

## Article

# Petrogenesis of the Ore-Related Intrusions of the Aikengdelesite Mo (–Cu) and Halongxiuma Mo Deposits: Implication for Geodynamic Evolution and Mineralization in the East Kunlun Orogen, Northwest China

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**Abstract:** The East Kunlun Orogenic Belt (EKOB) is the most important Triassic polymetallic metallogenic belt in China. A study about the petrogenesis of the ore-related intrusions is of great significance to the geodynamic evolution of orogenic belts. In this study, analysis of U–Pb zircon dating, whole-rock major and trace element compositions, and zircon Hf isotopes for the granitoids hosting the Aikengdelesite Mo (–Cu) and Halongxiuma Mo deposits in the EKOB are studied to determine their chronology and petrogenesis. Zircon date results show that the Aikengdelesite granite porphyry and the Halongxiuma granodiorite porphyry formed at  $244.2 \pm 1.7$  Ma and  $230.0 \pm 1.0$  Ma respectively. All samples of the Aikengdelesite granite porphyry and the Halongxiuma granodiorite porphyry which have high SiO<sub>2</sub> and K<sub>2</sub>O contents, and low MgO and Cr, belong to the high-K calc-alkaline series. The Aikengdelesite granite porphyry samples show I-type geochemical affinities, whereas the Halongxiuma granodiorite porphyry samples are A-type granitoids. They all show negative zircon  $\epsilon_{\text{Hf}}(t)$  values (–7.4 to –3.3 and –3.7 to –2.5). We suggest that the Aikengdelesite granite porphyry may have been derived from the lower continental crust. While the Halongxiuma granodiorite porphyry could have formed by partial melting of basic lower crustal materials. By combining the results of this study with previous data, two magmatic and mineralization peak periods (278–237 Ma and 230–210 Ma) were observed in the Paleo-Tethys of the EKOB. Porphyry–skarn deposits occurring in the first episode were formed in the setting of an active continental margin related to the Paleo-Tethys Ocean plate subduction (e.g., Aikengdelesite porphyry deposit), while deposits occurring in the second episode were formed in a post-collisional setting (e.g., Halongxiuma porphyry deposit).

**Keywords:** geochemistry; petrogenesis; east Kunlun orogenic belt; Paleo-Tethys Ocean; geodynamic evolution



**Citation:** Xu, Q.; Sun, Y.; Mao, G.; Xin, W.; Yang, Y. Petrogenesis of the Ore-Related Intrusions of the Aikengdelesite Mo (–Cu) and Halongxiuma Mo Deposits: Implication for Geodynamic Evolution and Mineralization in the East Kunlun Orogen, Northwest China. *Minerals* **2023**, *13*, 447. <https://doi.org/10.3390/min13030447>

Academic Editor: Rubén Díez-Fernández

Received: 16 February 2023

Revised: 7 March 2023

Accepted: 12 March 2023

Published: 22 March 2023

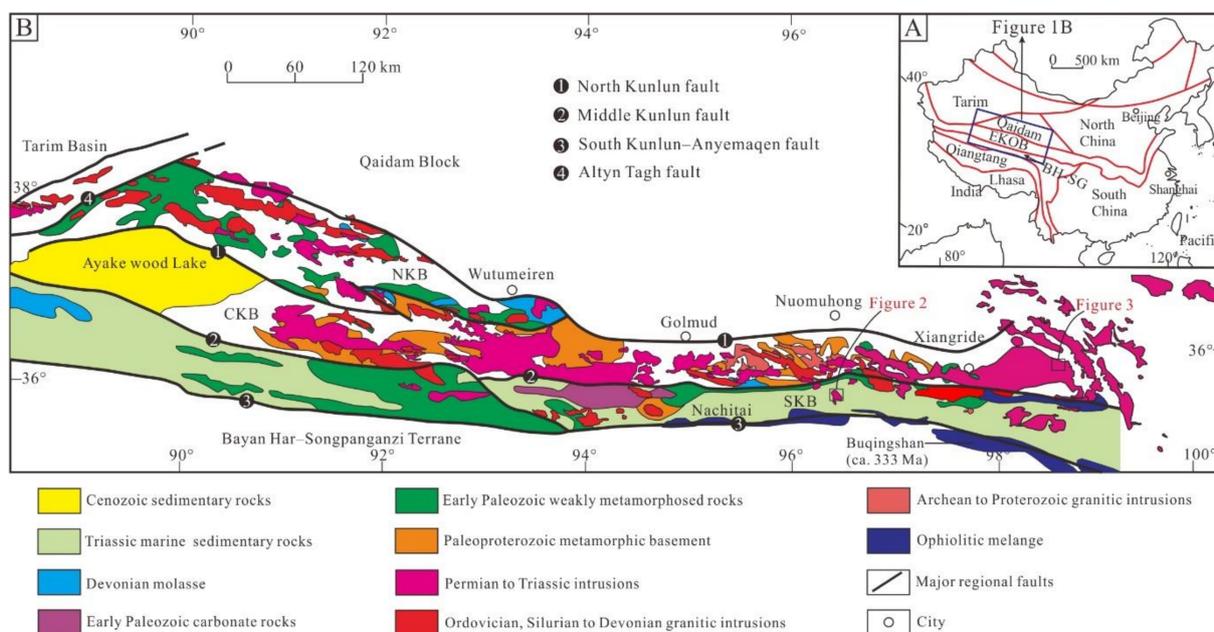


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## 1. Introduction

The East Kunlun Orogenic Belt (EKOB) extends >1500 km in the east–west direction and 50–200 km in width along the northern Tibetan Plateau in northwest China (Figure 1A) [1,2]. The EKOB is characterized by a complex evolution history of the Paleo-Tethys Ocean [3,4] and records the widespread magmatism [5] rocks during the Permian–Triassic (Figure 1B) [6]. However, the tectonic setting of these magmatic rocks remains controversial. Some scholars believe that Middle Permian–Middle Triassic magmatic rocks were induced by the northward subduction of the Paleo-Tethys Ocean [7–9], whereas others have suggested that Early Triassic felsic magmatism was related to the collision between the Bayan Har–Songpanganzi Terrane and the EKOB [10–12]. Therefore, evolution of the

Paleo-Tethys from oceanic slab subduction to continental collision in EKOB, which is also an important polymetallic belt, remains to be discussed [2]. The porphyry and skarn deposits in EKOB occur mostly in Triassic granites (Figure 1B), such as the Yazigou, Hutouya, Saishitang, Yemaquan, Wulanwuzhuer, and Jiandanggen deposits [1,13]. The Aikengdelesite Mo (–Cu) and Halongxiuma Mo deposits are important breakthroughs for porphyry Mo prospecting in the eastern section of EKOB during the past decade. Many studies have been carried out, which were only published in Chinese and mainly focused on its geological characteristics [14–16], preliminary fluid inclusion analyses [17,18], geochronology, and geochemistry about the associated intrusions [16,19,20]. In addition, a consensus that the Aikengdelesite Mo (–Cu) and Halongxiuma Mo deposits are porphyry deposits has been reached. The Aikengdelesite porphyry Mo (–Cu) deposit was formed in the Early Triassic [16], and the Halongxiuma porphyry Mo deposit was formed in the Middle Triassic [21]. The tectonic setting of Triassic porphyry–skarn deposits in the EKOB is controversial, and they may be attributed either to subduction, collisional, or post-collisional setting [2,22]. Therefore, a study on petrogenesis of the Triassic Aikengdelesite and Halongxiuma ore-related intrusions can provide theoretical guidance for metallogenic research and the evolution of the Paleo-Tethys Ocean in the EKOB.



**Figure 1.** (A) Tectonic map of China (modified after [23]). EKOB, the Eastern Kunlun Orogen Belt; BH-SG, the Bayan Har–Songpanganzi Terrane; (B) Schematic geological map of the Eastern Kunlun Orogen Belt (modified after [1,3,7]). NKB, the North Kunlun Belt; CKB, the Central Kunlun Belt; SKB, the South Kunlun Belt.

To address the above issues, we performed zircon LA-ICP-MS U–Pb dating, whole-rock major and trace element geochemistry, and zircon Hf isotope analyses to identify the petrogenesis of granitoids hosting the Aikengdelesite Mo (–Cu) and Halongxiuma Mo deposits and associated tectonic setting. This study will also provide new constraints on the transition from Paleo-Tethys oceanic slab subduction to continental collision in the EKOB.

