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# The Metallogenic Mechanism of Skarn Sn-Polymetallic Deposits in the Southern Great Khingan Range, China: Constraints on the Geological and Geochemical Characteristics of Damogutu Sn–Fe and Dashishan Sn–Pb–Zn Deposits



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**Abstract:** Skarn Sn-polymetallic deposits, located in the southern Great Khingan Range, can be divided into Sn–Fe and Sn–Pb–Zn deposits. By systematically studying the geochemical characteristics of source granitoid and deposits, the ore-forming mechanisms were established, and the differences in ore-forming processes between Sn–Fe and Sn–Pb–Zn deposits are discussed. The main findings are as follows: (1) these two deposits were formed in the Late-Yanshanian period; (2) the source granitoid evolved at an early stage in a reducing environment, while the oxygen fugacity increased at a late stage through the influence of a deep-seated fault; (3) fine-grained syenogranite from Dashishan showed a higher degree of evolution than the syenogranite from Damogutu; (4) the Damogutu Sn–Fe and Dashishan Sn–Pb–Zn deposits shared a source of ore-forming fluid, and Fe, Sn, Pb, and Zn all derived from Late-Yanshanian granitoids; and (5) the ore-forming fluid experienced a continuous evolution process from the magmatic to hydrothermal stage, and the magmatic–hydrothermal transitional fluid played a very important role in skarnization and mineralization.

**Keywords:** Damogutu Sn–Fe deposit; Dashishan Sn–Pb–Zn deposit; source granitoid; ore-forming fluids; skarn deposit

# 1. Introduction

Many Sn-polymetallic deposits are present in the Southern Great Khingan Range (Figure 1) with high economic potential for Fe, Sn, Pb, and Zn [1], and can be classified as magmatic–hydrothermal or skarn type.



**Figure 1.** Geological maps: (**a**) simplified map of Northeast China (modified after [2]); (**b**) the southern Great Khingan Range (modified after [1]). I: Xinlin–Xiguitu suture; II: Erlian–Hegenshan suture; III: Xar Moron suture; IV: Mudanjiang–Yilan suture; i: Derbugan Fault; ii: Nenjiang–Balihan Fault; iii: Songliao Basin Central Fault; iv: Jiamusi–Yilian Fault; v: Dunhua–Mishan Fault.

Systematic study of magmatic–hydrothermal deposits has led to substantial progress in the knowledge of their spatial and temporal distributions, features of related granitoids, fluid sources, evolution, and precipitation mechanisms [3–8]. While, several researchers have focused on the genesis of skarn deposits, in particular, Huanggangliang Sn–Fe deposit, Baiyinnuoer and Haobugao Sn–Pb–Zn deposits [9–12], they neglected the relationship between Sn–Fe and Sn–Pb–Zn mineralization.

The Damogutu Sn–Fe and Dashishan Sn–Pb–Zn deposits are two typical skarn deposits in the southern Great Khingan Range. They show a close spatio–temporal relationship and share similar regional geology and local geology. In this paper, by systematically studying their geochemical characteristics, the relationship and differences in ore-forming processes between Sn–Fe and Sn–Pb–Zn deposits are discussed.

#### 2. Regional Geology

The southern Great Khingan Range is located in the east part of the Xing'an–Mongolian Orogenic Belt and belongs to the Central Asian Orogenic Belt. It has undergone multiple phases of tectonic reworking, which have led to the closure of the Paleo–Asian Ocean, the formation of Central Asian Orogenic Belt, and the subduction and modification of Mongolia–Okhotsk and the Paleo–Asian Ocean [2,13–16].

The geological terrane in the southern Great Khingan Range comprises rocks of Proterozoic to Cenozoic ages (Figure 1b). The Proterozoic is mainly middle- to low-grade metamorphic rocks of the Baoyintu Group, which are exposed near Weilasituo and Bairendaba (Figure 1b). The Paleozoic are mainly composed of clastic and volcanic rocks, and it is worth noting that the Dashizhai and Zhesi Groups of the Middle Permian period are the most important ore-bearing strata [5,7,9,11]. The Jurassic continental volcano-clastic rocks are most widely distributed within the units of Mesozoic. The Cenozoic strata primarily consists of glutenite, mudstone, large amounts of basalt, and are distributed in a continental rift–subsidence basin controlled by the northeast deep-seated fault, such as the Great Khingan West slope, Daqingmuchang, Great Khingan Main Ridge, and Xar Moron faults (Figure 1b) [1].

Under the influence of multiple tectonic movements, different stages of faults and folds were formed. The northeast deep-seated fault formed during the NNW-directed subduction of the Pacific plate and controlled the distribution of strata, granitic intrusions, and ore deposits [2].

Granitoids, including monzonitic, biotite, and highly evolved alkali–feldspar granites are the most common types of magmatic rocks in the southern Great Khingan Range, with an exposed area of 150 km<sup>2</sup>. Spatially, the large granitoid plutons are distributed in the NE between the Great Khingan West Slope Fault and the Great Khingan Main Ridge Fault, while the small granitoid stocks are scattered between the Great Khingan Main Ridge Fault and the Xar Moron Fault (Figure 1b). Temporally, the granitoid magma intruded from the Caledonian to the Late-Yanshanian periods. The Late-Yanshanian period (155–114 Ma) was not only the most important period of granitoid magma emplacement (Figure 2) but also a major period of Sn-polymetallic mineralization [14,17–20].



**Figure 2.** Frequency histogram of the Late-Yanshanian granitoid and Sn-polymetallic deposits in the southern Great Khingan Range. The age data regarding granitoid are from References [14,17,18,20–23]. The age data on Sn-polymetallic deposits are from References [3,5–8,11,12,24–28].

