensive analyses suggest that the Shangxiahua granite porphyry is a A-type granite, which is consistent with the reported type of the Daping granite porphyry, which is also located in the Yongding region [13].

### 5.2.2. Magma Source

The genesis of A-type granites is controversial, especially the nature of their source and formation processes. Currently, there are four main models for the genesis of A-type granites: (1) direct fractional crystallisation of mantle-derived Mg-Fe magma [51,57,58]; (2) partial melting of crustal felsic rocks [35,36,59,60]; (3) melting of lower crustal granulite remnant [58,61,62] and (4) melting of mixture of crustal felsic magma with mantle-derived magma [63–67].

In general, granites produced through direct fractional crystallisation of mantle-derived magma may exhibit elevated Nb/Ta (>17.5) and Nd/Th (>15) ratios [31]. Nevertheless, the Nb/Ta and Nd/Th ratios of the Shangxiahua granite porphyry are comparatively low, at 5.8 to 14.3 and 0.2 to 0.4, respectively. Furthermore, Taylor and McLennan (1995 [68]) observed that the high SiO<sub>2</sub> content (71.19 wt%~75.49 wt%) and low MgO content (0.17 wt%~0.49 wt%) are not characteristic of granites formed by direct fractional crystallisation of mantle-derived magma. Furthermore, the Shangxiahua granite porphyry exhibits low (<sup>87</sup>Sr/<sup>86</sup>Sr)<sub>i</sub> and negative ε<sub>Nd</sub>(t) values, indicating that the granite porphyry was not the result of direct fractional crystallisation of mantle-derived magma (Figures 7 and 8, [37,54]). Experimental petrology has demonstrated that the dewatered melting of crustal felsic rocks under high temperature and low pressure conditions can result in the formation of felsic melts that are analogous to aluminous A-type granites [61,69]. Furthermore, experimental petrology demonstrates that under conditions of elevated temperature and reduced pressure, the dewatered melting of crustal felsic rocks can result in the formation of felsic melts that are analogous to aluminous A-type granites. A-type granites formed by partial melting of crustal felsic rocks are classified as A2-type granites and exhibit a positively correlated partial melting trend on the La-La/Sm diagram [40,70]. However, the Shangxiahua granite porphyry is distinguished by low Y/Nb ratios, indicative of an A1-type granite (Figure 9), and an insignificant trend of horizontal differentiation on the La-La/Sm diagram (Figure S1). It can, thus, be concluded that partial melting of the ancient crystalline basement of the southeastern section of the Nanling Range in South China is an inadequate explanation for the genesis of the Shangxiahua granite porphyry, and the aluminous A1-type granites cannot be derived directly from partial melting of crustal igneous rocks. Furthermore, experimental studies have corroborated that granites derived from lower crustal granulite facies belt tend to exhibit low <sup>T</sup>FeO/(<sup>T</sup>FeO + MgO) (0.65~0.88) [61], whereas the Shangxiahua granite porphyry displays elevated <sup>T</sup>FeO/(<sup>T</sup>FeO + MgO) (0.83~0.93). It can, thus, be concluded that the first three hypotheses are not applicable to the genesis of Shangxiahua granite porphyry.

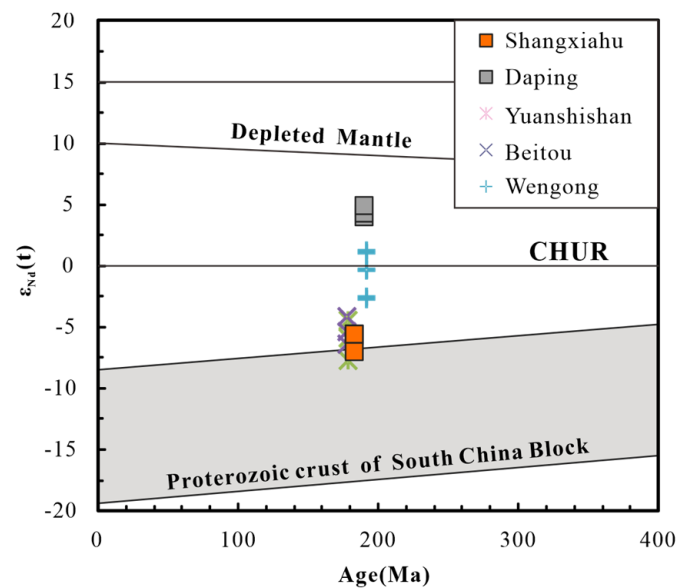


**Figure 7.**  $\epsilon_{Nd}(t)$ -Age (Ma) diagram of granite porphyry from the Shangxiaihu Nb-Ta deposit and Early Jurassic A-type granite in South China. The Early Jurassic A-type granite data in South China were obtained from Zhou et al., 2018 [71], including the Yuanshishan data from Jia et al., 2014 [72]; the Beitou data from He et al., 2010 [73] and the Wengong data from Zhu et al., 2010 [74]; the same are below.