## 2. Regional Geology

The EKOB lies between the Qaidam Block in the north and the Bayan Har–Songpanganzi Terrane in the south (Figure 1A,B) [24,25]. The EKOB is divided into three parts by the North Kunlun, Middle Kunlun, and South Kunlun–Anyemaqen faults: the North Kunlun Belt (NKB), the Central Kunlun Belt (CKB), and the South Kunlun Belt (SKB) (Figure 1B) [24,25]. At least two stages of orogeny have been identified in the EKOB by previous studies:

Neoproterozoic–Early Devonian and Carboniferous–Late Triassic, corresponding to the evolution of the Proto-Tethys and Paleo-Tethys oceans, respectively [3,4,10,25,26]. Early Cambrian (522–509 Ma) and Early Carboniferous (345–333 Ma) ophiolite belts lay along the eastern section of the Middle Kunlun and South Kunlun–Anyemaqen faults record the opening of the Proto-Tethys and Palaeo-Tethys oceans, respectively (Figure 1B) [3,10,27]. The basement of the EKOB is dominated by Paleo-Mesoproterozoic middle to high grade metamorphic rocks, which consist of paragneiss, amphibolite, marble, orthogneiss, and migmatite [6,10,24,28].

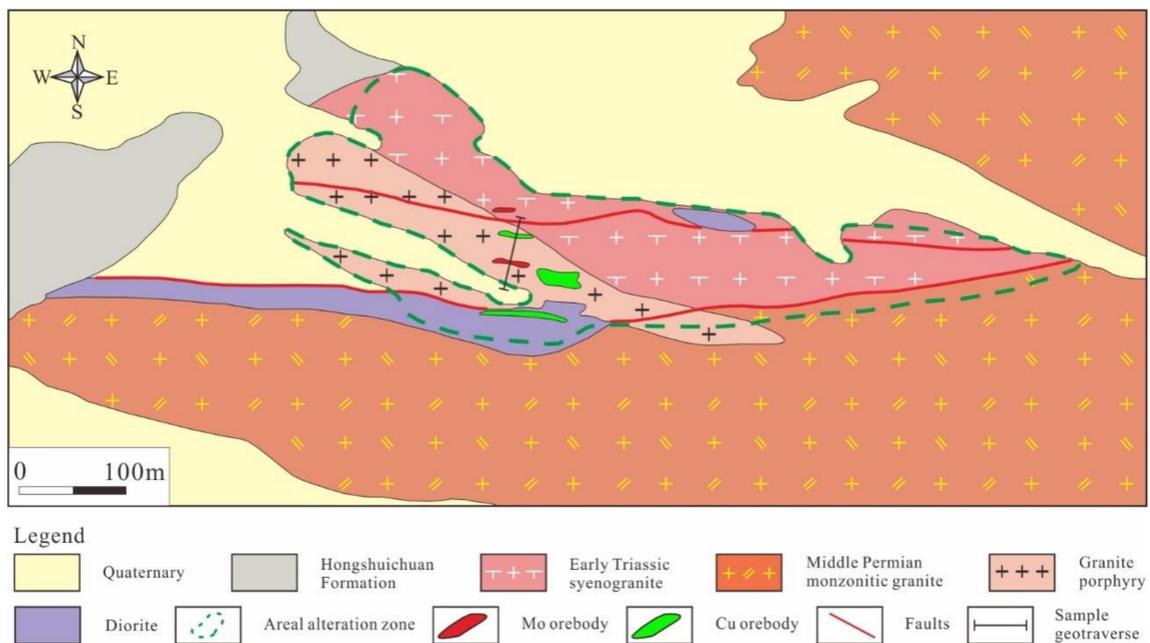
The NKB is characterized by thick early Paleozoic weakly metamorphosed sedimentary clastic and carbonate rocks that are interlayered with intermediate-basic volcanic rocks [7,29,30], which are partly overlain by Devonian molasse sediments unconformably (Figure 1B). These strata are intruded by widespread Paleozoic intrusions (Figure 1B). The CKB is characterized by widespread EW-trending Permian-Triassic arc magmatic rocks, which are parallel to the Paleo-Tethys ophiolite melange belt (Figure 1B), corresponding to the evolution of the Paleo-Tethys Ocean [3,4,24,31,32]. The SKB is characterized by the early Paleozoic Naij-Tai Group, which consists of weakly metamorphosed sedimentary and volcanic rocks [10,32]. The Naij-Tai Group is overlain by Triassic marine sedimentary rocks unconformably [32]. A small number of Early Paleozoic and Mesozoic granitic bodies are exposed in SKB (Figure 1B).

It is worth mentioning that the Bayan Har–Songpanganzi Terrane is characterized by extensive coverage of huge Late Triassic turbidite sequences with thicknesses of up to 10–15 km, which were accumulated during the Ladinian through the Norian time [33,34]. This terrane thus had previously been interpreted to be floored by oceanic crust [35]. However, deep seismic investigations [36], geochemical and isotopic studies on the magmatic rocks [34], and tectonic modeling [37,38] indicate that it may currently be underlain by a South China–type continental basement at least at its eastern corner.

### 3. Ore Deposit Geology and Sample Descriptions

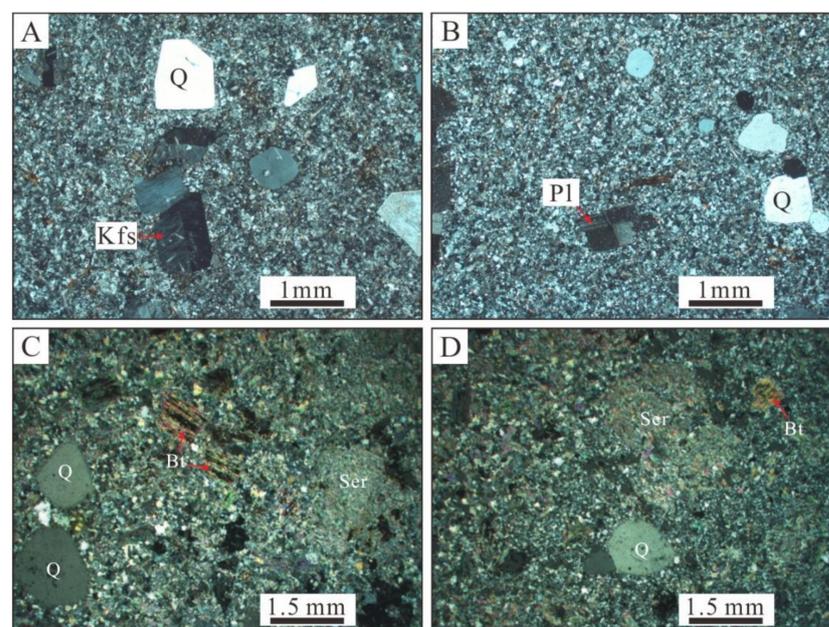
#### 3.1. Aikengdelesite Mining Area

The Aikengdelesite porphyry Mo (–Cu) deposit is located in the eastern section of the SKB (Figure 1B). The exposed strata in the mining area comprise the Lower Triassic Hongshuichuan Formation and Quaternary sediments (Figure 2). The lithology of the Lower Triassic Hongshuichuan Formation is mainly andesite, dacite, and andesitic tuff lavas interbedded with small amounts of siliceous rocks and carbonaceous slates. Two nearly parallel EW-trending faults are distributed in the middle of the mining area (Figure 2). Multi-stage intrusive rocks are exposed in the Aikengdelesite mining area, including a Middle Permian medium-fine-grained monzonitic granite (ca. 268 Ma [19]), an Early Triassic medium-fine-grained syenogranite (ca. 245 Ma [16]), and a Triassic granite porphyry and medium-grained diorite (Figure 2) [14,16]. The granite porphyry intrudes the medium-fine-grained monzonitic granite rocks. The Mo–Cu orebodies in the Aikengdelesite deposit are mainly hosted within the granite porphyry. Hydrothermal alteration is extensively developed in granite porphyry and its surrounding rocks (Figure 2). The above indicates the granite porphyry, which is closely related to hydrothermal alteration of deposits, is the main host rock of the Mo–Cu mineralization. The alteration of the Aikengdelesite Mo (–Cu) deposit can be divided into potassic, silicified, phyllic, and propylitization. The first two kinds of alteration are closely associated with Mo–Cu mineralization, and the intensity of these alterations is positively related to the Mo–Cu grade. The main ore minerals of the Aikengdelesite deposit are mainly molybdenite, chalcopyrite, pyrite, and small amounts of sphalerite and galena. Gangue minerals include mainly quartz, K-feldspar, sericite, muscovite, chlorite, and calcite.