The most important characteristics of the southern Great Khingan Range are the large amount of polymetallic deposits, including Sn–Fe, Cu, Pb–Zn–Ag, and Mo deposits (Figure 1b), which can be classified into three systems: (1) Sn-polymetallic systems, including most Sn–W deposits and Pb–Zn–Ag deposits, which are closely associated with the Late-Yanshanian granitoid in time and space (Figure 1b, Figure 2, and Figure 3a); (2) Mo-polymetallic systems, including many porphyry Mo-polymetallic deposits such as Aolunhua and Nianzigou [27,29], mainly formed during the Indosinian–Yanshanian

epoch; and (3) Cu-polymetallic systems, including Naoniushan, Lianhuashan, and Bianbianshan, intimately linked to Mesozoic terrestrial volcanism [30,31].

# 3. Deposit Geology

The Damogutu Sn–Fe and Dashishan Sn–Pb–Zn deposits are located less than 30 km northeast of Linxi county and no more than 10 km from each other (Figures 1b and 3a). As they share similar geology, they are discussed together in this section.

# 3.1. Host Rocks

The geology of the two deposits is relatively simple. Quaternary, Jurassic Xinmin group, Permian Zhesi group, and Dashizhai group are the main sedimentary formations (Figure 3b,c).



**Figure 3.** Geological maps of deposits: (**a**) the Damogutu–Dashishan area (modified after [1]); (**b**) the Damogutu Sn–Fe deposit (modified after [32]); (**c**) the Dashishan Sn–Pb–Zn deposit (modified after [33]).

The Zhesi Formation hosts Sn–Fe and Sn–Pb–Zn mineralization and is primarily composed of limestone and sandy slate. Because of the contact metamorphism, some limestone has been turned into hornfels with a well-developed garnet skarn zone (Figure 4).



**Figure 4.** Geological cross-sections: (**a**) the Damogutu Sn–Fe deposit (modified after [32]); (**b**) the Dashishan Sn–Pb–Zn deposit (modified after [33]).

## 3.2. Intrusive Rocks

Syenogranite is the only intrusive rock found in the Damogutu Sn–Fe deposit and is closely related to Sn–Fe mineralization (Figures 3a and 4b). In the Dashishan Sn–Pb–Zn deposit, in addition the syenogranite, there is a fine-grained syenogranite vein, which is related to Pb–Zn mineralization (Figures 3b and 4b).

The syenogranites in the Damogutu Sn–Fe deposit and the fine-grained syenogranites of the Dashishan Sn–Pb–Zn deposit share similar characteristics, such as a light fleshy red to off-white color, and a medium- to fine-grained granitic texture (Figure 5a). The main minerals include quartz (30%), K-feldspar (45%), plagioclase (20%), and small amounts of biotite (<5%) (Figure 5c). The quartz is usually colorless and shaped, granular crystals (Figure 5c). The K-feldspars are mainly orthoclases and microclines, with stumpy Carlsbad or cross-hatched twins (Figure 5d). The plagioclases are typically idiomorphic, long columnar albites with a grey interference color and a polysynthetic twin (Figure 5d). The biotites are mainly brown and idiomorphic (Figure 5e). Accessory minerals include magnetite (Figure 5e,f), zircon and a few pyrites.

The fine-grained syenogranite in the Dashishan Sn–Pb–Zn deposit is off-white and has a fine-grained texture (Figure 5b) comprising quartz (40%), K-feldspar (45%), plagioclase (13%), and small amounts of biotite (<3%). The characteristics of quartz, plagioclase, and biotite are similar to those described above for syenogranite, while the K-feldspars are mainly microclines, or even amazonite (Figure 5g). Moreover, some sulfide minerals, such as pyrite and sphalerite, can be found in the fine-grained syenogranite (Figure 5h).

Both the syenogranite and fine-grained syenogranite all show characteristics of highly evolved granites, e.g., miarolitic cavities with idiomorphic quartz, fluorite, and some tourmaline (Figure 6a–c). Pegmatite masses and greisen veins are also very common (Figure 6d–g).



**Figure 5.** Photos of the intrusive rocks: (**a**) the hand specimen of syenogranite; (**b**) the hand specimen of fine-grained syenogranite; (**c**) photomicrograph of syenogranite; (**d**) photomicrograph of plagioclase with polysynthetic twin embedded in K-feldspar; (**e**, **f**) photomicrographs of biotite with magnetite; (**f**) photomicrograph of microcline with cross-hatched twins; (**g**) photomicrographs of pyrite and sphalerite. Qz: quartz, Kf: K-feldspar, Pl: plagioclase, Bi: biotite, Mc: microcline, Mt: magnetite, Py: pyrite, Sp: sphalerite.



**Figure 6.** Photos of the intrusive rocks: (**a**) miarolitic cavity with euhedral quartz; (**b**) miarolitic cavity with euhedral fluorite; (**c**) miarolitic cavity with tourmaline; (**d**) pegmatite mass; (**e**,**f**) photos of greisen vein; (**g**) photomicrograph of greisen vein. Qz: quartz; Ms: muscovite; Fl: fluorite, Tur: tourmaline.

#### 3.3. Ore Bodies and Mineralogy

The ore bodies of the Damogutu Sn–Fe and Dashishan Sn–Pb–Zn deposits are irregular veins and occur in the skarn zones between granitoid and limestone. The ore bodies are controlled by the faults and are lenticular (Figure 4).

Texturally, ores can be classified as a layered, massive, or vein type (Figure 7a–c). In terms of the occurrence form, they can be garnet-skarn (Figure 7d–g), diopside-skarns (Figure 7h), epidotes-skarn (Figure 7i) or quartz veins (Figure 7j). Garnet-skarn ores can be divided into Fe (Figure 7d,e) and Pb–Zn garnet ores (Figure 7f,g), which are the most important types of ore in the Damogutu Sn–Fe and the Dashishan Sn–Pb–Zn deposits, respectively. Furthermore, using a handheld XRF (X-ray fluorescence) instrument, garnet and magnetite were determined to also be very important Sn-hosting minerals, and Sn was as an isomorphism hosting in the lattice of these minerals because of Sn's siderophile affinity.