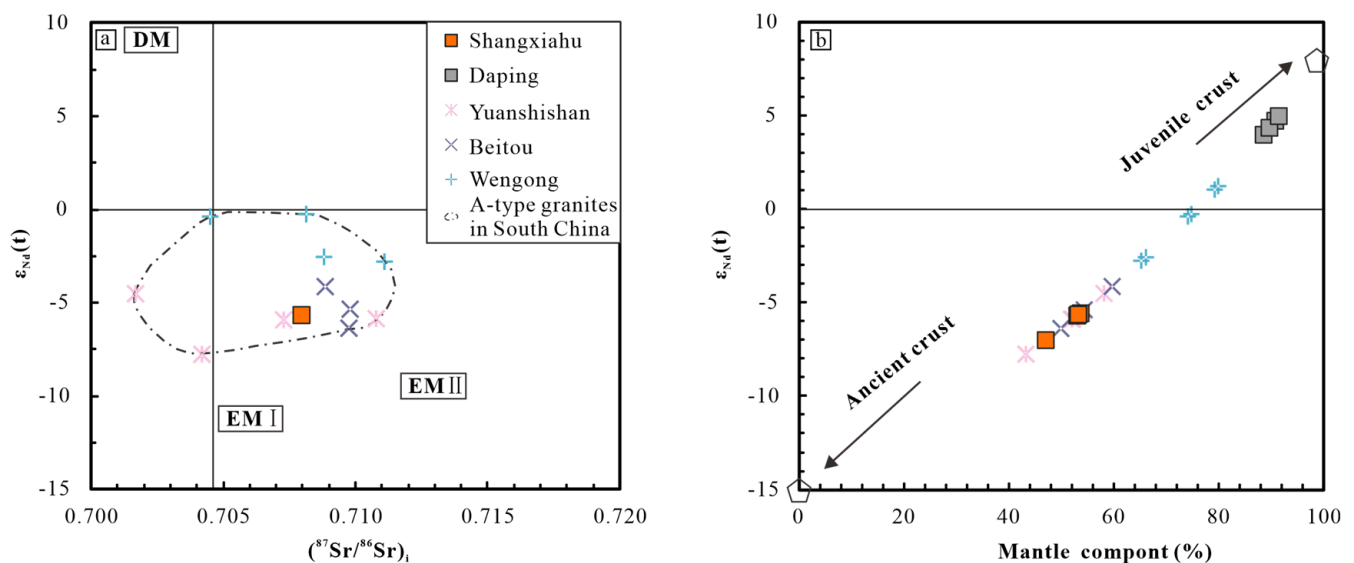


**Figure 8.**  $\epsilon_{Nd}(t)$ - $(^{87}\text{Sr}/^{86}\text{Sr})_i$  (a) and  $\epsilon_{Nd}(t)$ -estimated proportions of the mantle component (b) diagrams of granite porphyry from the Shangxiaihu Nb-Ta deposit and Early Jurassic A-type granite in South China. Mantle component (%) =  $(\text{Nd}_c/\text{Nd}_m)/((\text{Nd}_c/\text{Nd}_m) + (\epsilon_m - \epsilon_s)/(\epsilon_s - \epsilon_c))$  [75] in (b). The results of the data are detailed in Table 3, where  $\text{Nd}_c$  and  $\text{Nd}_m$  denote the Nd concentration in the crustal and mantle compositions, respectively.  $\epsilon_m$ ,  $\epsilon_s$  and  $\epsilon_c$  denote Nd isotopic compositions for the juvenile crust, the test sample and the crust, respectively. Parameters used as follows:  $\epsilon_m = +8$ ,  $\epsilon_c = -15$ ,  $\text{Nd}_c = 25$  ppm and  $\text{Nd}_m = 15$  ppm. Nd isotope data for the end members are from Wu et al., 2003 [76].

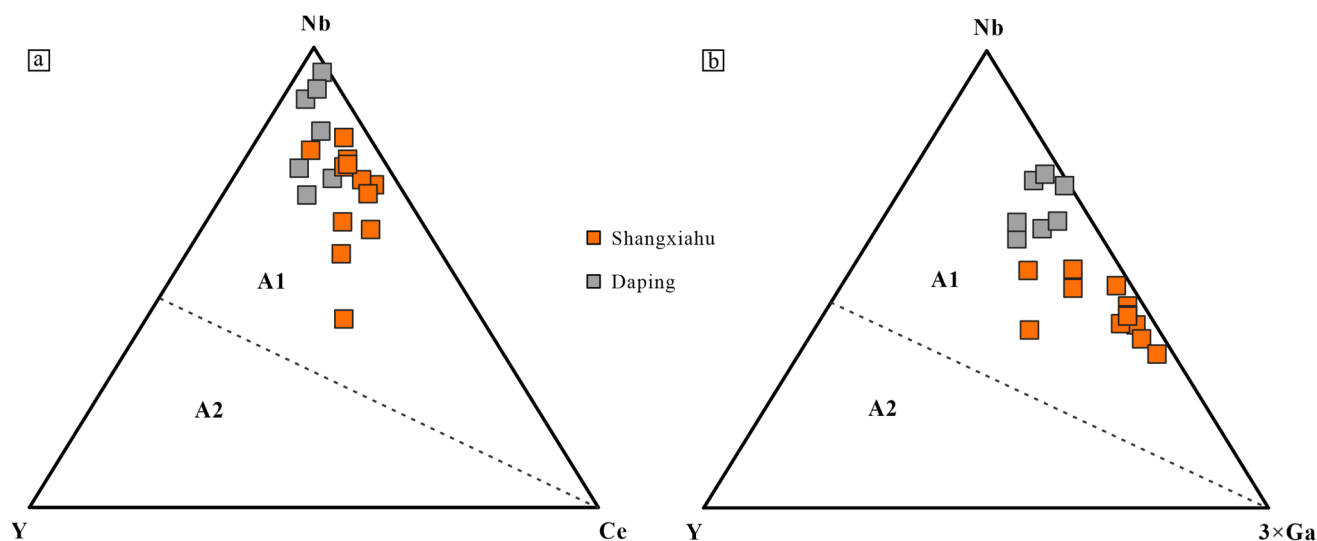


**Figure 9.** Y-Nb-Ce (a) and Y-Nb-3 × Ga (b) triangular diagrams of granite porphyry from the Shangxiahu Nb-Ta deposit (modified from Eby (1992) [77]). Where A1 represents non-orogenic A-type granite, A2 represents orogenic A-type granite.