**Figure 2.** Geological map of the Aikengdesite porphyry Mo (–Cu) deposit (modified from [17]).

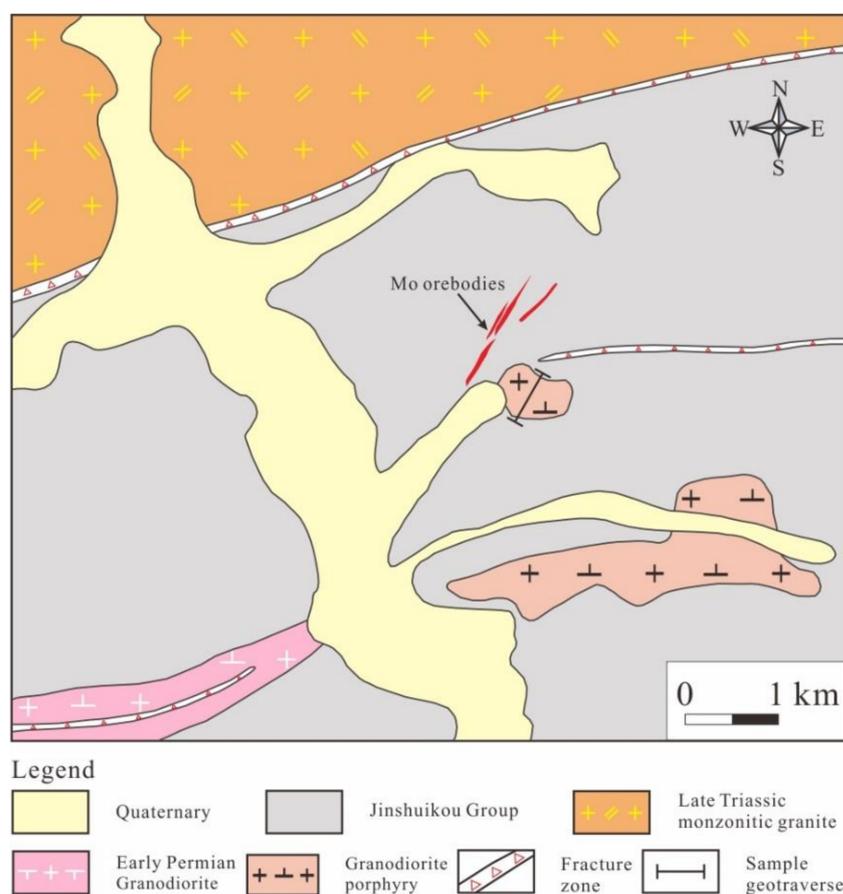
Six fresh granite porphyry samples were collected from surface exposures (Figure 2). The granite porphyry is composed of 30–35 vol.% phenocrysts (which mainly consists of quartz (~10 vol.%), K-feldspar (~10 vol.%), plagioclase (~5 vol.%), and biotite (~5 vol.)) and 65–70 vol.% matrix. The groundmass has the same mineral components as phenocrysts (Figure 3A,B).



**Figure 3.** Photomicrographs of the ore-related porphyry bodies from the Aikengdesite Mo (–Cu) and Halongxiuma Mo deposits. (A,B) Aikengdesite granite porphyry with porphyritic texture; (C,D) Halongxiuma granodiorite porphyry with porphyritic texture. All photomicrographs were captured under transmitted lights. Abbreviations: Q = Quartz; Kfs = K-feldspar; Pl = Plagioclase; Bt = Biotite; Ser = Sericite.

### 3.2. Halongxiuma Mining Area

The Halongxiuma porphyry Mo deposit is located in the eastern section of the CKB (Figure 1B). The exposed strata in the mining area comprise the Paleoproterozoic Jinshuikou Group and Quaternary sediments (Figure 4). The lithology of the Jinshuikou Group is mainly gneiss, schist, and marble. Near-EW-trending fracture zones are developed within the Proterozoic basement (Figure 4). Multiphase magmatism occurs in the Halongxiuma mining area, mainly consisting of Early Permian granodiorite, Triassic monzonitic granite, and granodiorite porphyry (Figure 4). Porphyry Mo mineralization is developed mainly in the Triassic granodiorite porphyry bodies that intruded the Proterozoic Jinshuikou Group at or near the contact zones between the porphyry bodies and metamorphic rocks (Figure 4). Therefore, the Mo mineralization is more closely related to granodiorite porphyry bodies. In addition, Pb–Zn mineralization has also been observed in several drill cores in the Halongxiuma mining area.



**Figure 4.** Geological map of the Halongxiuma porphyry Mo deposit (modified from [21]).

Five fresh granodiorite porphyry samples were collected from surface exposures (Figure 4). The granodiorite porphyry consists of ~30 vol.% phenocrysts (which are dominantly composed of quartz (~15 vol.%), plagioclase (~10 vol.%), and biotite (~5 vol.)) and ~70 vol.% matrix. Mineral composition of the matrix is the same as that of the phenocrysts (Figure 3C,D).

## 4. Analytical Methods

### 4.1. LA-ICP-MS Zircon U–Pb Dating

The sorting of zircons was completed by the Laboratory of Langfang Regional Geology and Mineral Resources Survey. After sample crushing, magnetic separation and heavy liquid separation were adopted. Zircons with good crystal shape, with no cracks, and

no obvious inclusions were selected manually through binocular microscopes. The inner structures of zircons were revealed through cathode luminescence (CL) microphotographs. Laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) Zircon U–Pb dating was carried out in the Key Laboratory of Institute of Mineral Resources, Chinese Academy of Geological Sciences in Beijing, using a Finnigan Neptune LA-MC-ICPMS instrument equipped with a New Wave UP 213 LA system produced by Thermo Fisher Scientific in Germany [39]. The sampling method was single point denudation with a 30  $\mu\text{m}$  laser beam spot, and all signals were simultaneously received in static mode for data collection. Zircon GJ1 was used as an external standard, and zircon M127 was used as an external standard for elemental mass fraction. The method of [40] was used to correct the results for common lead. The isotope ratio and mass fraction of the samples were calculated using a 10.9 version of ICP-MS-Data Cal program [41]. Isoplot 3.0 was used to calculate the weighted-mean age and plot the concord diagram [42]. Table S1 presents the zircon U–Pb isotopic data.

#### 4.2. Whole-Rock Major and Trace Element Analyses

The whole rock geochemical analysis was completed in the Analysis and Test Center of the Beijing Institute of Geology, Nuclear Industry. The main elements were determined by X-ray fluorescence spectrometry (XRF). The experimental instrument was the serial scanning X-ray fluorescence spectrometer PW2404 of FHLISP Company from Amsterdam, The Netherlands. The trace and rare earth elements were determined by the inductively coupled plasma mass spectrometer of ELEMENT I produced by Finnigan-MAT of Bremen, Germany. For elements greater than 20  $\mu\text{g/g}$ , the error is  $\pm 5\%$ , and for elements less than 20  $\mu\text{g/g}$ , the error is  $\pm 10\%$ . Major- and trace-element data are presented in Table S2.

#### 4.3. Zircon Hf Isotopic Analyses

Zircon Hf isotope analysis was performed at the Key Laboratory of Mineralization and Resource Evaluation, Ministry of Land and Resources, Institute of Mineral Resources, Chinese Academy of Geological Sciences. A Finnigan Neptune Multi-receive Inductively coupled Plasma Mass Spectrometer (LA-MC-ICPMS) was used. A laser denudation system is the Newwave UP213 laser. The sampling method was single point denudation, and all signals were received simultaneously in static mode. The zircon Hf isotopes were denudated using 40–65  $\mu\text{m}$  diameter spots. For details of the test process and post-processing, refer to [28,29]. The present-day chondritic ratio (CHUR) of  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282772$  and  $^{176}\text{Lu}/^{177}\text{Hf} = 0.0332$  were adopted to calculate  $\epsilon_{\text{Hf}}(t)$  values [43]. In the calculation of Hf model ages,  $^{176}\text{Lu}/^{177}\text{Hf}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  were set as 0.0384 and 0.28325, respectively [43]. The analytical techniques and data calculated using a 10.9 version of ICP-MS Data Cal software have been described by [44]. Hf isotopic composition data are presented in Table S3.