This kind of Sn is also very common in the Huanggangliang skarn deposit [34], but with little economic value. Diopside and epidote ore types, which mainly contain Pb and Zn (Figure 7h,j), are very common in the Dashishan Sn–Pb–Zn deposit but are scarce in the Damogutu Sn–Fe deposit. The quartz-vein ore type mainly contains cassiterite (Figure 7j) and is only found in the Damogutu Sn–Fe deposit.



**Figure 7.** Photos of different ore types: (**a**) layered magnetite ore; (**b**) massive magnetite ore; (**c**) vein-type magnetite ore; (**d**) garnet-skarn type magnetite ore; (**e**) garnet-skarn type magnetite ore with specularite; (**f**) garnet-skarn type galenite ore; (**g**) garnet-skarn type sphalerite ore; (**h**) diopside-skarn type sphalerite ore; (**i**) epidote-skarn type galenite ore; (**j**) quartz-vein type cassiterite ore. Grt: garnet, Mt: magnetite, Gn: galenite, Sp: sphalerite, Sp: specularite, Di: diopside, Ep: epidote, Cst: cassiterite, Py: pyrite.

The two deposits have different ore assemblages. In the Damogutu Sn–Fe deposit, magnetite and cassiterite are the dominant ore minerals, with minor specularite, arsenopyrite, pyrite, chalcopyrite, among others (Figure 8a–d). In contrast, in the Dashishan Sn–Pb–Zn deposit, the most important ore minerals are galena and sphalerite (Figure 8e,f), followed by magnetite, specularite, pyrite, and chalcopyrite.



**Figure 8.** Photomicrographs of ore minerals. (**a**) subhedral magnetite; (**b**) acicular specularite replacing magnetite; (**c**) euhedral arsenopyrite; (**d**) anhedral pyrite and chalcopyrite replacing magnetite; (**e**) anhedral galena and sphalerite and residue of chalcopyrite; (**f**) anhedral chalcopyrite replaced by pyrite and sphalerite. Mt: magnetite, Spe: specularite, Apy: arsenopyrite, Py: pyrite, Ccp: chalcopyrite, Gn: galena, Sp: sphalerite.

## 3.4. Periods and Stages of Mineralization

Based on the cross-cutting relations and mineral assemblages, the mineralization processes at the Damogutu Sn–Fe and Dashishan Sn–Pb–Zn deposits took place in three main intervals: (1) the granite crystallization period, (2) the main metallogenic period, and (3) the supergenic period. The main metallogenic period can be further divided into three stages (Figure 9):





The prograde alteration stage (Stage I) is marked by the crystallization of anhydrous silicate minerals, such as wollastonite, diopside, and garnet. This stage was not the major metallogenic stage, and little magnetite was formed.

The retrograde alteration stage (Stage II) is characterized by the formation of hydrosilicate minerals, such as epidote, actinolite, and amphibole. With the reduction of temperature, anhydrous silicate minerals were replaced by hydrosilicate minerals, and a high amount of magnetite was precipitated (also known as the magnetite stage). Furthermore, plagioclase, K-feldspar, muscovite, quartz, cassiterite, and specularite were formed in this stage. This stage was the main metallogenic stage of the Damogutu Sn–Fe deposit.

The quartz–sulfide stage (Stage III) is characterized by the precipitation of quartz and sulfide minerals. This was the last stage of the main metallogenic period; it occurred at a lower temperature and fewer skarn minerals were formed. The main minerals formed in this stage were quartz, fluorite, pyrite, chalcopyrite, arsenopyrite, sphalerite, and galena. This stage was the major metallogenic stage in the Dashishan Sn–Pb–Zn deposit.

For this study, granitoid and ore samples were collected. The granitoid samples, including syenogranites and fine-grained syenogranites, were collected at the surface. The sampling locations are shown in Figure 3. The ore samples were mainly collected at the ore heap.

Zircons were separated using heavy-liquid and magnetic separation methods at the Langfang Geoscience Exploration Technology Service Company Limited, and the cathodoluminescence (CL) images were obtained by a Tescan Mira 3 field emission scanning electron microscope from Beijing GeoAnalysis Company Limited. In situ U–Pb dating was carried out by a New Wave 193ss Laser Ablation and Agilent 7500a ICP-MS at the State Key Laboratory of Geological Process and Mineral Resources (GPMR), China University of Geosciences (Beijing). The diameter of the laser spot was 36 µm, and helium was used as a carrier gas to transport the ablated aerosol from the laser-ablation cell to the ICP-MS torch. Isotopic ratios and element concentrations were calculated using GLITTER 4.4.1 (Macquarie University) and were corrected for both the depth-dependent element and U–Pb isotope fractionation effect and the instrumental mass bias using Harvard zircon 91500 as an external standard [35], and QH as a secondary standard [36]. The zircon trace element concentrations were calibrated using 610 glass as a reference standard and <sup>29</sup>Si as the internal calibrant. Common Pb concentrations were evaluated using the method of Andersen [37]. The weighted average of the ages was evaluated with a 95% confidence level.

Analyses of major and trace element were done at the analytical laboratory of the Beijing Research Institute of Uranium Geology. Major elements were analyzed by XRF using a Philips PW244 sequential spectrometer with a 1–5% precision rate. Trace elements were analyzed using a Finnigan MAT Element I–type ICP-MS with a precision rate > 5%. The Chinese national standards GB/T14506 and DZ/T0223 were considered for the analytical process and for quality control. Details of the test method were introduced in Reference [38].