The Early Yansha igneous in the Nanling Range are characterised by a basalt, A-type acid volcanics and a "bimodal" igneous rock assemblage of their intrusive facies gabbro and A-type granites, which are distributed in a nearly EW-trending area. This indicates that they were formed in an extensional setting [13,78], with a certain degree of crust–mantle interaction [13,79]. The Lu/Yb ratios of the mantle-derived magma (0.14–0.15) are lower than those of the continental crust (0.16–0.18) [31], while the Lu/Yb ratios of the Shangxiahu granite porphyry are between 0.127 and 0.210. This indicates that the magma source of the Shangxiahu granite porphyry is likely a mixed source comprising both mantle- and crust-derived magmas. Moreover, the Shangxiahu granite porphyry exhibits negative  $\varepsilon_{\text{Nd}}(t)$  values (−5.6–−7.0), like other Early Jurassic A-type granites in South China (e.g., Daping: [13]; Yuanshishan: [72]; Beitou: [73]; Wengong: [74]); the  $\varepsilon_{\text{Nd}}(t)$ –Age (Ma) diagram (Figure 7) shows that the samples of the Shangxiahu granite porphyry partly fall within the South China Proterozoic crustal region, with a  $T_{2\text{DM}}$  (Ma) range of 1422–1538 Ma (Table 3). This suggests that the Shangxiahu granite porphyry may have been derived from partial melting of the South China Mesoproterozoic crust, with the addition of mantle-derived magma. The  $(^{87}\text{Sr}/^{86}\text{Sr})_i$  values (0.379801–0.707960) of the Shangxiahu granite porphyry are lower than those of other Early Jurassic granites in South China (Figure 8a), which may be attributed to the alteration of some samples, resulting in a larger Rb/Sr ratio, affecting the correction of Sr isotopes. In order to evaluate the degree of participation of crust- and mantle-derived magma, the following continental crust (LCC) and depleted mantle (DM) are calculated and assessed as two end-member components [76]. The resulting calculations demonstrate that the parent magma of the Shangxiahu is composed of 52% mantle-derived magma and 48% Mesoproterozoic crust-derived magma (Figure 8b). Furthermore, the presence of gabbros in the Shangxiahu area further indicates that the granite porphyry in this area was formed by the mixing of mantle- and crust-derived magma.

### 5.3. Nb-Ta-Bearing Magma Evolution and Nb-Ta Enrichment

A synthesis of the previous research data reveals that the contents of the whole-rock  $\text{SiO}_2$ , Rb, Cs and Nb in the Yongding granite porphyries are higher, while those of Sr, Ba, Ti and Eu are lower. The average value of the differentiation index ( $\text{DI} = \text{Q} + \text{Or} + \text{Ab} + \text{Ne} + \text{Lc} + \text{Kp}$ ) of the Shangxiahu granite porphyry is 91.47 (Table 1), and that of the Daping granite porphyry is 95.05 (according to the data obtained from Wang et al., 2020 [13]), indicating that the rock bodies have undergone highly fractional crystallisation [80]. Based

on the analysis of granite types and parental magma components, combined with the analysis of Nb-Ta enrichment and mineralisation processes, and supplemented by previous research on the Yongding region, the formation process of the Yongding Yanshanian granite porphyries Nb-Ta deposit can be inferred as follows:

1. Partial melting of the crust induced by asthenospheric material upwelling

Previous studies indicate that the Paleo-Pacific Plate commenced a northwestward movement during the Jurassic period [81] and subsequently subducted at a low angle beneath the Eurasian continent [82]. Due to the northwestward subduction of the Paleo-Pacific Plate, the eastern continental margin of China became an active continental margin, and the remelting of the subducted plate occurred along the Qinhang Paleo-Plate welding zone and the Nanling Range. It is possible that the 172–145 Ma Nanling granites in the Qinhang Belt were formed in a post-arc extensional setting related to the low-angle subduction of the Paleo-Pacific [82,83]. At the same time, the continental crust may have been continuously thickened, and a series of crust-scale extensional faults have been developed in the post-arc area [82,84]. The bimodal magmatism (158–179 Ma [85]), the development of A-type granites (including Daping, Yuanshishan, Beitou, Wengong, etc., [13,71–74] and alkaline intrusions (165–173 Ma [86]) and the low  $T_{DM}$  and high  $\epsilon_{Nd}$  granite belts in Hangzhou, Jiangxi, Hunan, Guangdong and Fujian provinces all indicate that the eastern Qinhang metallogenic belt was in an extensional state during the Early-Middle Jurassic. In the Rb-Y + Nb diagram and Nb-Y diagram (Figure 10) [87], the samples of Shangxiahu granite porphyry all fall into the within-plate granites (WPG) area, which also indicates that the magma was formed through lithospheric thinning. In addition, Eby (1992) [77] divided A-type granites into A1- and A2-type granites according to the tectonic environment: A1-type granites have a certain geochemical similarity with oceanic crust and are the products of partial melting of mantle-derived basic cumulate in accretionary orogenic belts; A2-type granites are closer to continental crust in composition and are the product of partial melting of crustal residues in collisional orogenic belts. The classification diagram (Figure 9) of Eby (1992) [77] is used to identify the tectonic environment in which the formation of Shangxiahu granite porphyry occurred. It was determined that all samples are distributed within the A1 granite region, which is consistent with the tectonic environment of non-orogenic intraplate extension in the study area. In summary, the South China crust may have undergone extensional thinning during the Mesozoic, which may have triggered mantle upwelling along the extensional continental margins and underplating of mantle-derived materials along the fault [88–91]. This may have induced partial melting of the crust at the bottom of the Shangxiahu area.