## 5. Results

### 5.1. LA-ICP-MS Zircon U–Pb Ages

Results of zircon U–Pb dating are given in Table S1. All analyzed zircons from samples AKD-TW1 (granite porphyry) and HLXM-TW1 (granodiorite porphyry) are euhedral-subhedral (Figure 5). Their oscillatory growth zoning and the Th/U ratios (0.71–1.54) of all these analyzed zircons indicate a magmatic origin [45]. Zircons from the granite porphyry yielded  $^{206}\text{Pb}/^{238}\text{U}$  ages of 251–242 Ma and a weighted-mean age of  $244.2 \pm 1.7$  Ma (MSWD = 0.48;  $n = 15$ ) (Figure 6A,B). Zircons from the granodiorite porphyry yielded  $^{206}\text{Pb}/^{238}\text{U}$  ages of 231–229 Ma and a weighted-mean age of  $230.0 \pm 1.0$  Ma (MSWD = 0.11;  $n = 18$ ) (Figure 6C,D).



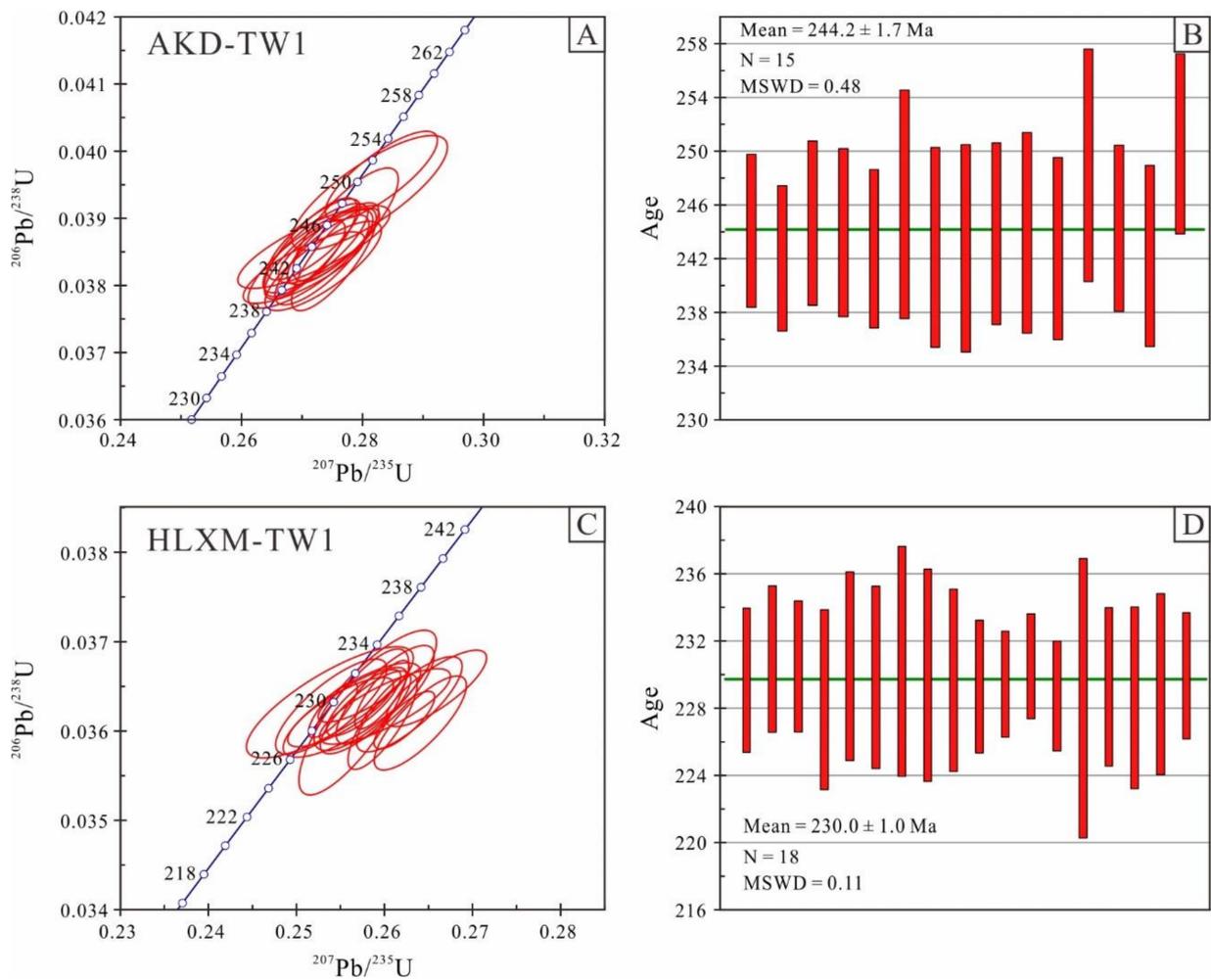
**Figure 5.** CL images of zircons from the ore-related porphyry bodies of Aikengdelesite Mo (–Cu) and Halongxiu Mo deposits.

## 5.2. Whole-Rock Major and Trace Element Compositions

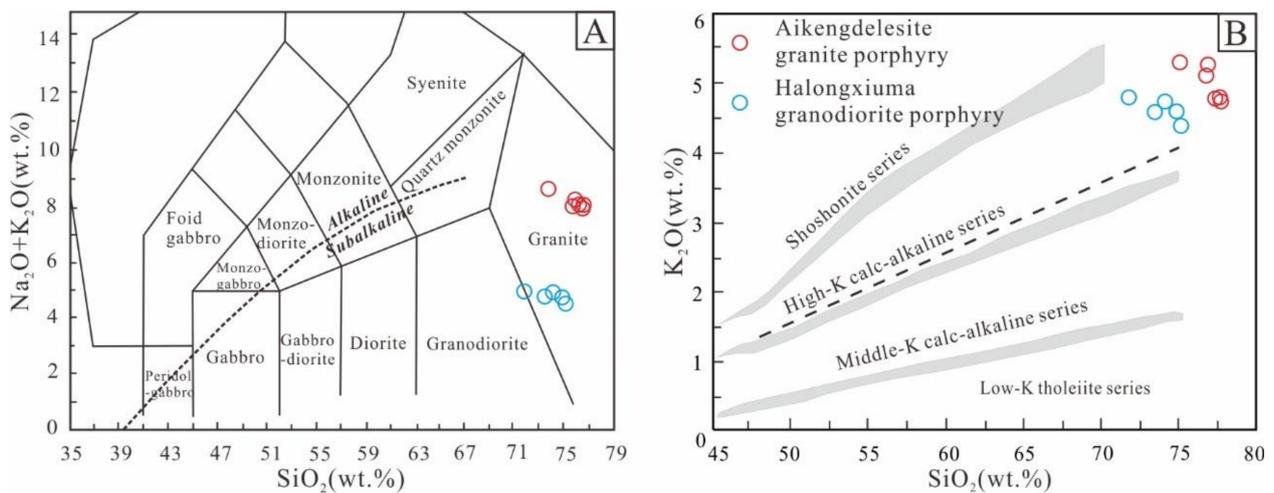
### 5.2.1. The Aikengdelesite Granite Porphyry

The whole-rock major and trace element analytical results are presented in Table S2 and illustrated in Figure 7. The six analyzed samples of the Aikengdelesite granite porphyry are characterized by relatively high  $\text{SiO}_2$  (73.85–76.72 wt.%),  $\text{Al}_2\text{O}_3$  (12.64–13.91 wt.%), and  $\text{K}_2\text{O}$  (4.67–5.21 wt.%), and low  $\text{Na}_2\text{O}$  (2.89–3.33 wt.%),  $\text{MgO}$  (0.13–0.28 wt.%) with  $\text{Mg}^\#$  values of 17–29. These signatures denote the granite porphyry as high-K and calc-alkalic granite (Figure 7).

