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# Petrogenesis and Tectonic Setting of Ore-Associated Intrusive Rocks in the Baiyinnuoer Zn–Pb Deposit, Southern Great Xing'an Range (NE China): Constraints from Zircon U–Pb Dating, Geochemistry, and Sr–Nd–Pb Isotopes

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**Abstract:** The Baiyinnuoer skarn Zn–Pb deposit, located in the Southern Great Xing'an Range, Northeast China, is the largest Zn–Pb deposit of the northern China, with a total reserve of 32.74 Mt at average grades of 5.44% Zn and 2.02% Pb. The Zn–Pb ore bodies are hosted in the Lower Permian Huanggangliang Formation. The results of zircon U–Pb geochronology show that the ore-associated granodiorite porphyry, granodiorite, and diorite were emplaced at  $248 \pm 1.3$ ,  $251 \pm 1.8$ , and  $249 \pm 1.4$ Ma, respectively. The granodiorites and granodiorite porphyry have low P<sub>2</sub>O<sub>5</sub> (0.13–0.23 wt %) and A/CNK (0.79–1.05) values, and their SiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> contents are negatively correlated, indicating I-type affinity. The positive  $\varepsilon$ Nd(t) values (+1.3 to +1.8) and young two-stage model ages ( $T_{DM2}$ ) (880–916 Ma) of the Baiyinnuoer intrusive rocks suggest that they might have formed by the mixing of both mantle and crustal materials. The variations in the major elements, Rb, Sr, and Ba, and the negative Nb–Ta–Ti anomalies indicate that fractional crystallization might have occurred during magma ascent. In combination with the regional geology, the new geochronological, geochemical, and isotopic data reveal that the ore-associated intrusive rocks at Baiyinnuoer were formed in a post-collision setting in the Late Permian.

Keywords: Late Permian; I-type granitoid; skarn Zn–Pb deposit; Baiyinnuoer; Great Xing'an Range

# 1. Introduction

The Southern Great Xing'an Range (SGXR), Northeast (NE) China, located in the eastern part of the Central Asian Orogenic Belt (CAOB), is considered to be one of the most important metallogenic belts, hosting a number of skarn, porphyry, and magmatic–hydrothermal Pb–Zn–Ag–Cu–Mo polymetallic deposits [1–4] (Figure 1). Complex tectonic events have occurred in the region, including the closure of the Paleo-Asian Ocean in the Late Palaeozoic, the opening and closure of the Mongol–Okhotsk Ocean in the Mesozoic, and the subduction of the Paleo-Pacific Ocean in the Mesozoic [5–13].

The Baiyinnuoer skarn Zn–Pb deposit, located in the SGXR, is the largest Zn–Pb deposit in this region of northern China (Figure 1), with a total reserve of 32.74 Mt at average grades of 5.44% Zn, 2.02% Pb, and 31.4 g/t Ag [1,12,13]. Many recent investigations have focused on the geochronology, geochemistry, S–Pb isotopes, and fluid inclusions of the deposit [7,8,13–17]. Most scholars have regarded the Baiyinnuoer deposit as a skarn-type deposit, whereas Zeng et al. [7] considered it to



be a sedimentary exhalative deposit, on the basis of the S isotopic data of the sulfides. The age of the ore-associated intrusions and the related skarn-type Zn–Pb mineralization in the Baiyinnuoer deposit is still controversial. Shu et al. [1] reported the zircon U–Pb ages of the ore-associated granites and granodiorites (approximately 275 and 273 Ma, respectively) and suggested a Middle Permian age for the Zn–Pb mineralization. Yi et al. [16] estimated the age of the ore-related granodiorites as 242–245 Ma, proposing a Late Permian age for the Baiyinnuoer Zn–Pb mineralization. Jiang et al. [13] later identified skarn and vein types of mineralization, and suggested that the skarn mineralization was related to the granodiorites (Late Permian) and the vein-type mineralization was associated with the feldspar porphyries (Late Jurassic). Therefore, these key problems lie in the interpretation of the genetic relationships between the granitoids and the mineralization, and they require more precise geochemical, geochronological, and isotopic data.



**Figure 1.** (**A**) Tectonic sketch map of the Central Asian Orogenic Belt (modified after [1,9,18]). (**B**) Simplified geological map of northeast China, showing the igneous rocks distributions within the Great Xing'an Range (modified after [1,6]). (**C**) Simplified geological map of the Southern Great Xing'an Range, showing the distributions of the main mineral deposits (modified after [1,3]).

In this study, we performed zircon U–Pb geochronological, whole rock geochemical, and Sr–Nd–Pb isotopic analyses of the ore-associated intrusive rocks in the Baiyinnuoer Zn–Pb deposit. These new data are used to better understand the ages, petrogenesis, and tectonic setting of the ore-associated intrusive rocks.