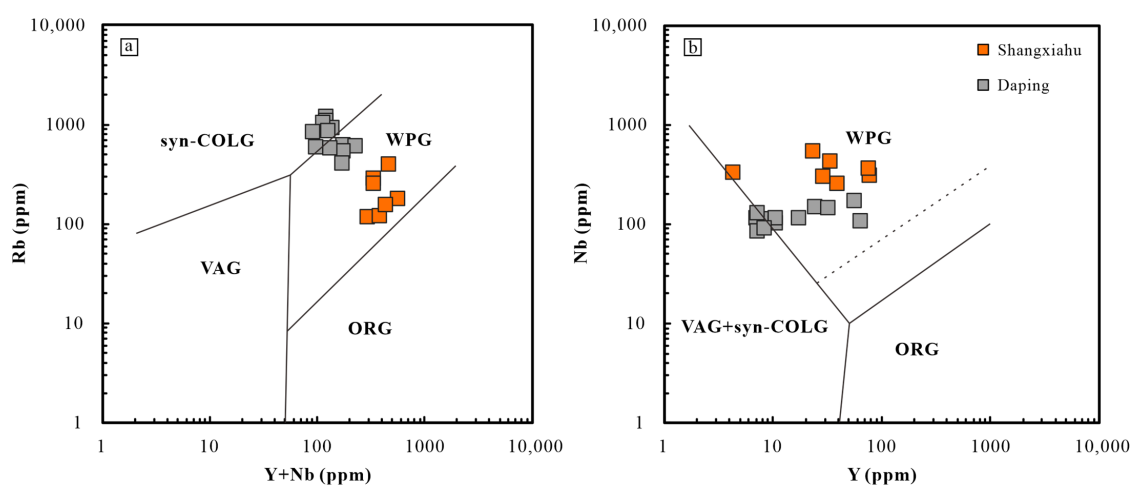


Figure 10. Rb-Y + Nb (a) and Nb-Y (b) diagrams of granite porphyry from the Shangxiahu Nb-Ta deposit.

## 2. Mixing of mantle-derived and crust-derived magmas

The compressive stress caused by the subduction of the Paleo-Pacific Plate resulted in the activation of the nearly EW-trending Indosinian fault zone in the Nanling Range. This led to the extension of the local lithosphere, which in turn promoted the upwelling of asthenospheric materials to form gabbro-diabase [92]. The upwelling of asthenospheric materials induced the partial melting of the Mesoproterozoic basement crust to form mixed magma, which subsequently underwent highly fractional crystallisation, evolving into highly fractionation granites [7]. Previous studies have indicated that the mantle-derived basaltic magma in southwestern Fujian could intrude along the Zhenghe-Dapu fault zone at approximately 180 Ma, potentially inducing the melting of lower crustal materials [93]. Tectonically, the Shangxiahu area is situated along the Zhenghe-Dapu fault zone. The upwelling of basaltic magma along the fracture channel will induce the melting of some ancient crustal materials, thus mixing the mantle- and crust-derived magmas to form a weakly peraluminous parent magma. The Sr-Nd isotope analysis of the Shangxiahu granite porphyry also demonstrated that its parent magma is composed of 52% mantle-derived magma and 48% crust-derived magma, and that the parent magma of the Daping granite porphyry contains a high proportion of mantle-derived magma (90%), which is basically consistent with the findings of Wang Jinrong (2020) [13]. This suggested that the mixing of mantle- and crust-derived magmas formed the parent magmas of the Shangxiahu and Daping granite porphyry.

## 3. Magmatic fractional crystallisation

The geochemical characteristics of the Shangxiahu granite porphyry indicate that it underwent a highly fractional crystallisation process during the magmatic evolution (Figure 11). As shown in Figure 11c, the Shangxiahu granite porphyry exhibits low whole-rock Sr and Eu contents, and the correlation trend indicates the fractional crystallisation of biotite and feldspar, a conclusion supported by the negative correlation between Rb and Ba (Figure 11d). The fractional crystallisation of plagioclase in the Shangxiahu granite porphyry resulted in high Rb contents (116.3–397.0 ppm) and high Rb/Sr ratios (2.04–41.0) in the residual magma. Furthermore, the Shangxiahu granite porphyry also exhibits low Ti contents, with  $\text{TiO}_2$  contents as low as 0.04 wt%. Stepanov et al. (2014) [94] proposed that fractional crystallisation of biotite, iron-titanium oxide or titanite may lead to Ti depletion. The Daping granite porphyry adjacent to Shangxiahu also exhibits similar characteristics, as described above (Figure 11). In conclusion, the geochemical characteristics and field geological features of the Yongding granite porphyries indicate that their genesis is related to fractional crystallisation, especially the fractional crystallisation of biotite and feldspar.