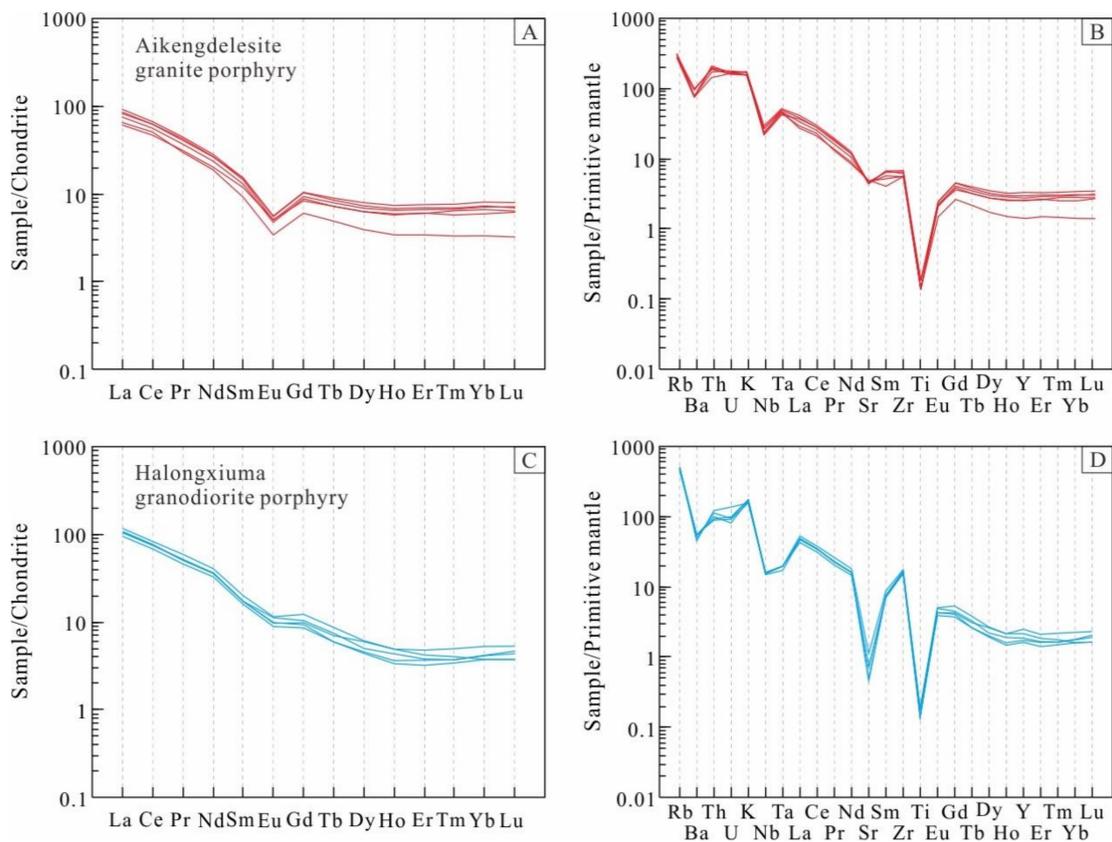
The chondrite-normalized REE patterns in all granite porphyry samples show a slightly enrichment of LREEs relative to HREEs and a moderate degree of negative Eu anomalies ( $\text{Eu}/\text{Eu}^* = 0.42$  to  $0.51$ ; Figure 8A). The granite porphyry samples exhibit enrichment in LILEs (e.g., Rb, Th, U, and K) and depletion in Ba, Nb, Sr, and Ti (Figure 8B).



**Figure 6.** (A) Zircon U–Pb concordia diagram and (B) weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  ages for the ore-related porphyry bodies of Aikengdesite Mo (–Cu); (C) Zircon U–Pb concordia diagram and (D) weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  ages for the ore-related porphyry bodies of Halongxiuma Mo deposits.



**Figure 7.** (A) TAS diagram (after [46]); (B)  $\text{K}_2\text{O}$  vs.  $\text{SiO}_2$  diagram (after [47]) for the ore-related porphyry bodies from the Aikengdesite Mo (–Cu) and Halongxiuma Mo deposits.



**Figure 8.** (A) Primitive mantle normalized spider diagrams and (B) chondrite-normalized REE patterns for the ore-related porphyry bodies from the Aikengdelesite Mo (–Cu); (C) Primitive mantle nor-normalized spider diagrams and (D) chondrite-normalized REE patterns for the ore-related porphyry bodies from the Halongxiuma Mo deposits. The chondrite values are from [48], the primitive mantle values are from [49].

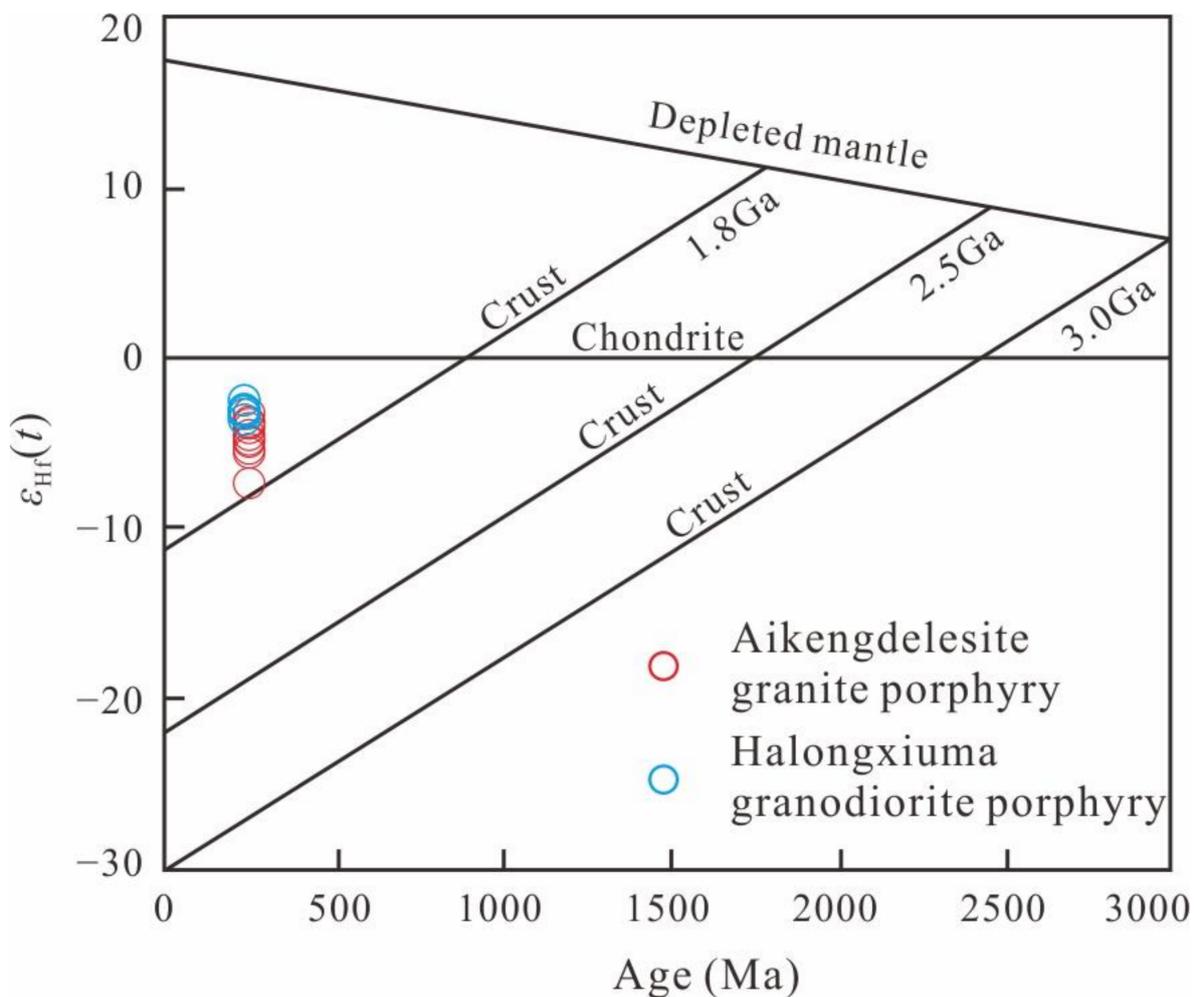
### 5.2.2. The Halongxiuma Granodiorite Porphyry

The whole-rock major and trace element analytical results are presented in Table S2 and illustrated in Figure 7. The six analyzed samples of the Halongxiuma granodiorite porphyry are characterized by relatively high  $\text{SiO}_2$  (71.81–75.18 wt.%),  $\text{Al}_2\text{O}_3$  (13.67–14.42 wt.%), and  $\text{K}_2\text{O}$  (4.40–4.81 wt.%), and low  $\text{Na}_2\text{O}$  (0.06–0.12 wt.%),  $\text{MgO}$  (0.64–0.85 wt.%) with  $\text{Mg}^\#$  values of 32–48. These signatures denote the granodiorite porphyry as high-K and calc-alkalic granite (Figure 7).