Analyses of stable isotope analyses, including sulfur and lead isotopic composition, were undertaken using a Finnigan MAT–253 mass spectrometer at the Isotope laboratory of Beijing Research Institute of Uranium Geology. For sulfur isotope analyses, the sulfide samples were oxidized to sulfate by Cu<sub>2</sub>O. The sulfate was then purified to pure BaSO<sub>4</sub> by the carbonate-zinc oxide semi-melt method, and SO<sub>2</sub> was prepared by the V<sub>2</sub>O<sub>5</sub> oxide method. The sample pre-treatment procedure described by Robin et al. [39] was used for lead isotope analyses. This involved washing the sulfide minerals with HCl, dissolving them in the aqua regia under heating, and finally, converting them to an HBr chromatographic solution.

The composition of single inclusions was determined using a LabRam HR laser Raman spectrometer (laser wavelength: 532 nm; the spectrometer resolution:  $<0.65 \text{ cm}^{-1}$ , horizontal spatial resolution:  $<1 \mu m$ , and longitudinal spatial resolution:  $<2 \mu m$ ) at the Fluid Inclusion Research Laboratory, Institute of Geology and Geophysics, Chinese Academy of Sciences.

The micro thermometric measurements of inclusions were carried out using a Carl Zeiss Axioskop 40 Optical Microscope and a THMSG 600 freezing-heating unit at the Beijing Institute of Geology for Mineral Resources. The temperature was controlled between -196 and 600 °C, and the cooling/heating rate ranged from 0.01 to 130 °C /min.

## 5. Results

#### 5.1. U–Pb Age and Trace Element Composition of Zircon

The trace element composition and U–Pb isotope data of zircons from syenogranite (DMGT-1) and fine-grained syenogranite (DSS–5) are shown in Tables S1 and S2, respectively. According to the CL (Cathode Luminescence) images, most zircons in these two samples had similar characteristics, such as euhedral crystals with length–width ratios ranging from 2:1 to 4:1 and a commonly concentric oscillatory zone (Figure 10a,b). In terms of the trace element composition, the zircons showed relatively high Th and U concentrations, high Th/U ratios (>0.4) (Table S1), and left-dipping REE (Rare Earth

Elements) or HREE (Heavy Rare Earth Elements) enrichment distribution curves with Eu-negative and Ce-positive anomalies (Figure 10c,d). The CL images and trace element compositions all indicated that these zircons are typically magmatic [40–43].



**Figure 10.** Characteristics of the zircons: (**a**,**b**) cathodoluminescence (CL) images of the main analyzed zircon grains; (**c**,**d**) chondrite-normalized REE patterns of the analyzed zircon grains. Chondrite normalizing values were from: (**e**,**f**) U–Pb isotopic diagrams of the syenogranite and fine-grained syenogranite, including zircon U–Pb concordia diagrams and <sup>206</sup>Pb/<sup>238</sup>U probability density histograms.

Seventeen zircons of the syenogranite (DMGT-1) were chosen for LA-ICP-MS U–Pb dating, and twelve data points fell near the U–Pb concordia curve, yielding a weighted mean  $^{206}$ Pb/ $^{238}$ U age of 148.8 ± 1.1 Ma (Mean Standard Weight Deviation or MSWD = 0.083) (Table S2 and Figure 10e) (the other five data were located far from the concordant curve due to the suspected lead loss). Twenty zircons of the fine-grained syenogranite (DSS-5) were analyzed, and ten valid data points were obtained with a weighted mean  $^{206}$ Pb/ $^{238}$ U age of 143.5 ± 3.3 Ma (MSWD = 3.8) (Table S2 and Figure 10f) (the other ten data were located far from the concordant curve due to the suspected lead loss). These two ages were consistent within the error range and represented the best estimates of the crystallization ages of the syenogranite and fine-grained syenogranite, suggesting that the two may have been formed from the same magmatic event in the Late-Yanshanian period.

#### 5.2. Major and Trace Element Composition of Granites

As shown in Table S3, the syenogranite and fine-grained syenogranite had similar major element compositions and constituted peraluminous granite (Figure 11), with high SiO<sub>2</sub> (73.64–78.75 wt %), Al<sub>2</sub>O<sub>3</sub> (11.90–13.88 wt %), and alkali (6.93–9.25 wt %) contents and low Fe<sub>2</sub>O<sub>3</sub><sup>T</sup> (0.03–1.57 wt %), MgO (0.05–0.24 wt %), and CaO (0.06–1.27 wt %) contents.



**Figure 11.** Diagrams of the major elements and trace elements: (**a**) Tas diagram (after [44]); (**b**) A/NK versus A/CNK diagram (after [45]); (**c**) chondrite-normalized REE; and (**d**) N-MORB-normalized trace element spider diagram. The values of chondrite and N-MORB are from Boynton [46] and Sun and McDonough [47], respectively. A/NK = molar  $Al_2O_3/(Na_2O + K_2O)$ ; A/CNK = molar  $Al_2O_3/(CaO + Na_2O + K_2O)$ .

Except for a few samples, the trace element compositions of syenogranite and fine-grained syenogranite were also very similar (Table S3). The chondrite-normalized REE distribution patterns showed a gently right-dipping V-type curve with high  $\sum$ REE (45.88–324.27 ppm) and an obvious Eu-negative anomaly (0.01–0.16) (Figure 11c). According to the N-MORB-normalized trace element patterns (Figure 11d), nearly all syenogranites and fine-grained syenogranites showed enrichment of high-strength elements (e.g., Zr, Y, W, Nb, La, and Ce) and depletion of large ion lithophile elements (e.g., Ba, Sr, Eu, P, and Ti).