#### 2. Geological Setting

Northeast China, which is located in the eastern part of the CAOB, is bounded by the North China Craton (NCC) to the south, and the Siberian Craton (SC) to the north [1,9,18–22] (Figure 1A). The Palaeozoic tectonic evolution of NE China includes the subduction of the Paleo-Asian Ocean and the amalgamation of multiple microcontinental blocks (e.g., the Jiamusi, Songliao, Xing'an, and Erguna blocks) [6,21–24] (Figure 1B). The Mesozoic tectonic evolution of this region is characterized by the Pacific plate tectonic regime in the east and the Mongol–Okhotsk plate tectonic regime in the northwest [6,21–24].

The SGXR, located in the western Songliao block [6,25,26] (Figure 1B), is characterized by widespread Late Paleozoic to Mesozoic volcanic-sedimentary successions (Figure 1C), and a number of world-class Pb–Zn–Ag–Cu–Mo polymetallic deposits are hosted in these successions (e.g., the Bairendaba, Huanggangliang, Bianjiadayuan, Dajing, and Haobugao deposits) [27–29]. The NE-trending Huanggang–Ganzhuermiao and EW-trending Xilamulun faults dominate this region and control the emplacement of the intrusions and the distributions of the polymetallic deposits [28–30] (Figure 1C). Moreover, intense magmatic events have been identified in this region, which has broadly distributed I- and A-type granitoids [5,6,21]. On the basis of a precise framework, these granitoids were considered to be emplaced in two geotectonic stages. The first group includes granodiorite, diorite, and tonalite with ages ranging from 321 to 237 Ma, which originated in the mantle and recycled ancient crustal materials, where the magmatism was associated with the closure of the Paleo-Asian Ocean, post-orogenic extension, and plate subduction [5,30–33]. The second group consists of monzogranite, syenogranite, and granodiorite with ages ranging from 150 to 131 Ma, which were derived from lower crustal materials, where the magmatism was related to plate subduction, lithospheric delamination, and extension [5,10,34,35].

According to the distributions of the polymetallic deposits, the SGXR metallogenic belt can be divided into three metallogenic sub-belts from west to east: the Xilinhot–Xilinguole Pb–Zn–Ag–Cu metallogenic sub-belt (e.g., the Bairendaba, Weilasituo, and Daolundaba deposits), the Huanggang–Ganzhuermiao Sn–Pb–Zn–Fe–Cu metallogenic sub-belt (e.g., the Huanggang, Dajing, Bianjiadayuan, and Haobugao deposits), and the Linxi–Lindong–Tianshan–Tuquan Cu–Mo metallogenic sub-belt (e.g., the Aoergai deposit) [5,13] (Figure 1C).

The Baiyinnuoer Zn–Pb deposit is a typical skarn Zn–Pb deposit in the SGXR, which belongs to the Huanggang–Ganzhuermiao Sn–Pb–Zn–Fe–Cu metallogenic sub-belt (Figure 1C). Exposed rocks include the Lower Permian Huanggangliang Formation and the Upper Jurassic Manketouebo Formation (Figure 2). The Huanggangliang Formation can be divided into three parts. The lower part is composed of sandy and argillaceous slates, and the middle part contains limestones, marbles, and skarns, with minor tuffs and andesites, and the upper part consists of slates with minor sandy and argillaceous slates (Figure 2). The Manketouebo Formation, unconformably overlaid on the Huanggangliang Formation, comprises tuffs and breccias. These units at Baiyinnuoer were intruded by Indosinian subvolcanic rocks (Late Permian-Middle Triassic), Yanshanian plutonic rocks (Late Jurassic-Early Cretaceous), and post-mineralization quartz porphyry dike (Early Cretaceous) [1] (Figure 2). Indosinian subvolcanic rocks consist of granodiorite, granodiorite porphyry, diorite, and syenite porphyry, which are genetically associated with the dominant skarn-type Zn–Pb mineralization [1]. Yanshanian plutonic rocks are composed of feldspar porphyry and feldspar-quartz porphyry, which are related to minor vein-type Zn–Pb mineralization [13]. Recent geochronological investigations indicated that the granodiorite, diorite, and feldspar porphyry were emplaced at approximately 244, 242, and 136 Ma, respectively [13,15,16].



**Figure 2.** Geological map of the Baiyinnuoer Zn–Pb deposit, showing the north and south ore zones (modified after [1]).

The Baiyinnuoer Zn–Pb deposit is divided into the north and south ore zones (Figure 2). The south ore zone is approximately 2800 m long and 200–400 m wide, and it contains 55 ore bodies. The north ore zone is 1800 m long and 400–600 m wide, and it includes 108 ore bodies. The ore bodies contain galena and sphalerite with Pb and Zn grades of 2.02% and 5.44%, respectively [1,13]. Other ore minerals include chalcopyrite, pyrrhotite, and pyrite. The gangue minerals contain mainly chlorite, epidote, allanite, pyroxene, actinolite, garnet, feldspar, quartz, and calcite.