The chondrite-normalized REE patterns in all granodiorite porphyry samples show a slightly enrichment of LREEs relative to HREEs and weak negative Eu anomalies ( $\text{Eu}/\text{Eu}^* = 0.71$  to  $0.81$ ; Figure 8C). The granodiorite porphyry samples exhibit enrichment in LILEs (e.g., Rb, Th, U, and K) and depletion in HFSEs (e.g., Nb, Ta, and Ti) (Figure 8D).

### 5.3. Zircon Hf Isotopic Compositions

In situ Lu–Hf isotope analysis was carried out for U–Pb dating of AKD-TW1 and HLXM-TW1 samples. The results are given in Table S3 and plotted in Figure 9. Ten zircon grains Lu–Hf isotope analyses for the granite porphyry (AKD-TW1) yielded  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios of 0.282422 to 0.282539 and negative  $\varepsilon_{\text{Hf}}(t)$  values of  $-7.4$  to  $-3.3$ . The two-stage model ages ( $T_{\text{DM}2}$ ) are in the range of 1743–1483 Ma. Ten zircon grains Lu–Hf isotope analyses for the granodiorite porphyry (HLXM-TW1) yielded  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios of 0.282531 to 0.282563 and negative  $\varepsilon_{\text{Hf}}(t)$  values of  $-3.7$  to  $-2.5$ . The two-stage model ages ( $T_{\text{DM}2}$ ) are in the range of 1494–1422 Ma.



**Figure 9.** Plots of zircon U–Pb ages vs.  $\epsilon_{\text{Hf}}(t)$  values for the ore-related porphyry bodies from the Aikengdesite Mo (–Cu) and Halongxiuma Mo deposits.

## 6. Discussion

### 6.1. Timing of Magmatism and Mo Mineralization

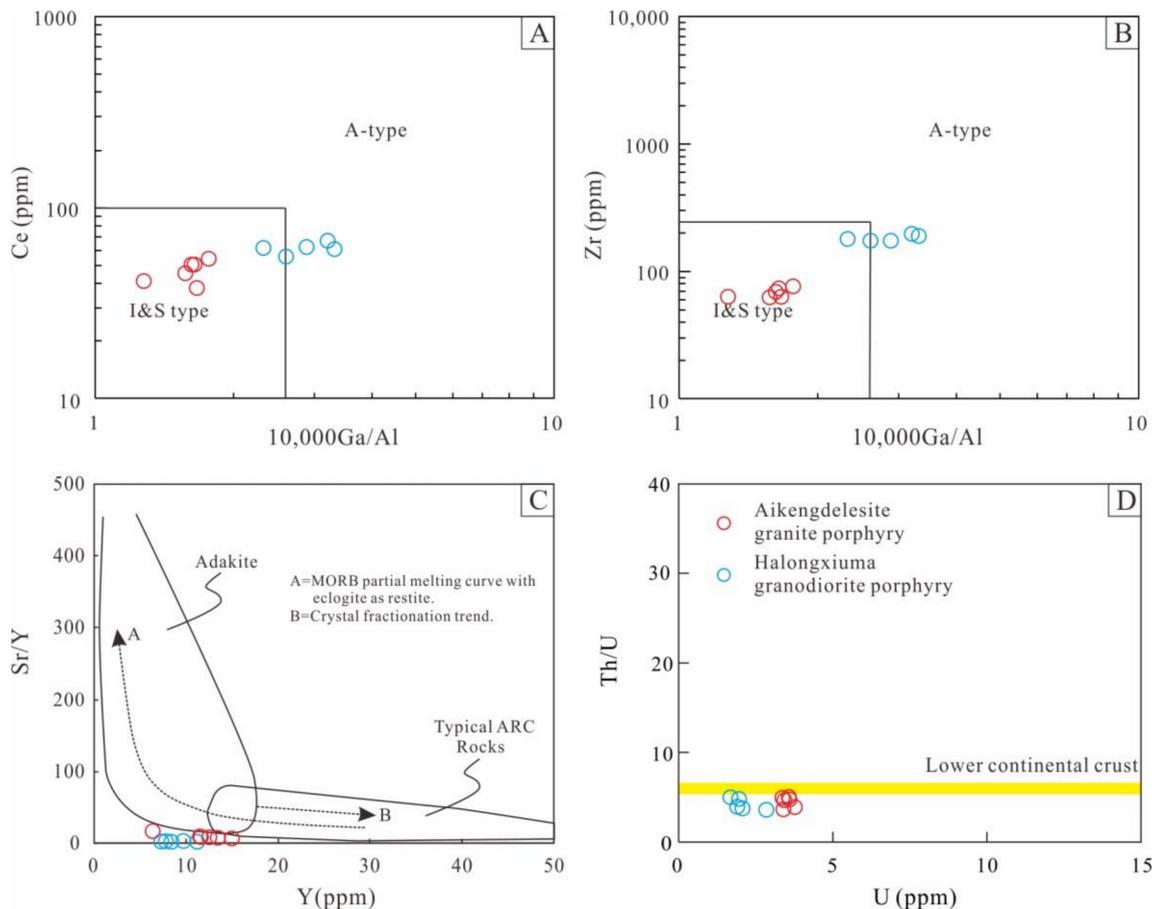
According to the geology of the Aikengdesite Mo (–Cu) mining area, the granite porphyry is closely related to the space of ore body, indicating that the granite porphyry is genetically related to the Mo mineralization in the Aikengdesite Mo (–Cu) deposit, providing ore-forming materials and fluid sources for mineralization. Therefore, the time of Mo mineralization (ca. 245 Ma) can be approximated as the crystallization age of the ore-related granite porphyry. Similarly, the Late Triassic granodiorite porphyry (ca. 230 Ma) is the most likely rock mass to cause porphyry Mo mineralization in the Halongxiuma Mo deposit. In addition, a large number of existing geochronological data from the EKOB [22,50–57] show that porphyry and skarn deposits constitute the Triassic Cu–Mo polymetallic metallogenic belt in this area, indicating that this area has great porphyry metallogenic potential.

### 6.2. Petrogenesis

For Triassic granitoids in the EKOB, enriched mantle derived melt [8,58,59], oceanic crust and overlying sediments [12], and lower crust derived melts [60] could be potential magmatic sources.

### 6.2.1. The Aikengdesite Granite Porphyry

The  $10,000\text{Ga}/\text{Al}$  ratios of the Aikengdesite granite porphyry samples vary from 1.28 to 1.77, which are lower than the minimum value of 2.6 for typical A-type granitoids [61]. In the  $10,000\text{Ga}/\text{Al}$  vs. Ce and  $10,000\text{Ga}/\text{Al}$  vs. Zr diagrams (Figure 10A,B), these samples almost all plot in the overlapping region of I- and S-type granitoids. The Aikengdesite granite porphyry samples commonly contain hydrous minerals (e.g., biotite) but carry no typical aluminum-rich minerals (e.g., muscovite, cordierite, garnet, or andalusite) (Figure 3A,B), precluding the possibility of S-type granitoids [62]. These characteristics clearly indicate that the granite porphyry samples are I-type granitoids.



**Figure 10.** (A)  $10,000\text{Ga}/\text{Al}$  vs. Ce; (B)  $10,000\text{Ga}/\text{Al}$  vs. Zr; (C) Y vs. Sr/Y; and (D) U vs. Th/U diagrams for the ore-related porphyry bodies from the Aikengdesite Mo (–Cu) and Halongxiuma Mo deposits. The average Th/U ratio ( $\sim 6$ ) of the lower continental crust is from [63].