#### 5.3. Stable Isotope Geochemistry

## 5.3.1. Sulfur Isotope

The main sulfide minerals in the Damogutu Sn–Fe and Dashishan Sn–Pb–Zn deposits are arsenopyrite, pyrite, pyrrhotite, chalcopyrite, galena, sphalerite, and molybdenite. The  $\delta^{34}S_{V-CDT}$  values of the deposits are listed in Table S4 and can be used to characterize the source of sulfur [48,49]. For the former deposit, two arsenopyrites and one pyrite were chosen for sulfur isotope analyses, and three positive  $\delta^{34}S_{V-CDT}$  values close to zero were obtained (2.9‰ and 2‰ for the two arsenopyrites and 1.1‰ for the pyrite). For the latter deposit, five samples were chosen. One arsenopyrite had a

 $\delta^{34}S_{V-CDT}$  value of -1.9%, two galenas had  $\delta^{34}S_{V-CDT}$  values of -1.2% and 1.3%, and two sphalerites had  $\delta^{34}S_{V-CDT}$  values of -0.1% and -4.3%. The range for  $\delta^{34}S_{V-CDT}$  values in sulfides from both deposits were relatively narrow.

## 5.3.2. Lead Isotope

The lead isotope ratios of minerals usually depend on the initial concentration of U, Th, and the minerals' age [50]. Compared to ordinary minerals, the lead isotopic composition of the Pb-bearing minerals usually remained constant once the mineral was formed, because of their low U/Pb and Th/Pb ratios [51,52]. Therefore, investigation of the lead isotope is important for understanding the genesis of Pb-bearing minerals [53,54].

The lead isotope ratios of sulfide minerals from the Damogutu Sn–Fe and Dashishan Sn–Pb–Zn deposits were shown to be similar and are listed in Table S5. For the three sulfide minerals from the Damogutu Sn–Fe deposit, including two arsenopyrites and one pyrite, ratios of 38.181–38.474 <sup>208</sup>Pb/<sup>204</sup>Pb, 15.562–15.629 <sup>207</sup>Pb/<sup>204</sup>Pb, and 18.280–18.428 <sup>206</sup>Pb/<sup>204</sup>Pb were obtained. For the five sulfide minerals (one arsenopyrite, two galenas, and two sphalerites) from the Dahsishan Sn–Pb–Zn deposit, ratios of 37.976–38.301 <sup>208</sup>Pb/<sup>204</sup>Pb, 15.517–15.587 <sup>207</sup>Pb/<sup>204</sup>Pb, and 18.120–18.289 <sup>206</sup>Pb/<sup>204</sup>Pb were obtained.

## 5.4. Characteristics of Inclusions

The inclusions from the Damogutu Sn–Fe and the Dashishan Sn–Pb–Zn deposits showed similar characteristics. Composition determination and microthermometric measurements were conducted on inclusions in quartz (from the granite crystallization period), garnet and diopside (from Stage I), and quartz (from Stage III). The fluid inclusions in the minerals from Stage II—minerals such as epidote, actinolite, and amphibole—were too small.

## 5.4.1. Types and Petrography of Fluid Inclusions

The inclusions of these two deposits were divided into three categories, and their features are described below.

The melt inclusions, which are common in quartz from granite and garnet from skarn, mainly comprise a solid phase at normal temperature and cannot be fused when the temperature is higher than 500 °C. Those in quartz from granite are usually small (10–20  $\mu$ m) with an irregular shape (Figure 12a), while those in garnet are relatively large (>40  $\mu$ m) (Figure 12b).

The fluid–melt inclusions, which are very common in quartz from granite and garnet, are composed of solid, liquid, and vapor at room temperature, and the solid phase showed similar features to those of the melt inclusions (Figure 12c,d). The solid–liquid ratios varied widely (1:5–5:1) and were usually greater in quartz than granites.

The fluid inclusions are the most common type and could be found in granite, skarn minerals, and quartz veins (Figure 12e–i). Based on their components, they can be divided into L-type and S-type fluid inclusions. L-type fluid inclusions consisted of liquid and vapor phases at room temperature, and their vapor phase occupied <50 vol %. These inclusions were oval or irregular, 6–20  $\mu$ m in diameter, and had a vapor–liquid ratio of 1:3–1:6 (Figure 12e–g). The S-type fluid inclusions had a composition that was similar to that of the fluid–melt inclusions but with daughter minerals (Figure 12h,i), which disappeared when the temperature was higher than 400 °C. These inclusions are only found in the quartz vein (Stage III).



**Figure 12.** Photomicrographs of inclusions: (**a**) melt inclusion in quartz from granite; (**b**) melt inclusion in garnet; (**c**) fluid–melt inclusion in quartz from granite; (**d**) fluid–melt inclusion in garnet; (**e**) L-type fluid inclusion in quartz from granite; (**f**) L-type fluid inclusion in garnet; (**g**) L-type fluid inclusion with different vapor–fluid ratios in quartz vein; (**h**) L-type and S-type fluid inclusions in quartz vein; (**i**) S-type inclusions in quartz vein. S: solid; L: liquid; V: vapor.

# 5.4.2. Inclusions in Quartz from Granites

The quartz from granites was usually pure with a few inclusions. The inclusions were primarily melt and fluid–melt inclusions (Figure 12a,c) and secondary melt and L-type fluid inclusions (Figure 12e).

The fluid–melt inclusions were relatively large  $(10-20 \,\mu\text{m})$  with an irregular shape. The solid–liquid ratios ranged from 5:1 to 1:5 and were usually greater than 1:1 (Figure 12c). The laser Raman spectroscopic analyses showed that the solid phase of the fluid–melt inclusions was mainly and radite  $(875 \,\text{cm}^{-1})$  and fluorite  $(908 \,\text{cm}^{-1}, 926 \,\text{cm}^{-1}, 944 \,\text{cm}^{-1}, 1359 \,\text{cm}^{-1})$ , and 1393  $\text{cm}^{-1}$ ) (Figure 13a).

Melt inclusions were usually situated in the center of the quartz and were relatively small (10–20  $\mu$ m) with irregular shapes.

Fluid inclusions were L-type and mainly had a linear distribution along growth zones or micro-cracks in the host quartz. Their compositions were similar to those of the liquid and vapor phases of fluid–melt inclusions. According to microthermometric measurements, the temperature exhibited pronounced modes at 168.5–251.3 °C, and the estimated salinities were 1.2–4.3 wt % NaCl equiv. (Table S6 and Figure 14a,b).