Detailed field observation around the south ore zone at Baiyinnuoer in this study revealed that the skarn-type Zn–Pb ore bodies occurred extensively, and these ore bodies developed along the contact zones between the Indosinian subvolcanic rocks and marbles.

## 3. Samples and Analytical Methods

#### 3.1. Samples

In the Baiyinnuoer south ore zone, 11 samples, which belonged to the Indosinian subvolcanic group, were collected from underground tunnels, and the locations of the samples are shown in Figure 2. These studied ore-associated intrusions are composed of seven granodiorite samples, one granodiorite porphyry sample, and three diorite samples. The granodiorite is fine-grained and massive, and contains plagioclase (35%), K-feldspar (30%), quartz (15%), amphibole (15%), and minor biotite; all percentages are approximates (Figure 3A,B). The granodiorite porphyry shows porphyritic texture, and the phenocrysts contain amphibole (15%), plagioclase (15%), K-feldspar (5%), quartz (5%), and minor biotite, and the matrix consist of plagioclase (25%), K-feldspar (20%), quartz (10%), and amphibole (5%) (Figure 3C,D). The diorite consists of plagioclase (55%), amphibole (30%), and quartz (15%) (Figure 3E,F). Among these samples, one granodiorite sample, one granodiorite porphyry sample, and one diorite sample were analyzed by zircon U–Pb in situ LA-ICP-MS geochronology. One granodiorite porphyry sample and one diorite sample were analyzed for Sr–Nd–Pb isotopic analysis. Whole-rock geochemical analysis of all 11 samples was performed.



**Figure 3.** Photographs and photomicrographs of (**A**,**B**) granodiorite, (**C**,**D**) granodiorite porphyry, and (**E**,**F**) diorite in the Baiyinnuoer Zn–Pb deposit. Abbreviations: Qz—quartz, Pl—plagioclase, Kfs—K-feldspar, Am—amphibole, Bt—biotite.

#### 3.2. Analytical Technique

#### 3.2.1. Whole-Rock Geochemical Analysis

The major and trace element compositions were determined at the Institute of Geophysics and Geochemistry, Chinese Academy of Geological Sciences, Langfang, China. Each sample was crushed and powdered to less than 200 mesh in an agate mortar. The major elements were analyzed by X-ray fluorescence spectroscopy (Shimadzu WD-1800, Kyoto, Japan) using Chinese Standard GB/T14506.28–2010 [36]. Uncertainties were given at the 95% confidence level. The trace elements and rare earth elements (REE) were measured by ICP-MS using Chinese Standard Materials GSR-1, GSR-2, and GSR-3. Uncertainties were given at the 90% confidence level.

#### 3.2.2. Whole-Rock Sr-Nd Isotopic Analysis

Whole-rock Sr–Nd isotopic analysis was performed at the Beijing Research Institute of Uranium Geology, China National Nuclear Corporation, Beijing, China. The sample was crushed and powdered to less than 200 mesh in an agate mortar. The Sr–Nd isotopes were identified by thermal ionization mass spectrometry (TIMS; Thermo-Finnigan Triton, Davis, CA, USA). The isotopic mass fractionation was corrected by normalizing to  ${}^{88}$ Sr/ ${}^{86}$ Sr = 8.375209 and  ${}^{146}$ Nd/ ${}^{144}$ Nd = 0.7219. In the analysis, measurement correction using the American Standard Materials NBS 987 yielded  ${}^{87}$ Sr/ ${}^{86}$ Sr = 0.710250 ± 0.000007 (2 $\sigma$ ) and  ${}^{143}$ Nd/ ${}^{144}$ Nd = 0.512109 ± 0.000003 (2 $\sigma$ ). The precision of the Sr–Nd isotopic analysis was better than 0.005%.

#### 3.2.3. Whole-Rock Pb Isotopic Analysis

Whole-rock Pb isotopic analysis was performed at the Beijing Research Institute of Uranium Geology, China National Nuclear Corporation, Beijing, China. Each sample was crushed and powdered to less than 200 mesh in an agate mortar. A 0.2 g powder sample was digested by a mixed acid in a low-pressure airtight vessel. The aqueous solution was evaporated to dryness when it was fully dissolved after 24 h. After reacting with HCl to form chloride, the sample was separated by centrifugation. The Pb was dissociated using HCL, and the Pb isotopes were identified by TIMS (Isoprobe). The uncorrected results for NBS 981 were  $^{206}$ Pb/ $^{204}$ Pb = 16.895 ± 0.002,  $^{207}$ Pb/ $^{204}$ Pb = 15.437 ± 0.002, and  $^{208}$ Pb/ $^{204}$ Pb = 36.537 ± 0.004.