The Aikengdesite granite porphyries gave high  $\text{SiO}_2$  (73.85–76.72 wt.%) and  $\text{K}_2\text{O}$  (4.67–5.21 wt.%), low MgO (0.13–0.28 wt.%), and Cr (3.82–6.14 ppm) contents (Table S2), implying little or no mantle contribution [64]. The Aikengdesite granite porphyries do not have an adakitic affinity (Figure 10C). Hence, they are different in origin from adakites derived from the subducted oceanic crust. The samples of the Aikengdesite granite porphyry belong to high-K calc-alkaline series, indicating that they are mainly crust-derived [65]. The Aikengdesite granite porphyry samples have negative zircon  $\varepsilon_{\text{Hf}}(t)$  ( $-7.4$  to  $-3.3$ ) values, which are similar to the continental crustal Hf isotope compositions (Figure 9). In addition, the Nb/Ta ratios of the Aikengdesite granite porphyry are between 8.86 and 10.07 (average 9.34), which are lower than that of mantle derived magmas ( $17.5 \pm 2$  [66]) and close to the value of crust derived magmas (11–12 [66]), showing that the magma source area was dominated by the crust. Th/Nb ratios (0.75–1.03, average 0.87) of the Aikengdesite granite porphyry samples reflect the crustal characteristics (average value

of continental crust and primitive mantle: Th/Nb of 0.44 and 0.177, respectively [67,68]). In the U vs. Th/U plot (Figure 10D), all of the samples occur near the lower continental crust, showing that the Aikengdelesite granite porphyries were dominantly derived from the lower continental crust.

### 6.2.2. The Halongxiuma Granodiorite Porphyry

The Halongxiuma granodiorite porphyry samples commonly contain hydrous minerals (e.g., biotite) but carry no typical aluminum-rich minerals (e.g., muscovite, cordierite, garnet, or andalusite) (Figure 3C,D), precluding the possibility of S-type granitoids [66]. The  $10,000\text{Ga}/\text{Al}$  ratios of the Halongxiuma granodiorite porphyry samples vary from 2.32 to 3.32, which are primarily higher than the minimum value of 2.6 for typical A-type granitoids with only one value less than 2.6 [61]. These samples also almost all plot in the region of A-type granitoids (Figure 10A,B). These characteristics clearly indicate that the granite porphyry samples are A-type granitoids.

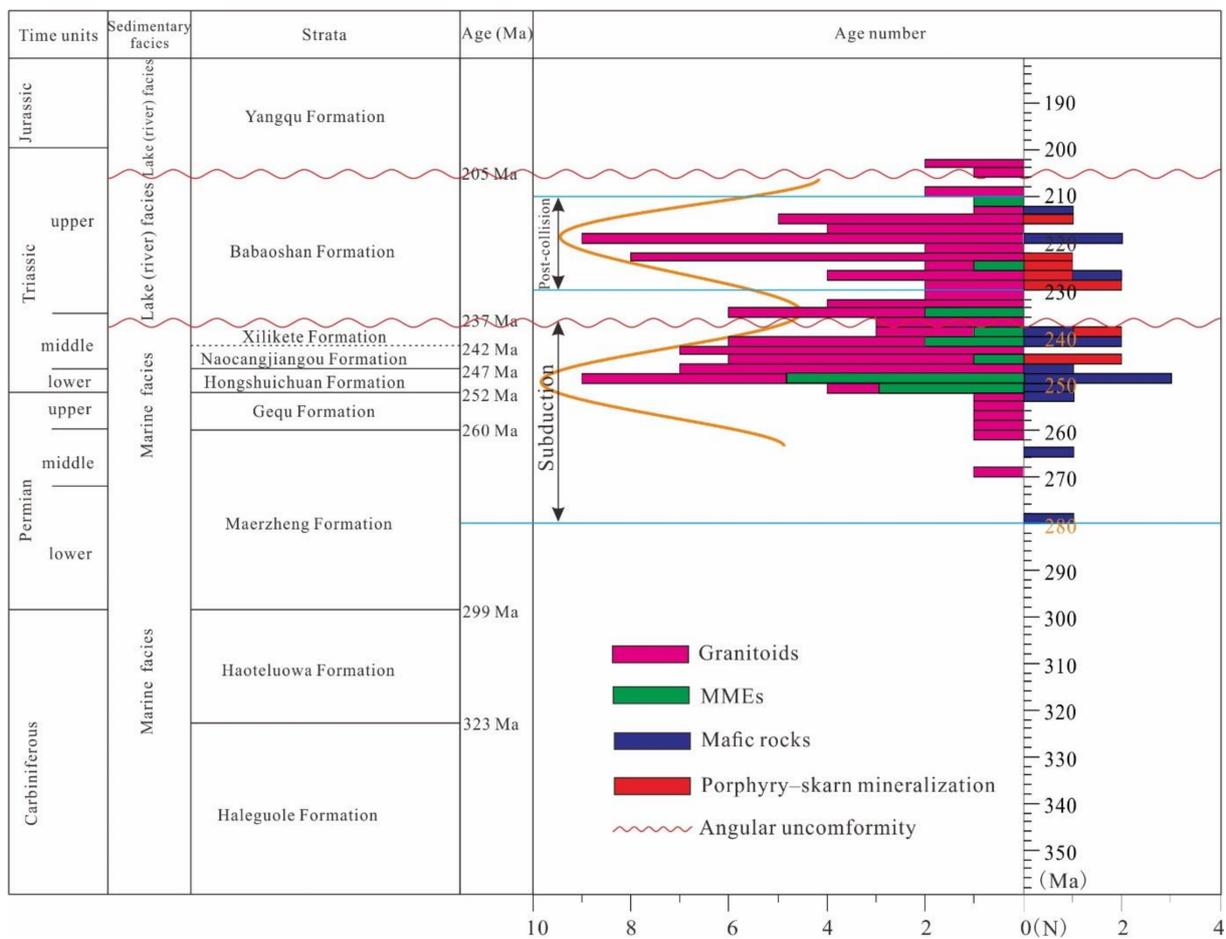
The Halongxiuma granodiorite porphyries are characterized by display high  $\text{SiO}_2$  (71.81–75.18 wt.%) and low MgO (0.64–0.85 wt.%) contents (Table S2), which is probably the product of partial melting of the lower crust without the interaction with the mantle. Furthermore, the granodiorite porphyries do not have the characteristics of adakites (Figure 10C). Therefore, subducted oceanic crust cannot be the main source area of the Halongxiuma granodiorite porphyries. The Halongxiuma granodiorite porphyry samples have negative zircon  $\varepsilon_{\text{Hf}}(t)$  (−3.7 to −2.5) values, which are similar to the continental crustal Hf isotope compositions (Figure 9). The Nb/Ta ratios of the Halongxiuma granodiorite porphyry are between 13.50 and 15.14 (average 14.18), which are lower than that of mantle derived magma ( $17.5 \pm 2$  [59]) and close to the value of crust derived magma (11–12 [66]), showing that the magma source area is dominated by the crust source. La/Nb ratios (2.70–3.19, average 2.96) and Th/Nb ratios (0.67–0.95, average 0.79) of the Halongxiuma granodiorite porphyry samples all reflect the crustal characteristics (average value of continental crust and primitive mantle: La/Nb of 2.2 and 0.94, Th/Nb of 0.44 and 0.177, respectively [67,68]). All of the Halongxiuma granodiorite porphyry samples occur near the lower continental crust (Figure 10D). Therefore, the Halongxiuma granodiorite porphyries likely formed by partial melting of basic lower crustal materials.

### 6.3. Implication for Geodynamic Evolution and Two Episodes of Metallogenic Events

The Kunnan-A'nyemaqen ophiolite belt is composed of the EKOB's Paleo-Tethys ophiolite, which is distributed along the south Kunlun fault [69]. The study of Buqingshan ophiolite (333 Ma [27]) in the greenstone belt shows that the Paleo-Tethys Ocean began to expand in the Early Carboniferous. Liu et al. [70] studied the age of pyroxene in Xiaomiao mafic rocks ( $277.8 \pm 2.7$  Ma), indicating the initial subduction of the Paleo-Tethys Ocean. However, the closure time of the Paleo-Tethys Ocean has been controversial. It may be Late Permian [12], Early–Middle Triassic [71], or Late Triassic [1,22,25,72].