**Figure 13.** Laser Raman spectra of fluid–melt inclusions in quartz from granite: (**a**) Laser Raman spectra of solid phase; (**b**) Laser Raman spectra of liquid phase; (**c**) Laser Raman spectra of vapor phase. S: solid; L: liquid; V: vapor. Gn: garnet; Fl: fluorite.

#### 5.4.3. Inclusions in Garnet (Stage I)

There were a large number of inclusions in the garnet of skarn, including melt, fluid–melt, and L-type fluid inclusions (Figure 12b,d,f). These melt inclusions were bigger than those in the quartz from granite (>40  $\mu$ m) and usually possessed the crystal shape of garnet (Figure 12b). The fluid–melt and L-type fluid inclusions were small (approximately 20  $\mu$ m) and oval (Figure 12d). The laser Raman spectra of inclusions in garnet were masked by the background peaks of the host garnet. Moreover, the homogenization temperature of the L-type fluid inclusions was 230–350 °C, and the estimated salinities were 1.0–14.1 wt % NaCl equiv. (Table S6 and Figure 14c,d).

#### 5.4.4. Inclusions in Quartz from Quartz Veins (Stage III)

In the quartz vein (Stage III), there were only fluid inclusions, which could be divided into L–types and S–types (Figure 12f–h). The L-type fluid inclusions (10–20  $\mu$ m) were mainly liquid-rich inclusions, but their vapor–liquid ratios varied (approximately 1:2.5–1:10) (Figure 12g). The main component of the gas and liquid phases was H<sub>2</sub>O. The homogenization temperature was 104–224 °C, and the estimated salinities are 3.4–13.6 wt % NaCl equiv. (Table S6 and Figure 14e,f). The S-type fluid inclusions (6–20  $\mu$ m) were associated with the L-type fluid inclusions and had similar gas and liquid

phase components, with a cubic halite solid phase (Figure 12a). The homogenization temperature was 409–410 °C, and the estimated salinities were 48.4–48.6 wt % NaCl equiv. (Table S6 and Figure 14e,f).



**Figure 14.** Histograms of homogenization temperatures and salinities of fluid inclusions: (**a**,**b**) L-type fluid inclusions in quartz from granite; (**c**,**d**) L-type fluid inclusions in garnet; (**e**,**f**) L-type and S-type fluid inclusions in quartz vein.

## 6. Discussions

#### 6.1. Ore-forming Event Age

Syenogranites from the Damogutu Sn–Fe deposit and fine-grained syenogranites from the Dashishan Sn–Pb–Zn deposit both show close relationships with the ore bodies in terms of spatial distribution (Figure 12). Although no obvious skarn mineral was found in these two granites, the fluid–melt inclusions in quartz contained garnet and fluorite (Figure 13a), illustrating that these two granites are directly involved in skarnization and that they are the source granitoid of Damogutu and Dashishan. Therefore, the ore-forming event ages of the Damogutu Sn–Fe and Dashishan Sn–Pb–Zn deposits are 148.8  $\pm$  1.1 and 143.5  $\pm$  3.3 Ma (Figure 10), respectively.

According to previous studies, Sn-polymetallic mineralization, such as that of the Huanggangliang (136.5–134.6 Ma) [26], Weilasituo (135–138 Ma) [6], Yindu (135 Ma) [55], Baiyinchagan (141.4 Ma) [56], and Dajing (146–133 Ma) [57] took place during the Late-Yanshanian period (approximately 150–130 Ma), which is known as the most important Sn-polymetallic mineralization period. Damogotu and Dashishan formed during this metallogenic epoch.

## 6.2. Geochemical Evolution of the Source Granitoids

Two main types of Sn-polymetallic deposits (magmatic–hydrothermal type and skarn type), whose metallogenic granitoids are all highly evolved granites, formed during the Late-Yanshanian period. In this chapter, we discuss the different geochemical characteristics of the source granitoid of these two deposit types based on previous research.

#### 6.2.1. Oxygen Fugacity

Oxygen fugacity is one of the most important physicochemical parameters during the evolution of magma and can determine the precipitation and migration of elements [58].

Trail et al. [59] proposed that the magma oxygen fugacity can be calculated considering the zircon Ce anomaly and the Ti–in–zircon temperature through a new empirical formula:

$$\ln(Ce/Ce^*) = (0.1156 \pm 0.0050) \times \ln(fO_2) + \frac{13860 \pm 708}{T_{zircon}(K)} - 6.125 \pm 0.484$$
(1)

Watson et al. [60] presented the formula for the Ti–in–zircon temperature:

$$T_{zircon}(K) = \frac{5080 \pm 30}{(6.01 \pm 0.03) - \log(Ti_{zircon})}$$
(2)

In general, the  $Ce/Ce^*$ , which represents Ce anomalies, was computed by La–Pr interpolation. However, because of the influence of tiny inclusions and the low concentrations of La and Pr, the attained value had large errors. Hence, we used the thermodynamically based lattice strain model to calculate  $\delta Ce$ , which was described in detail by Blundy and Wood [61].

As shown in Table S1, the calculated  $\log(fO_2)$  and the Ti–in–zircon temperature of syenogranite (DMGT-1) from Damogutu ranged from –34.13 to –8.06 and from 631 to 1128 °C, respectively. The calculated  $\log(fO_2)$  and the Ti–in–zircon temperature of fine-grained syenogranite (DSS-5) from Dashishan ranged from –34.21 to –7.52 and from 606 to 807 °C, respectively. In the  $\log(fO_2)$ –T diagram (Figure 15a), the syenogranite (DMGT-1) and fine-grained syenogranite (DSS-5) showed similar  $\log(fO_2)$  values and Ti–in–zircon temperatures coinciding with the granites of Weilasituo and Shuangjianzishan, which indicates that their zircon was formed in a reducing environment [20]. Therefore, considering the line of evidence above, we concluded that the granites at Damogutu and Dashishan formed initially under reducing conditions.