#### 3.2.4. Zircon U-Pb in Situ LA-ICP-MS Geochronology

Cathodoluminescence (CL) imaging of zircon grains was performed using an electron microscope at the Institute of Mineral Resources, China Academy of Geological Science, Beijing, China. Zircon U–Pb

geochronology was conducted using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Testing Center of the Shandong Bureau of the China Metallurgical Geology Bureau, Jinan, China. A Coherent COMPex Pro ICP-MS instrument was used to acquire the ion signal intensities. Helium mixed with argon was used as a carrier gas. Each type of analysis incorporated a background acquisition followed by data acquisition from the sample. NIST 610 glass and Si were used as standards to perform the calibrations for the zircon analyses. Zircon 91,500 was used as an external standard for correcting U–Pb isotope fractionation effects. Concordia diagrams and weighted mean calculations were performed using Isoplot 3.0 [37]. Uncertainties were given at the 95% confidence level.

# 4. Results

#### 4.1. Whole-Rock Geochemistry

The whole-rock major and trace element contents and REE data from seven granodiorite samples, one granodiorite porphyry sample, and three diorite samples are listed in Table S1. The granodiorite samples were slightly altered as the Loss on ignition (LOI) values ranging from 0.54 to 1.35 wt %. One granodiorite porphyry sample (BY02) and two diorite samples (BY09 and BY11) might experience modest alteration, leading their LOI values to be 3.24, 4.60, and 3.00 wt %, respectively (Table S1).

The granodiorites and granodiorite porphyry in the Baiyinnuoer deposit have high SiO<sub>2</sub> contents of 65.05–68.25 wt % (Figure 4A), with an average value of 67.38 wt %. The Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, FeO<sub>t</sub>, MgO, and CaO contents are 13.11–14.30, 2.09–4.42, 2.40–5.42, 1.66–3.70, 1.21–2.15, and 1.93–4.39 wt %, respectively. They also have low TiO<sub>2</sub> (0.37–0.55 wt %) and P<sub>2</sub>O<sub>5</sub> (0.13–0.23 wt %) contents. The Mg# values of the granodiorites (porphyries) range from 43 to 65. In the K<sub>2</sub>O versus SiO<sub>2</sub> diagram (Figure 4A), most samples plot into the high-K calc-alkaline field. The granodiorites and granodiorite porphyry are metaluminous with A/CNK (molar Al<sub>2</sub>O<sub>3</sub>/CaO + Na<sub>2</sub>O + K<sub>2</sub>O) values of 0.79–1.05 and A/NK (molar Al<sub>2</sub>O<sub>3</sub>/Na<sub>2</sub>O + K<sub>2</sub>O) values of 1.21–1.69 (Figure 4B). Moreover, the granodiorites and granodiorite porphyry have REE contents of 97.03–144.36 ppm and are enriched in light rare earth element (LREE), with (La/Yb)<sub>N</sub> ratios of 7.60–13.27. The granodiorites and granodiorite porphyry also show slight Eu anomalies ( $\delta$ Eu = 0.54–0.82;  $\delta$ Eu = 2 × (Eu/0.0735)/((Sm/0.195) + (Gd/0.259))) and negligible Ce anomalies ( $\delta$ Ce = 0.86–1.06;  $\delta$ Ce = 2 × (Ce/0.808)/((La/0.310) + (Pr/0.122))) (Figure 5A). As shown in the primitive-mantle-normalized trace element spider diagram (Figure 5B), the granodiorites and granodiorite porphyry are enriched in Rb, Th, and U, and depleted in Nb, Ta, and Ti.



**Figure 4.** Geochemical classification diagrams of the Baiyinnuoer intrusive rocks. (**A**) K<sub>2</sub>O versus SiO<sub>2</sub> (modified after [38]). (**B**) A/NK versus A/CNK (modified after [39,40]).



**Figure 5.** Chondrite-normalized rare earth element (REE) patterns and primitive-mantle-normalized multi-element spidergrams for the granodiorite and granodiorite porphyry (**A**,**B**) and the diorite (**C**,**D**) in the Baiyinnuoer Zn–Pb deposit. Chondrite-normalized and primitive-mantle-normalized values are from [41].