In general, the less evolved granites are mainly associated with copper, molybdenum, lead and zinc mineralisation, while the high-evolution granites are more related to tungsten, rare metals and heavy rare earth elements [7]. The granitic magma would gradually evolve towards a melt and fluid with the incompatible elements accumulation during the process of high fractional crystallisation, and lead to a decrease in Nb/Ta, K/Rb and Zr/Hf ratios. Therefore, granites with a higher degree of differentiation are more closely related to Ta, Rb and Hf mineralisation [7,95]. Furthermore, the Rb/Sr ratio is also generally considered as an indicator of the extent of magma evolution [96–98]. The Nb/Ta, K/Rb and Zr/Hf ratios of the Shangxiahu granite porphyry are lower than those of the Daping granite porphyry, while the Rb/Sr ratios are relatively lower (Figure 12), indicating that the differentiation degree of the Shangxiahu granite porphyry is lower than that of the Daping granite porphyry.

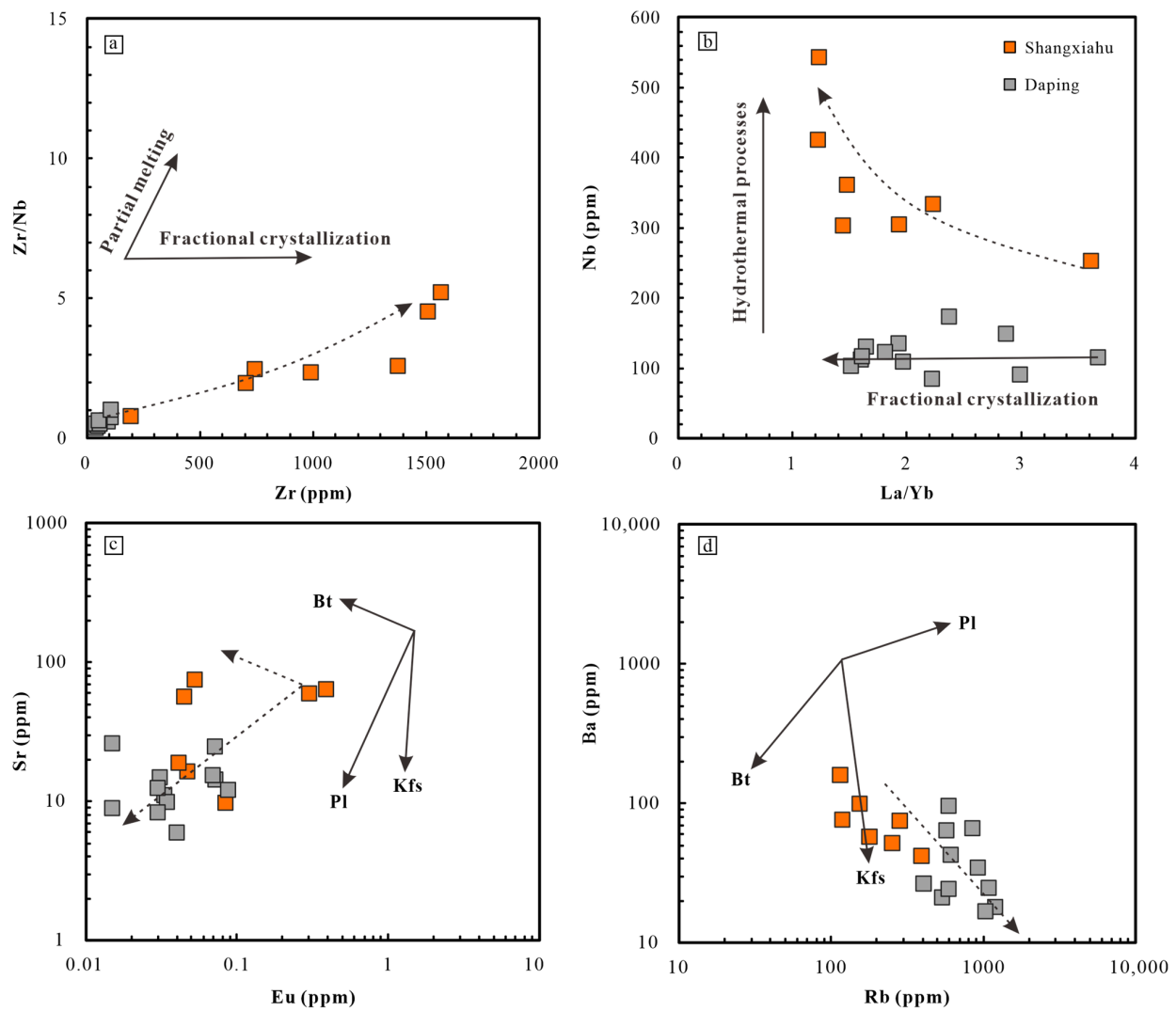


**Figure 11.** Zr/Nb-Zr diagram (a); Nb-La/Yb diagram (b); Sr-Eu diagram (c); Ba-Rb diagram (d) of granite porphyry from the Shangxiahu Nb-Ta deposit.