In addition, the whole-rock  $Fe_2O_3$ /FeO ratio was one of the most important indexes reflecting oxygen fugacity [62]. In the  $Fe_2O_3$ /FeO-SiO\_2 diagram (Figure 15b), granitoids from Damogutu and Dashishan mainly belong to the ilmenite series. However, compared to granitoids from Weilasituo and Shuangjianzishan,  $Fe_2O_3$ /FeO ratios were higher and a lot of magnetite was formed, which all means that the solidification of the magma proceeded with relatively high oxygen fugacity, and thus, the oxygen fugacity of the late stage of magma activity increased.



**Figure 15.** Diagrams of oxygen fugacities: (**a**)  $\log(fO_2)$ -T diagram (after [58]); (**b**) Fe<sub>2</sub>O<sub>3</sub>/FeO-SiO<sub>2</sub> diagram [62].

The increase in oxygen fugacity may be related to deep-seated faults. In addition to granites from Dashishan and Damogutu, many magnetites have been found in granites from Huanggangliang, Beidashan, Wushijiazi, and Haliheiba pluton, which are all located near the Great Khingan Main Ridge Fault. It is noteworthy that a mass of large-scale skarn deposits, such as those from Huanggangliang, Baiyinnuoer, and Haobugao, are also located near the Great Khingan Main Ridge Fault.

## 6.2.2. Evolution Degree

The granites from Damogutu and Dashishan have a close spatio–temporal relationship (Figures 1 and 10) and show similar petrographic and geochemical characteristics (Figure 5, Figure 10, Figure 12, and Figure 15). Furthermore, in the Harker diagrams (Figure 16), granites from Damogutu and Dashishan exhibited a good linear relationship, suggesting that the granites from Damogutu and Dashishan resulted from magmatic differentiation of the same magma.

On the other hand, these granites all showed highly evolved features, such low concentration of dark-colored minerals, a lot of albite, and formation of microcline, miarolitic cavity, pegmatite mass, a greisen vein, fluorite, and tourmaline (Figures 5 and 6) [63,64]. The gently right-dipping V-type REE distribution pattern (Figure 11c) also confirmed the highly evolved nature of the granites [63,65]. However, both the syenogranite from the Damogutu Sn–Fe deposit and the fine-grained syenogranite showed differences. Firstly, the fine-grained syenogranite had less biotite and more microcline than syenogranite and some amazonite. Secondly, the fine-grained syenogranite showed smaller Nb/Ta and Zr/Hf ratios (Figure 17a) and was located nearer to Rb in the Rb–Ba–Sr triangular diagram, which are two of the most important geochemical indicators of the degree of granite evolution [63,66,67]. All geological and geochemical features indicated the syenogranite formed in the early stage of magmatic evolution and the fine-grained syenogranite formed in the late stage.



**Figure 16.** Harker diagrams: (**a**) Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> diagram; (**b**) CaO–SiO<sub>2</sub> diagram; (**c**) Fe<sub>2</sub>O<sub>3</sub><sup>T</sup>–SiO<sub>2</sub> diagram; (**d**) MgO–SiO<sub>2</sub> diagram; (**e**) TiO<sub>2</sub>–SiO<sub>2</sub> diagram; (**f**) Na<sub>2</sub>O–SiO<sub>2</sub> diagram.



**Figure 17.** Discrimination diagram of granite's evolution degree: (**a**) Nb/Ta–Zr/Hf diagram (after [63]); (**b**) Rb–Ba–Sr triangular diagram.

## 6.3. Source of Ore-Forming Fluids

The  $\delta^{34}S_{V-CDT}$  values of the sulfide minerals from Damogutu ranged from 1.1 to 2.9‰, and those from Dashishan ranged from -4.3 to -0.1‰, which were similar to the values of most Sn-polymetallic deposits. All of these values converged at 0‰ (Figure 18). On the other hand, the lead isotopic data of Damogutu and Dashishan show features that were similar to those of Huanggangliang and Weilasituo, which were located between the mantle and the upper crust's Pb evolutionary curves (Figure 19). Hence, the sulfur and lead isotopic signatures of Damogutu and Dashishan suggest that the ore-forming fluids were sourced from the underlying granitoids and are compatible with other Sn-polymetallic deposits from the Southern Great Kahingan Range.



**Figure 18.** Sulfur isotopic compositions of different Sn-polymetallic deposits: Huanggangliang [68]; Baiyinnuoer [69]; Haobugao [70]; Bianjiadayuan [71]; Dajing [72]; Baiyinchagan [73]; and Weilasituo (unpublished).



**Figure 19.** Lead isotopic composition of different Sn-polymetallic deposits: (**a**) <sup>207</sup>Pb/<sup>204</sup>Pb–<sup>206</sup>Pb/<sup>204</sup>Pb diagram; (**b**) <sup>208</sup>Pb/<sup>204</sup>Pb–<sup>206</sup>Pb/<sup>204</sup>Pb diagram. The Pb tectonic models are from Zartman and Doe (after [74]). The data regarding Huanggangliang are from Liu et al. [68] and Yao et al. [75]. A: mantle; B: orogenic belt; C: upper crust; D: lower crust.

Previous researchers have suggested that Sn–Pb–Zn mainly comes from Late-Yanshanian granitoids [68,76]; however, the Fe concentration of granites is too low to provide sufficient Fe to form the mineralization, and thus, mainly came from basaltic andesite [77], which is an important component of Dashizhai formation. If the basaltic andesite was the source of Fe for Fe mineralization in the Late-Yanshanian period, then these rocks would have been altered by magmatic or hydrothermal activity. However, there is no evidences of alteration in the basaltic andesite near the deposits, which means that the basaltic andesite could not have supplied Fe. The granitoids near the deposit show evidence of greisenization (Figure 6e–g) and skarnization (Figure 13a), and a large amount of magnetite has been found in the biotite. Hence, we believe that the Fe of the Damogutu Sn–Fe deposit, like Sn–Pb–Zn, came from syenogranite.