With respect to the diorite samples, the SiO<sub>2</sub> contents range from 53.53 to 60.14 wt %, with an average of 57.16 wt %. The diorites have high FeO<sub>t</sub> (5.04–6.82 wt %), TiO<sub>2</sub> (0.59–0.64 wt %), MgO (3.02–4.06 wt %), and CaO (4.64–11.69 wt %) contents, and low Al<sub>2</sub>O<sub>3</sub> (12.71–14.07 wt %) and Na<sub>2</sub>O (2.06–2.56 wt %) contents. The diorites yield Mg# values of 50–55. In the K<sub>2</sub>O versus SiO<sub>2</sub> diagram, the diorites are all plotted in the shoshonitic field (Figure 4A). The diorites are metaluminous, with A/CNK values of 0.44–0.74 (Figure 4B). Moreover, the diorites have REE contents of 113.7–199.0 ppm and (La/Yb)<sub>N</sub> ratios of 10.55–22.23, indicating a distinct fractionation between heavy rare earth element (HREE) and LREE (Figure 5C). The diorites show negligible Eu and Ce anomalies ( $\delta$ Eu = 0.60–0.98;  $\delta$ Ce = 0.76–0.99) (Figure 5C) and negative Nb–Ta–Ti anomalies (Figure 5D).

#### 4.2. Whole-Rock Sr-Nd Isotopic Results

The Sr–Nd isotopic compositions of one granodiorite sample and one diorite sample, from the Baiyinnuoer deposit are listed in Table S2 and plotted in Figure 6. The granodiorite sample BY08 has an initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.7054, an  $\varepsilon$ Nd(*t*) value of +1.0 (*t* = 251 Ma), and a  $T_{DM2}$  value of 937 Ma. The diorite sample BY10 has an initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.7044, an  $\varepsilon$ Nd(*t*) value of +1.8 (*t* = 249 Ma), and a  $T_{DM2}$  value of 880 Ma.



**Figure 6.**  $\varepsilon$ Nd(*t*) versus (<sup>87</sup>Sr/<sup>86</sup>Sr)<sub>i</sub> for the Baiyinnuoer intrusive rocks, showing the mixing proportions of two end members: depleted mantle or juvenile components and crustal materials (modified after [42]). Abbreviations: DM–upper mantle peridotite; B–basalt; LCC–lower continental crust; UCC–upper continental crust. Data are from Jiang et al. [13] and this study.

#### 4.3. Whole-Rock Pb Isotopic Results

The Pb isotopic compositions of one granodiorite sample and one diorite sample from the Baiyinnuoer deposit are listed in Table S3 and plotted in Figure 7. The granodiorite sample BY08 shows <sup>208</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb, and <sup>206</sup>Pb/<sup>204</sup>Pb ratios of 38.56, 15.557, and 18.712, respectively. The diorite sample BY10 has <sup>208</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb, and <sup>206</sup>Pb/<sup>204</sup>Pb values of 38.203, 15.557, and 18.334, respectively.



**Figure 7.** Plot of Pb isotopic data for the Baiyinnuoer intrusive rocks. (**A**)  $^{207}$ Pb/ $^{204}$ Pb versus  $^{206}$ Pb/ $^{204}$ Pb. (**B**)  $^{208}$ Pb/ $^{204}$ Pb versus  $^{206}$ Pb/ $^{204}$ Pb (modified after [43]).

## 4.4. Zircon U-Pb Geochronology

The results of zircon U–Pb dating of one granodiorite porphyry sample, one granodiorite sample, and one diorite sample in the Baiyinnuoer deposit are presented in Table S4, and the representative CL images of zircon grains are shown in Figure 8, and the concordia diagrams of the zircon U–Pb isotopic data are illustrated in Figure 9.



#1 (252±3 Ma) #9 (250±3 Ma) #10 (245±3 Ma) #12 (248±4 Ma) #13 (242±4 Ma) #15 (246±3 Ma) #16 (247±3 Ma)



#5 (251±7 Ma) #6 (252±4 Ma) #7 (246±3 Ma) #9 (247±4 Ma) #12 (254±3 Ma) #13 (248±4 Ma) #20 (248±3 Ma)

**Figure 8.** Representative cathodoluminescence images of zircon grains from granodiorite porphyry (BY02), granodiorite (BY08), and diorite (BY10) samples from the Baiyinnuoer Zn–Pb deposit.

Zircon grains from the granodiorite porphyry sample BY02 are euhedral–subhedral prismatic grains with oscillatory zoning texture (Figure 8). They are 120–260  $\mu$ m in size, and their length/width ratios are 2:1–3:1 (Figure 8). Twenty-two zircon grains were analyzed, and their Th and U contents are 127.4–614.4 and 404.6–1517.9 ppm (Table S4), respectively. The Th/U ratios range from 0.25 to 0.46 (Table S4), indicating a magmatic origin [44]. These zircons show <sup>206</sup>Pb/<sup>238</sup>U ages of 242–253 Ma (Table S4) and yield a mean age of 248 ± 1.3 Ma (MSWD = 0.61, n = 22) (Figure 9A,B), which could represent the crystallization age of the granodiorite porphyry.