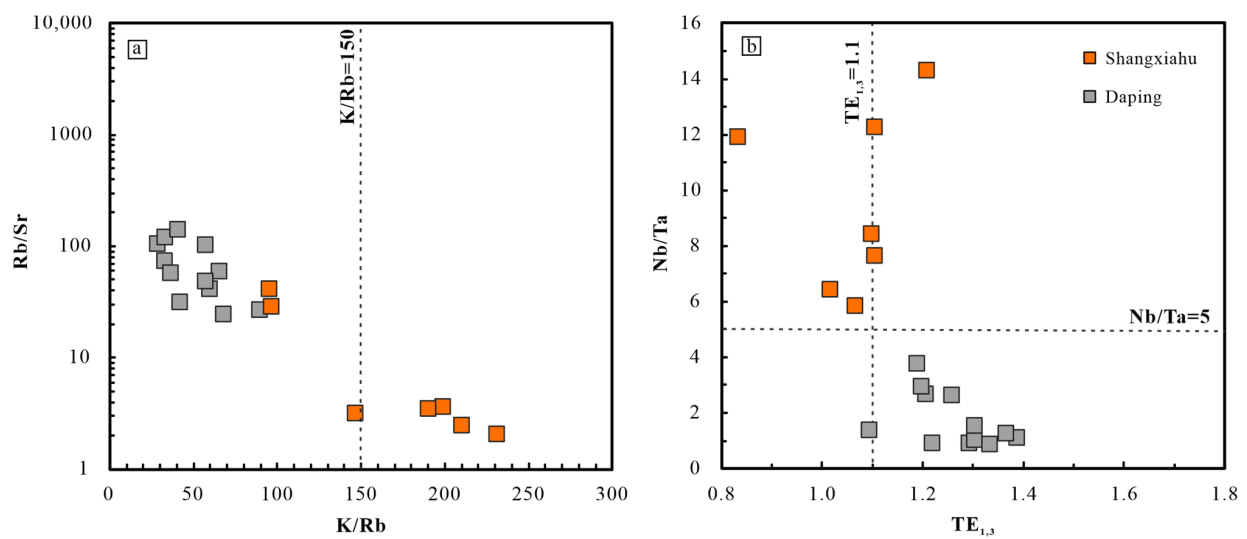


**Figure 12.** Cont.

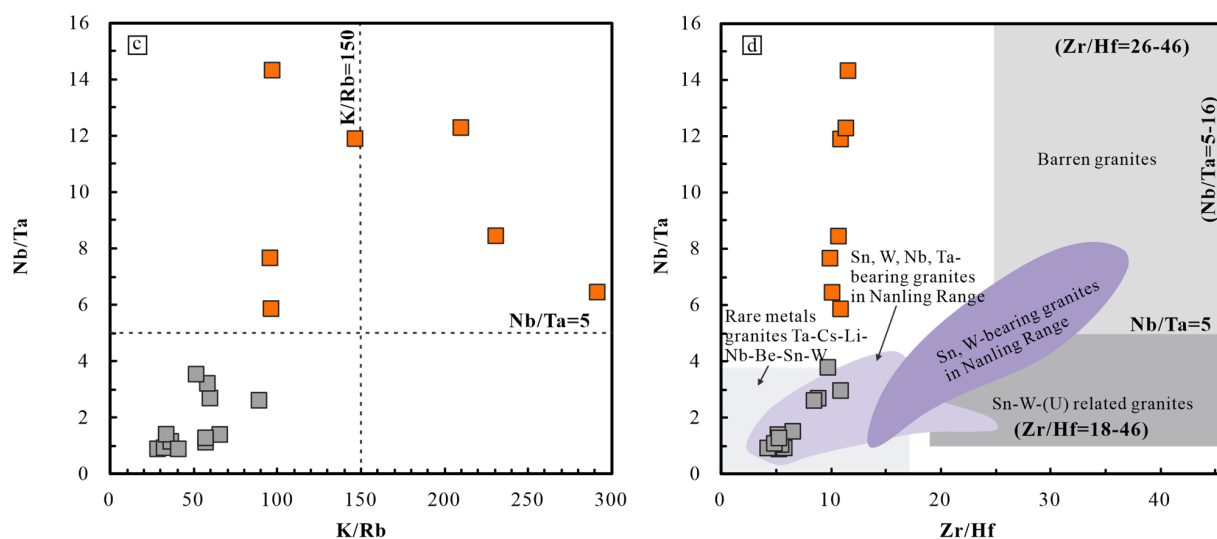


**Figure 12.** Rb/Sr-K/Rb diagram (a); Nb-Ta-TE<sub>1,3</sub> diagram (b); Nb-Ta-K/Rb diagram (c); Nb-Ta-Zr/Hf diagram (d) of granite porphyry from the Shangxiahu Nb-Ta deposit. Calculation of tetrad effect is  $TE_{1,3} = (t1 \times t3)^{0.5}$ ,  $t1 = (Ce/Ce^t \times Pr/Pr^t)^{0.5}$ ,  $t3 = (Tb/Tb^t \times Dy/Dy^t)^{0.5}$ ,  $Ce/Ce^t = Ce_{cn}/(La_{cn}^{2/3} \times Nd_{cn}^{1/3})$ ,  $Pr/Pr^t = Pr_{cn}/(La_{cn}^{1/3} \times Nd_{cn}^{2/3})$ ,  $Tb/Tb^t = Tb_{cn}/(Gd_{cn}^{2/3} \times Ho_{cn}^{1/3})$ ,  $Dy/Dy^t = Dy_{cn}/(Gd_{cn}^{1/3} \times Ho_{cn}^{2/3})$ , which is derived from Irber (1999) [99]. The data ranges of Sn-, W-, Nb- and Ta-rich granites and Sn- and W-rich granites in Nanling Range are from Xiang et al. 2020 [100]; the data ranges of barren granites, rare metal granites and Sn-W-(U)-related granites are from Ballouard et al. 2016 [98].