We summarize the chronological records of Permian to Triassic igneous activities in the EKOB in recent years, finding that the magmatic activities in the EKOB have the characteristics of double peaks in age (Figure 11). The first peak is concentrated between 278 and 237 Ma, the second peak is between 230 and 210 Ma, and it is in a state of gradual attenuation between 237 and 230 Ma. There is no doubt that this phenomenon must be closely related to the geodynamic process. A large number of the Permian–Middle Triassic subduction-related magmatic rocks (278–237 Ma; Figure 11), including the granitoids with mafic microgranular enclaves (MMEs) and mafic rocks [8,12,73–76], were identified in the EKOB. All the evidence indicates that the EKOB was still in an active continental margin environment before ca. 237 Ma. Although the termination time of oceanic subduction cannot be precisely constrained by subduction-related granitoids [8], the presence of significant volumes of adakites, mafic dike swarms, and A-type granites (230–210 Ma) in the EKOB [25,60,77] clearly reveals that the Paleo-Tethys Ocean should have closed before ca. 230 Ma [78–81]. Therefore, it can be concluded that the ocean basin

of the EKOB was closed at about 237 Ma, a collision occurred between 237 and 230 Ma and thickened the crust, while 230–210 Ma was the post-collisional extension stage (Figure 11). The sedimentary records in the EKOB also support this conclusion, although it has also been suggested that contact and collision never occurred due to buffering of the up to 10–15 km thick Upper Triassic flysch sequences accumulated on the Songpan–Ganzi Terrane [33,35]. The Gequ Formation (260–252 Ma) consists of oceanic molasse sediments and was deposited in an oceanic environment [82]. The Naocangjiangou and Xilikete formations (247–237 Ma) show marine facies (Figure 11). The Babaoshan Formation (237–205 Ma) above the angular unconformity shows lake or river facies (Figure 11). Therefore, all the evidence indicates that the Paleo-Tethys Ocean in the EKOB may have been open before 237 Ma, and 237 Ma probably represents the beginning of the continental collision (Figure 11).

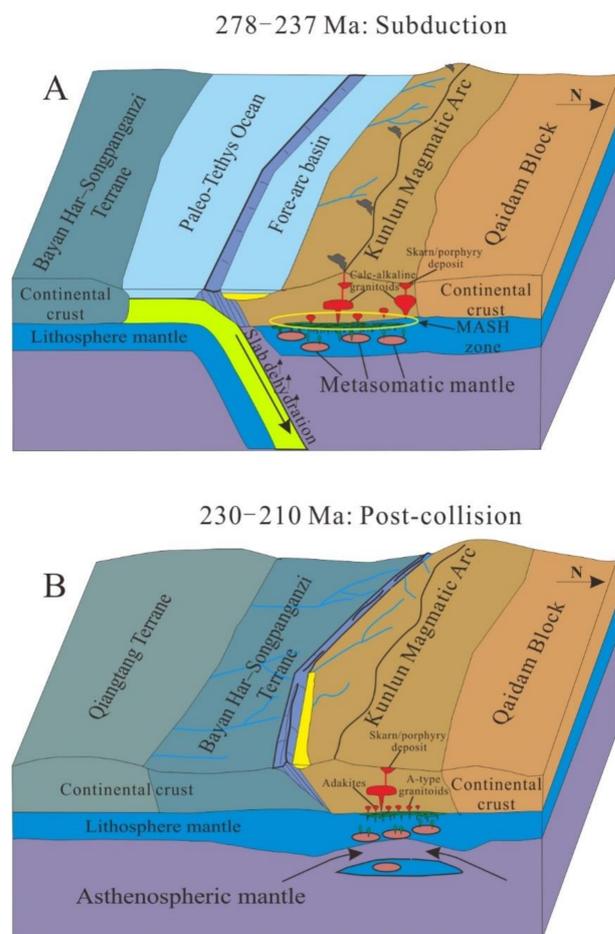


**Figure 11.** Histogram showing variations in the zircon U–Pb ages of the Permian–Triassic magmatic rocks in the EKOB, illustrating the geodynamic evolution of this region (modified after [60,76]).

Based on the geodynamic evolution of the Paleo-Tethys and mineralization ages for the porphyry–skarn deposits in the EKOB, two stages of metallogenic events were identified and similar to the peak age of magmatic activity (Figure 11; Table 1). The first stage of mineralization mainly occurred between 244 and 238 Ma. These porphyry–skarn deposits were formed in an active continental margin setting related to the subduction of the Paleo-Tethys Ocean plate (Figure 12A). The second episode happened after 230 Ma (230–215 Ma). These deposits were formed in a post-collisional setting (Figure 12B).

**Table 1.** High-precision magmatic and mineralization ages for the porphyry–skarn deposits in the EKOB.

Deposit	Type	Analytical Minerals/Rocks	Analytical Methods	Age (Ma)	Reference
Aikengdelesite	Porphyry (Cu, Mo)	Granite porphyry	Zircon LA-ICP-MS U-Pb	244.2 ± 1.7	This study
Xiadeboli	Porphyry (Cu, Mo)	Granite porphyry	Zircon SIMS U-Pb	244.2 ± 2.1	[83]
Maoniugou	Porphyry (Cu, Au)	Molybdenite	Re-Os	238.7 ± 1.4	[84]
Kaerqueka	Skarn-porphyry (Cu, Pb, Zn)	Molybdenite	Re-Os	238.8 ± 1.3	[53]
Halongxiuma	Porphyry (Mo)	Granodiorite Porphyry	Zircon LA-ICP-MS U-Pb	230.0 ± 1.0	This study
Hutouya	Skarn (Cu, Pb, Zn)	Molybdenite	Re-Os	230.1 ± 4.7	[85]
Jiadanggen	Porphyry (Cu, Mo)	Granodiorite porphyry	Zircon LA-ICP-MS U-Pb	227.0 ± 1.0	[86]
Yazigou	Porphyry (Cu, Mo)	Molybdenite	Re-Os	227.2 ± 1.9	[87]
		Granite porphyry	Zircon SHRIMP U-Pb	224.0 ± 1.6	
Saishitang	Skarn (Cu)	Molybdenite	Re-Os	224.7 ± 3.4	[88]
		Quartz diorite	Zircon LA-ICP-MS U-Pb	222.7 ± 2.3	
Wulanwuzhuer	Porphyry (Cu, Mo)	Molybdenite Granite porphyry	Re-Os Zircon SHRIMP U-Pb	223.4 ± 1.5 215.1 ± 4.5	[89]



**Figure 12.** Schematic cartoon illustrating the Permian–Late Triassic (280–210 Ma) geodynamic evolution in the EKOB. (A) subduction of the Paleo-Tethys Ocean plate (278–237 Ma); and (B) delamination of lower lithospheric mantle (230–210 Ma).

## 7. Conclusions

- (1) The ore-related intrusions emplaced at ca. 244 Ma for granite porphyry in the Aikengdelesite porphyry Mo (–Cu) deposit, and at ca. 230 Ma granodiorite porphyry in the Halongxiuma porphyry Mo deposit;
- (2) The Aikengdelesite I-type granite porphyry samples may have been derived from the lower continental crust. The Halongxiuma granodiorite porphyry samples should be formed by partial melting of basic lower crustal materials;
- (3) There are two magmatic and mineralization peak periods (278–237 Ma and 230–210 Ma), corresponding to two geodynamic evolution stages of subduction and post-collision extension, respectively.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13030447/s1>, Table S1: LA–ICP–MS zircon U–Pb dating data for the ore-related intrusions of the Aikengdelesite Mo (–Cu) and Halongxiuma Mo deposits; Table S2: Major (wt.%) and trace element (ppm) contents for the ore-related intrusions of the Aikengdelesite Mo (–Cu) and Halongxiuma Mo deposits; Table S3: Zircon Hf isotopic date for the ore-related intrusions of the Aikengdelesite Mo (–Cu) and Halongxiuma Mo deposits.

**Author Contributions:** Conceptualization, Q.X., Y.S. and W.X.; software, Q.X., Y.S. and W.X.; investigation, Q.X., Y.S., W.X. and Y.Y.; data curation, Q.X., Y.S. and W.X.; funding acquisition, Q.X., Y.S. and G.M.; project administration, Q.X., Y.S. and G.M.; writing—original draft preparation, Q.X., Y.S. and W.X.; and writing—review and editing, Q.X., Y.S. and W.X. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Natural Science Foundation of China (U22A20571, 42172087, 41572063), the Shandong Provincial Natural Science Foundation of China (ZR2019PD017), the Doctoral Scientific Research Start-Up Fund Project of Suzhou University (2022BSK009), the Shandong Provincial Natural Science Foundation of China (ZR2021QD086), and the Basic Scientific Research Project of colleges and universities of Liaoning Provincial Department of education in 2021 (LJKZ0369).

**Data Availability Statement:** Not applicable.

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

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