Zircon grains from the granodiorite sample BY08 are euhedral–subhedral prismatic grains with an oscillatory zoning texture (Figure 8). The sizes of these grains are 160–260  $\mu$ m, and their length/width ratios are 2:1–3:1 (Figure 8). Fourteen zircon grains were analyzed, and their Th and U contents are 74.4–506.5 and 289.5–931.1 ppm (Table S4), respectively. The Th/U ratios range from 0.31 to 0.54 (Table S4), indicating a magmatic origin [44]. These zircons show <sup>206</sup>Pb/<sup>238</sup>U ages of 247–253 Ma (Table S4) and yield a mean age of 251 ± 1.8 Ma (MSWD = 0.36, *n* = 14) (Figure 9C,D), which could represent the crystallization age of the granodiorite.

The zircons from the diorite sample BY10 present as euhedral–subhedral prismatic grains, with lengths of 160–300  $\mu$ m and length/width ratios of 2:1–3:1 (Figure 8). Twenty-three zircon grains were analyzed, and most of them exhibited oscillatory zoning texture (Figure 8). These grains have U = 315.3–1243.8 ppm, Th = 117.3–912.0 ppm, and Th/U = 0.29–0.73 (Table S4), indicating a magmatic origin [44]. Twenty-three analyzed spots show <sup>206</sup>Pb/<sup>238</sup>U ages ranging from 245 to 254 Ma (Table S4)

and yield a mean age of  $249 \pm 1.4$  Ma (MSWD = 0.74, n = 23) (Figure 9E,F), which could represent the magmatic crystallization age of the diorite.



**Figure 9.** Concordia diagrams of zircon U–Pb isotopic data from the granodiorite porphyry sample BY02 (**A**,**B**), granodiorite sample BY08 (**C**,**D**), and diorite sample BY10 (**E**,**F**) in the Baiyinnuoer Zn–Pb deposit.

# 5. Discussion

#### 5.1. Age of Magmatism

Several geochronological studies on Indosinian subvolcanic rocks at Baiyinnuoer have been undertaken to determine the precise age of magmatism. Yang et al. [17] reported that the granodiorites were emplaced at approximately 253 Ma. Jiang et al. [13] suggested that the crystallization age of the granodiorite was approximately 244 Ma. However, Shu et al. [1] reported that the granodiorites and granites were emplaced at approximately 273 and 275 Ma, respectively.

In this study, zircon grains from the granodiorite porphyry, granodiorite, and diorite commonly are euhedral–subhedral prismatic grains, and exhibit oscillatory zoning texture (Figure 8). These features, together with the high Th/U ratios, indicate a magmatic origin [44]. The zircons from the granodiorite porphyry sample BY02, the granodiorite sample BY08, and the diorite sample BY10 yield mean  $^{206}$ Pb/ $^{238}$ U ages of 248 ± 1.3, 251 ± 1.8, 249 ± 1.4 Ma, respectively. Accordingly, Indosinian

subvolcanic rocks were emplaced in the Late Permian and we can constrain the age of magmatism at Baiyinnuoer to 251–248 Ma.

In the Great Xing'an Range, ore-associated Indosinian magmatic rocks occur extensively. The zircon U–Pb geochronology in the Aoergai copper deposit showed that the ore-related granodiorites were emplaced at approximately 245 Ma [45]. Ore-related granite yielded a <sup>206</sup>Pb/<sup>238</sup>U age of approximately 243 Ma, which occurred widespread in the Badaguan Cu–Mo deposit [46]. The ages of mineralization of these deposits are similar to those of Indosinian magmatic rocks within the Great Xing'an Range. Further exploration in the Great Xing'an Range, therefore, might focus on the Late Permian–Early Triassic magmatism.

#### 5.2. Source and Petrogenesis of the Magma

#### 5.2.1. Granodiorite and Granodiorite Porphyry

Accurately recognizing the genetic type of the granitoids is important for understanding the source and petrogenesis of the magma and determining the tectonic setting [47]. The granitoids are classified as A-, I-, M-, and S-type [48–50]. In general, A-type granitoids have high (Na<sub>2</sub>O + K<sub>2</sub>O) and high field strength elements (HFSEs) contents and might be generated in extensional settings [51]. By contrast, I-type granitoids have low  $P_2O_5$  contents and high Th and Y values, and could have been derived from igneous rocks, whereas S-type granitoids are considered to be derived from metasedimentary rocks [52,53].

In the Baiyinnuoer Zn–Pb deposit, the high-K calc-alkaline granodiorites and granodiorite porphyry have high SiO<sub>2</sub> contents (65.05–68.25 wt %) and low FeO<sub>t</sub>/MgO ratios (0.94–2.33). They are metaluminous, with A/CNK values of 0.79–1.05, suggesting an important criterion for I-type granitoids [52,53]. In the discrimination diagrams, the granodiorites and granodiorite porphyry all plot into the unfractionated I-, M-, and S-type granitoids fields (Figure 10A,B). Moreover, all the granodiorites and granodiorite porphyry have low  $P_2O_5$  contents (0.13–0.23 wt %) and show negative correlations between SiO<sub>2</sub> and  $P_2O_5$  (Figure 10C), indicating I-type affinity. Accordingly, we consider that the granodiorites and granodiorite porphyry in the Baiyinnuoer Zn–Pb deposit are metaluminous, high-K calc-alkaline I-type granitoids.