#### 4. Magma–hydrothermal interaction and Nb-Ta enrichment

The enrichment of incompatible elements in magma–hydrothermal fluids is frequently regarded as a signature of magma–hydrothermal interaction in highly evolved peraluminous granites, given their strong affinity for magma–hydrothermal fluids [97,98,101–103]. The granite porphyries in the Yongding region exhibit two distribution patterns of incompatible elements, with low Li (3.36~14.4 ppm), Rb (120.3~397 ppm) and Cs (1.17~2.39 ppm) contents in the Shangxiahu granite porphyry, while the Daping granite porphyry displays high Li (5.02~388 ppm), Rb (539~1200 ppm) and Cs (1.18~5.45 ppm) contents, indicating different degrees of magma–hydrothermal interaction in different deposits. Ballouard et al. (2016) [98] proposed that whole-rock Nb/Ta ratios of < 5 can be regarded as geochemical markers of evolved melts with strong hydrothermal interactions. The Nb/Ta ratios > 5 (5.8~14.3) in Shangxiahu and < 5 (0.9~3.8) in Daping indicate that the magma–hydrothermal evolution is less pronounced in the Shangxiahu granite porphyry, while more pronounced in the Daping granite porphyry. Furthermore, K/Rb is frequently compared with Nb/Ta, as the former has also been proposed as a geochemical indicator of magma–hydrothermal alteration [96,97]. For example, Dostal and Chatterjee (2000) [97] identified K/Rb ratios < 150 as indicative of magma–hydrothermal alteration in the bedrock of the Southern Canadian Mountains. As illustrated in the Nb/Ta vs K/Rb diagram (Figure 12a,c), the majority of the Shangxiahu granite porphyry exhibit K/Rb < 150, a trend that is similarly observed in all Daping granite porphyry. This indicates that the hydrothermal activity in the Shangxiahu granite porphyry is localised, while it is widespread in the Daping granite porphyry.

Finally, whole-rock Nb/Ta ratios can be contrasted with the extent of the tetrad effect, which corresponds to the fractionation of internal rare earth elements (REEs) observed in REE patterns of highly fractionated igneous and hydrothermal precipitates [99]. Although Duc-Tin and Keppler (2015) [104] recently considered that the tetrad effect may be caused by the fractional crystallisation of monazite and xenotime, most scholars claim that this REE pattern actually reflects a selective complexation reaction of REEs during interactions between granitic melts and fluids rich in F and Cl [105]. Irber (1999) [99] quantified the extent of the tetrad effect (TE<sub>1,3</sub>) by determining the error of the first and third tetrads of

the granite REE pattern. This granite REE pattern is derived from a hypothetical tetrad effect, which is a pattern without REE. The calculation formulae are detailed in the notes to Figure 12. As illustrated in Figure 12b, the Shangxiahua granite porphyry exhibits an average  $TE_{1,3}$  value of approximately 1.1 (Table 1), while the Daping granite porphyry displays a strong tetrad effect ( $TE_{1,3} > 1.1$ ). This further indicates that the hydrothermal alteration of the Shangxiahua granite porphyry is weaker than that of the Daping granite porphyry.

The Zr/Hf ratio is commonly used as a marker for magma–hydrothermal interactions [96] or fractional crystallisation [106], with the Nb/Ta ratio often serving as a point of comparison. The Zr/Hf ratio is a geochemical indicator of rich mineralisation in granitic rocks, as it is expected to be roughly  $< 25$  in reported granites with mineralisation of Sn, W, Mo, Be and Ta [107]. In the Nb/Ta–Zr/Hf diagram (Figure 12d), most barren granites fall in the region of  $26 < \text{Zr/Hf} < 46$  and  $5 < \text{Nb/Ta} < 16$ . Conversely, peraluminous granites associated with Sn, W and/or U deposits have Zr/Hf ratios between 18 and 46 and Nb/Ta ratios  $< 5$  [96,98]. Rare metal granites are characterised by lower Zr/Hf ratios ( $< 18$ ) and Nb/Ta ratios ( $< 5$ ) [98]. The Nb/Ta and Zr/Hf ratios of the Shangxiahua granite porphyry range from 5.8 to 14.3 (with an average Nb content of 360.43 ppm and an average Ta content of 40.65 ppm) and from 9.9 to 11.5, respectively. This indicates that the Nb-rich and Nb/Ta  $> 5$  characteristics of the Shangxiahua granite porphyry may be related to the partial melting of the Mesoproterozoic Nb-rich crust. The Daping granite porphyry falls within the regional range of rare metal granites and coincides with the regional range of Sn- and W-rich granites in Nanling Range [100], which indicates the potential for the presence of ore bodies rich in Sn and W at the deep part or around the Daping area.