# 6.4. Evolution of the Ore-Forming Fluids

The ore–forming fluids of most magmatic–hydrothermal Sn-polymetallic deposits experienced a continuous evolution from the magmatic to a hydrothermal stage [20]. The features of the fluid, fluid–melt and melt inclusions indicate that the ore-forming fluid of the Damogutu Sn–Fe and Dashishan Sn–Pb–Zn deposits also experienced this process.

In the late granite crystallization period, the granite was not completely consolidated. The inclusions were mainly melt and fluid–melt inclusions, and the solid–liquid ratios were usually greater than 1:1 (Figure 12a,c), which means that magma was the main carrier of metals during the granite crystallization period. It is worth noting that the solid phase of the fluid–melt inclusions of this period mainly consisted of andradite and fluorite (Figure 13a), which means that skarnization began before the granite was completely consolidated and the fluid exsolution occurred at the late stage. The L-type fluid inclusions showed characteristics of secondary inclusions, consequently, the low temperature and salinity of the L-type fluid inclusions did not indicate ore-forming fluid (Figure 14a,b and Figure 20).



Figure 20. ω(NaCl)-Th diagram of L-type fluid inclusions from Damogutu and Dashishan.

At the prograde alteration stage (Stage I), the ore–forming fluid was completely the magmatichydrothermal transitional fluid, and the hydrothermal component started to increase. At this stage, the fluid inclusions in diopside are characteristics with high homogenization temperature and relatively uniform salinity, while for garnet the temperature and salinity exhibit a good linear relationship (Figure 20). At the beginning of this stage, the ore–forming fluid had high temperature (310–360 °C) and moderate salinity (4.3–10.2 wt %), and skarnization caused the sudden increase of salinity. As the skarnization progressed, the temperature and salinity gradually decreased. At the quartz–sulfide stage (Stage III), the ore-forming fluid completely corresponded to a purely hydrothermal stage, and the inclusions were all L-type and S-type fluid inclusions without any melt or melt–fluid inclusions (Figure 12g–i). Compared to the prograde alteration stage, the homogenization of this stage was lower (104–224 °C), but the salinity increased (3.4–13.6 wt % NaCl equiv.) (Figure 18e,f, and Figure 20). The appearance of S-type fluid inclusions means that the salinity of the ore-forming fluid was higher (Table S6). Relatively concentrated homogenization temperature and dispersed salinity indicate boiling of fluid at this stage, which lead to the coexistence of L–type and S–type inclusions (Figure 12h), and is in favor of mineralization.

# 6.5. Genetic Model

The Late-Yanshanian period (155–114 Ma) was one of the most important periods of granitoid magma intrusion in the southern Great Khingan Range (Figures 1b and 2). Under the influence of deep-seated faults, oxygen fugacity increased at the late stage of magma activity, leading to the crystallization of magnetite. The syenogranites and fine-grained syenogranites formed during different stages of magmatic evolution, and showed different geological and geochemical features, leading to different skarnization and formed different types of deposits.

By combining our results with previous studies, we propose two genetic models for the skarn Sn–Fe and Sn–Pb–Zn deposits in the southern Great Khingan Range:

(1) The skarn Sn–Fe deposit formed during the early stages of magmatic evolution, due to the contact metamorphism with the host limestones. The decrease in temperature and increase in oxygen fugacity during the retrograde stage of skarnization caused the introduction of Fe and Sn with the formation of large amounts of magnetite and minor specularite; Sn entered into the crystal lattice of magnetite and garnet forming isomorphous Sn, which is common in the Huanggangliang skarn deposit [34] (Figure 21).

(2) With the increasing fractionation of the granitic magma, the skarn Sn–Pb–Zn deposits formed due to the reaction with the carbonates. Continuous evolution of the melt led to a progressive enrichment in Sn, Pb, and Zn, and decreased in Fe in the fluids. The skarnization led to the formation of Sn-rich garnet ("isomorphous Sn" [34]), sphalerite, galena, and rare magnetite given the low availability of Fe (Figure 21).



**Figure 21.** Metallogenic model of the skarn Sn-polymetallic deposit in the southern Great Khingan Range.

# 7. Conclusions

(1) The Damogutu Sn–Fe and Dashishan Sn–Pb–Zn deposits were formed in the Late-Yanshanian period (approximately 148–143 Ma).

(2) The source granitoid evolved at an early stage in a reducing environment, while the oxygen fugacity increased at a late stage through the influence of a deep-seated fault.

(3) The granites from Damogutu and Dashishan experienced a similar evolution path and the same magmatic activity, but fine-grained syenogranite from Dashishan, showed a higher degree of evolution than the syenogranite from Damogutu.

(4) Damogutu Sn–Fe and Dashishan Sn–Pb–Zn deposits share the same source of ore-forming fluids, and Fe, Sn, Pb, and Zn all derived from Late-Yanshanian granitoids.

(5) The ore-forming fluid experienced a continuous evolution process from magmatic to hydrothermal fluid, and the magmatic–hydrothermal transitional fluid played a very important role in skarnization and mineralization.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2075-163X/9/7/418/s1, Table S1: Trace element of the granites' zircons from Damogutu and Dashishan; Table S2: LA-ICP-MS U–Pb isotopic analysis results of the granites' zircons from Damogutu and Dashishan; Table S3: Major and trace elements data of the granites from Damogutu and Dashishan; Table S4: Sulfur isotopic composition of sulfide minerals from Damogutu and Dashishan; Table S5: Lead isotopic composition of sulfide minerals from Damogutu and Dashishan; Table S6: Microthermometric data of fluid inclusions from Damogutu and Dashishan.

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