The petrogenesis of I-type granitoids remains controversial. Previous petrological investigations have demonstrated that I-type granitoids could have been formed by the partial melting of igneous rocks in the lower crust [54], the mixing of mantle-derived mafic magma and crust-derived felsic magma [55], or by the fractional crystallization of mantle-derived mafic magma [56,57]. The I-type granodiorites and granodiorite porphyry in the Baiyinnuoer deposit show a small positive correlation between La/Sm and La (Figure 10D), possibly suggesting partial melting rather than fractional crystallization. Therefore, a model of fractional crystallization of mantle-derived mafic magma was precluded. It is widely acknowledged that the magmas, which were derived from the partial melting of lower crustal mafic rocks, generally have low Mg# values (<40) and MgO contents [58]. The I-type granodiorites and granodiorite porphyry in the Baiyinnuoer deposit have higher Mg# (43-65) and MgO (1.36-2.15 wt %) values than typical crust-derived melts [59,60], suggesting that mantle components were involved in their genesis. Furthermore, the granodiorites and granodiorite porphyry have relatively low Nb/Ta ratios (8.48–15.01), which are lower than that of the primitive mantle (17) [61] but close to that of the crust (11) [61], suggesting the involvement of crustal materials. The low Zr/Hf (20.30–29.89) and Nb/La ratios (0.19–0.43) also indicate that crustal components were added to the magma source [61]. Accordingly, we consider that the I-type granodiorites and granodiorite porphyry in the Baiyinnuoer deposit resulted from mixing of mantle-derived and crust-derived magmas.



**Figure 10.** Discrimination diagrams of the Baiyinnuoer granodiorites and granodiorite porphyry (modified after [51]). (**A**) FeO<sub>t</sub>/MgO versus Zr + Nb + Ce + Y. (**B**) (Na<sub>2</sub>O + K<sub>2</sub>O)/CaO versus Zr + Nb + Ce + Y. (**C**) P<sub>2</sub>O<sub>5</sub> versus SiO<sub>2</sub>. (**D**) La/Sm versus La.

The Sr–Nd isotopic data might provide more evidence regarding their genesis. The granodiorite sample BY08 has a positive  $\varepsilon$ Nd(t) value (+1.3) and young  $T_{DM2}$  age (916 Ma), indicating a juvenile source. Wu et al. [42] proposed a two-component mixing model to constrain the proportions of ancient and juvenile materials. According to this model, as shown in Figure 6, the Baiyinnuoer granodiorite could have been generated from a mixture of approximately 20% mantle-derived components and 80% lower continental crustal materials. Accordingly, the parent magmas of the Baiyinnuoer granodiorites and granodiorite porphyry were originated in a mixture of mantle-derived components and lower continental crustal materials.

Moreover, the pronounced negative Eu, Nb, Ta, and Ti anomalies indicate that fractional crystallization might have occurred during magma ascent. The negative Eu anomalies might result from the fractionation of plagioclase and/or K-feldspar in the magma chamber. As shown in Figure 11A,B, the fractionating phases of amphibole and biotite might be included. The fractionation of Ti-bearing phases (e.g., ilmenite and titanite) and apatite might result in negative Nb–Ta–P–Ti anomalies (Figure 11C,D).



**Figure 11.** Discrimination diagrams of the Baiyinnuoer intrusive rocks (modified after [62]). (**A**) Ba versus Sr. (**B**) Eu versus Sr. (**C**) Ta/Nb versus Ta. (**D**) (La/Yb)<sub>N</sub> versus La.

## 5.2.2. Diorite

The diorites show metaluminous characteristics (Figure 4A,B), together with the fractionated REE patterns and Nb–Ta–Ti anomalies (Figure 5C,D), suggesting a close resemblance to typical arc-related rocks [58]. The diorites have low SiO<sub>2</sub> contents (53.53–60.14 wt %) and high MgO (3.02–4.06 wt %), Cr (76.9–121.3 ppm), Co (12.14–15.86 ppm), Ni (19.36–31.78 ppm), and Mg# (50–55) values, indicating that their parental magmas could not have been produced by the partial melting of crustal rocks, and thus a mantle source is favored [63]. The Nb/Ta (9.50–13.77), Zr/Hf (25.72–27.37), Nb/La (0.11–0.36), and Nb/U (1.67–3.58) ratios suggest the involvement of crustal components in their genesis [61]. Furthermore, the geochemical characteristics of the diorites are similar to those of the granodiorites and granodiorite porphyry in our study (Figure 5), possibly indicating that they have the same magma source. The diorite sample BY10 has a positive  $\varepsilon$ Nd(t) value (+1.8) and a young  $T_{DM2}$  age (880 Ma), indicating a juvenile magma source. As shown in Figure 6, the diorite could have been generated from a mixture of approximately 20% mantle-derived components and 80% lower continental crustal materials [42]. The fractionation of amphibole, biotite, ilmenite, titanite, and zircon might have occurred during magma ascent (Figure 11A,D).