## 6. Prospecting Prediction

From the previous section, it can be inferred that the low-angle subduction of the Pacific Plate led to the lithospheric extension and thinning, and the partial melting of the Mesoproterozoic basement crust was triggered by the upwelling of asthenospheric mantle materials, forming mixed magmas that underwent highly fractional crystallisation evolution. Simultaneously, further alteration and mineralisation occurred under the action of post-magmatic hydrothermal fluids, resulting in the formation of Nb-Ta granite porphyries in the Shangxiahua and Daping areas. Generally speaking, the more evolved or altered rocks are important parent rocks for rare metal mineralisation [7]. However, the degree of magmatic evolution and hydrothermal alteration of Shangxiahua granite porphyry is lower than that of Daping granite porphyry. In addition, its Nb content (253–542 ppm) is higher than that of Daping granite porphyry (84–173 ppm), and the Ta content (21.2–57.1 ppm) is lower than that of the Daping granite porphyry (38.1–125.0 ppm), which may be related to the differences in the composition and evolution of the parent magmas. The parent magma of the Shangxiahua granite porphyry has a much higher crustal component (48%) than that of the Daping granite porphyry (10%), suggesting the possibility of a lower crustal reservoir with a high Nb/Ta ratio [108] in the Shangxiahua area. This indicates the potential for prospecting in the area with high crustal source components in the crust–mantle interaction zone.

In addition, there are multi-stage magmatic activities in the Nanling Range, which may be responsible for the formation of Nb-Ta deposits. For example, granite-type Nb-Ta deposits such as Jianfengling, Jinzhuyuan and Dajishan developed on the Chenzhou–Linwu fault zone, and altered granite-type Nb-Ta polymetallic deposits such as Jiangkengli, Hailuoling, Hanjiaoshan and Niulingao developed in the eastern Nanling Range [11,92], which indicate that the magma in this area has been subjected to multiple intrusions, the residual magma has been extracted multiple times and the magmatic fractional crystallisation has been continuous. However, if the deep mafic magma is overheated, the heap crystals in the magma chamber will also be partially melted, that is, form activated crystal mush. At this time, the metallogenic capacity of the intruding magma will be reduced due to the "rejuvenation". Thus, the mineralisation ability of rare metals will be reduced in the source area with strong crust–mantle interaction [7], which may be the reason why the metallo-

genic capacity of Daping granite is lower than that of Shangxiahua granite. In addition, Nb and Ta tended to be enriched with volatiles in the late stage of the same magmatic process, resulting in the metasomatic alteration of volatile components such as F and Cl and alkaline components such as Na, K and Li at the top of the rock body, which led to the further mobilisation and transfer of metallogenic elements and the formation of associated Sn, W and Be ores [11]. Therefore, high volatile-rich Nb-Ta ore bodies may exist near the Daping mining area, and the above study shows that the Zr/Hf ratio of the Daping granite porphyry is  $< 46$ , which coincides with the regional scope of the Sn-rich and W-rich granite in the Nanling Range, indicating that there may be ore bodies rich in Sn and W at the deep part or around Daping area.

## 7. Conclusions

(1) The zircon U-Pb age of the Shangxiahua granite porphyry is  $183.2 \pm 3.2$  Ma, which represents the Early Jurassic granite porphyry Nb-Ta ore mineralisation.

(2) The Shangxiahua granite porphyry belongs to A1-type granite. Sr-Nd isotopic data indicate that its parental magma was derived from a mixed source of crust (48%) and mantle (52%), revealing that crust-mantle interaction is essential for generating Nb-Ta-rich magmas.

(3) The magmatic evolution and Nb-Ta enrichment of the Shangxiahua Nb-Ta deposit include four stages: the Early Jurassic extensional setting led to the upwelling of asthenospheric materials and the partial melting of the crust, the mixing of mantle-derived and crust-derived magmas, the magmatic fractional crystallisation and the magma-hydrothermal interaction.

(4) Combined with the existing studies, it is found that the Nb-rich nature of the Shangxiahua Nb-Ta deposit may be related to the presence of lower crustal reservoirs with high Nb/Ta ratio in this area, and it is speculated that the exploration should be conducted in the area with high crustal components in the crust-mantle mixing zone, and that there may be high volatile-rich Nb-Ta ore bodies at the shallow part of the Daping area near Shangxiahua and ore bodies rich in Sn and W at the deep part or around it.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14101005/s1>, Figure S1: La/Sm-La diagram of granite porphyry from the Shangxiahua Nb-Ta deposit.

**Author Contributions:** Conceptualization, H.L. and J.W.; methodology, H.L. and J.W.; software, H.L., Y.H. and X.L.; validation, H.L., Y.H. and X.L.; formal analysis, H.L. and Y.H.; investigation, H.L., J.W. and Q.C.; resources, J.W. and Q.C.; data curation, J.W.; writing—original draft preparation, H.L.; writing—review and editing, J.W. and F.X.; supervision, W.L. and B.C.; project administration, J.W. and Q.C. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Fujian Provincial Natural Science Foundation of China (general program) (No. 2021J01527).

**Data Availability Statement:** Data are contained within the article and Supplementary Materials.

**Acknowledgments:** Our special thanks go to editors and reviewers for their meaningful comments and help, which inspired us and helped us to improve the quality of our paper.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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