Accordingly, we consider that the 251–248 Ma intrusive rocks in the Baiyinnuoer deposit could have been derived from mixing of mantle-derived and crust-derived juvenile magmas, and little ancient crustal material was added to their genesis. The fractional crystallization of plagioclase and/or K-feldspar, amphibole, biotite, ilmenite, titanite, and apatite might have occurred in these intrusive rocks during magma ascent.

## 5.3. Tectonic Implications

Recent studies have shown that the Paleo-Asian Ocean developed mainly from the Mesoproterozoic, which was located in the CAOB between the NCC and SC [6,64]. However, controversy remains regarding where and when the Paleo-Asian Ocean closed. Several researchers have suggested that the Hegenshan–Heihe suture (between the Xing'an and Songliao blocks) could

represent the final closure of the ocean during the Late Devonian–Early Carboniferous [22,65,66], as evidenced by the palaeomagnetic data from the northern NCC. Nevertheless, most scholars consider that the Solonker–Xra Moron–Changchun suture (between the Songliao and Liaoyuan blocks) might represent the final collision zone and they suggested that the suturing might take place at 250 Ma [6,9,10,22,67–70], and this hypothesis is supported by the arc-related volcanic rocks and palaeontological evidence (e.g., fossils). Jian et al. [71] summarized the published zircon U–Pb age data of the ophiolite in the Solonker mélange and constrained the age of post-collisional magmatism in this region at 255–248 Ma, suggesting that this magmatic episode might follow the complete closure of Paleo-Asian Ocean in the Late Permian. In this study, our new data from the Baiyinnuoer intrusive rocks

could provide more clues for deciphering the geological setting of the SGXR during the Late Permian. The I-type granodiorites and granodiorite porphyry are enriched in LREE and HFSEs, and show typical calc-alkaline characteristics with negative Nb–Ta–Ti anomalies (Figures 4 and 5), indicating an arc-related setting. The Pb isotopic data of the Baiyinnuoer intrusive rocks suggest an orogenic setting during the Late Permian (Figure 7). Moreover, the tectonic discrimination diagrams show that the granodiorites and granodiorite porphyry all plot into the post-orogenic granite field (Figure 12), indicating that the Baiyinnuoer granodiorites and granodiorite porphyry were generated in a post-collision setting in the Late Permian. Accordingly, considering the regional geology, we propose a post-collision setting for the emplacement of the granodiorites and granodiorite porphyry in the Baiyinnuoer Zn–Pb deposit. In light of the new geochemical, geochronological, and isotopic data, the intrusive rocks were considered to be formed in a post-collision setting in the Late Permian (251–248 Ma), and could have been derived from the mixing of mantle-derived components and lower continental crustal materials, with subsequent fractional crystallization.



**Figure 12.** Discrimination diagrams of the Baiyinnuoer intrusive rocks. (**A**) Rb versus Yb + Ta. (**B**) Rb versus Y + Nb (modified after [72]). Abbreviations: WPG—with-in plate granites; VAG—volcanic arc granites; Syn-COLG—syn-collision granites; ORG—ocean ridge granites; POG—post-collision granites.

## 6. Conclusions

Geochronological data confirm that the Baiyinnuoer granodiorites, granodiorite porphyry, and diorites were formed in the Late Permian (251–248 Ma). The granodiorites and granodiorite porphyry are high-K calc-alkaline and show typical features similar to those of I-type granitoids. These intrusive rocks were likely derived from the mixing of mantle-derived components and lower continental crustal materials. The geochemical and isotopic results reveal a post-collision setting for the emplacement of these intrusive rocks at Baiyinnuoer. Therefore, the SGXR might experience the closure of the Paleo-Asian Ocean in the Late Permian.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2075-163X/10/1/19/s1, Table S1: Whole-rock geochemical data from the intrusive rocks in the Baiyinnuoer Zn–Pb deposit; Table S2: Sr–Nd isotopic data from the intrusive rocks in the Baiyinnuoer Zn–Pb deposit; Table S3: Pb isotopic data from

the intrusive rocks in the Baiyinnuoer Zn–Pb deposit; Table S4: LA-ICP-MS zircon U–Pb isotopic data from the intrusive rocks in the Baiyinnuoer Zn–Pb deposit.

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