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Article

Occurrences of Niobium and Tantalum Mineralization in Mongolia

Jaroslav Dostal [1,*] and Ochir Gerel [2]

[1] Department of Geology, Saint Mary's University, Halifax, NS B3H 3C3, Canada
[2] Geoscience Centre, Mongolian University of Science and Technology, Baga Toiruu 34, Ulaanbaatar 14191, Mongolia
* Correspondence: jarda.dostal@smu.ca

Abstract: Niobium and tantalum are two rare metals that have similar physical and chemical properties and occur together in nature. They are considered to be strategic and critical materials for the economy and national security of many industrial countries. Both elements are on the 2022 List of Critical Minerals of the USA as well as on the European Union's List of Critical Raw Materials. They rarely substitute for common elements in rock-forming minerals but are essential components in a range of rare minerals, particularly oxides and subordinately silicates. The economically important minerals are oxides. The columbite-tantalite and pyrochlore-microlite groups are the most common Ta- and Nb-bearing minerals. In Mongolia, primary niobium and tantalum mineralization includes two main types. The first type is mineralization associated with alkaline to peralkaline granites, pegmatites and syenites whereas the second type is related to the lithium-fluorine-rich peraluminous granites and related rocks (pegmatites and ongonites). The host rocks of both types of mineralization are the fractionated felsic rocks, which contain the primary magmatic ore assemblages associated with fractionation of magma rich in rare metals. Both assemblages were subsequently overprinted by the late magmatic to hydrothermal fluids, which remobilized and enriched the original mineralization. The newly formed ore mineral assemblages display complex replacement textures. In the case of peralkaline felsic rocks the processes produced the mineralization of Zr, Nb, heavy REE, Y, U, Th and Ta whereas peraluminous Li-F felsic rocks contain mainly mineralization of Sn, W, Ta, Li, and Nb. Mongolia hosts several promising occurrences of both types of Nb-Ta mineralization. However, they have not yet been sufficiently explored. Currently, the most promising is the occurrence in the Devonian Khalzan Buregtei peralkaline granites in northwestern Mongolia, where Nb-Ta is associated with REE and Zr mineralization. Mesozoic carbonatites of southern Mongolia do not host significant Nb and Ta mineralization.

Keywords: niobium; tantalum; mineralization; Mongolia; granite; pegmatite; rare metals; Central Asian Orogenic Belt

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1. Introduction

Niobium (Nb) and tantalum (Ta) are two transition metals that have similar physical and chemical properties and thus occur together in nature. They have been included into "rare metals", e.g., [1,2]. More recently, these two elements have been considered to be strategic and critical materials for the economy and national security of many industrial countries. Both elements are on the 2022 List of Critical Minerals of the USA as well as on the European Union's List of Critical Raw Materials. The main uses of niobium are in the production of high-strength steel alloys and superalloys needed in the aerospace industry, pipelines and various structural applications. Niobium is also used in making superconducting magnets for magnetic resonance imaging instruments. Tantalum is required for the production of electronic capacitators used in cell phones, computer hard drives, and implantable medical devices as well as in the production of corrosion resistant alloys, gas turbine blades and various superalloys.

Both elements are lithophile and high-field strength (HFSE). Their average crustal abundances are low: ~8 ppm Nb and 0.7 ppm Ta [3]. Compared to other highly incompatible elements such as light rare earth elements, Th and U, they are depleted in continental crust relative to the mantle abundances. They rarely substitute for common elements in rock-forming minerals but are essential components in a range of minerals, particularly oxides and subordinately silicates. The economically important minerals are oxides. Pyrochlore is the main ore mineral for Nb and tantalite is the principal ore mineral for Ta. Both minerals are parts of solid solution mineral groups, which have wide compositional ranges. The composition of two end members of the pyrochlore group is pyrochlore [$(Na,Ca)_2Nb_2O_6(OH,F)$] and microlite [$(Na,Ca)_2$ $Ta_2O_6(O,OH,F)$] whereas tantalite [$(Fe,Mn)Ta_2O_6$] is an end member of the solid solution series with columbite [$(Fe,Mn)Nb_2O_6$]. Other less common oxide minerals such as loparite ([$(Ce,La, Na, Ca, Sr) (Ti, Nb)O_3$]), which is a mineral of the perovskite group and tapiolite $(Fe, Mn)(Ta, Nb)_2O_6$ have a limited economic potential. Niobium and tantalum are also present in some common oxides such as rutile and ilmenite; however, their contents are mostly too low to make them of economic interest. The purpose of the paper is to report data on several promising occurrences of Nb and Ta in Mongolia, particularly on their mineralogical and geological characteristics and resources and to provide new whole-rock chemical analyses on some of the sites. The chemical analyses as well as the description of analytical methods are given in Appendix A. We have chosen Mongolia for the review of Nb and Ta mineralization as it lies between Russia and China, which both have in neighbouring parts of their territories significant reserves of these two rare metals. Nb and Ta occur as minor commodities of REE and Sn-W deposits. The review will be useful for future prospecting and research and for new discoveries of mineralization of these metals.

2. Deposits

Niobium- and tantalum-bearing minerals are relatively common but their economically significant accumulations are rare. The world's production of Nb and Ta ores comes from both primary magmatic deposits as well as secondary (residual and alluvial placer) deposits. In the primary mineralization, these two elements occur together with other rare metals including rare earth elements (REE), Zr, Rb, Cs, Be, Sn and W. According to the geological environment and composition of host rocks, several different types of primary deposits have been recognized [4–6]. In addition, secondary deposits include concentrations formed by weathering of primary deposits (laterites) and by sedimentary processes (placers). Unlike secondary deposits of some other rare metals (e.g., Zr, REE), the secondary Nb-Ta accumulations occur in close association with the primary deposits, e.g., [6]. The secondary deposits are economically important as their mining can be cheaper and their grade can be higher than those of the primary deposits. The three types of the deposits, which can be considered for Mongolia, e.g., [5–8] are:

1. Alkaline and peralkaline granites and syenites (Nb > Ta, also Zr, REE, U, Th).
2. Peraluminous rare metal granites also known as Li-mica albite granite, Li-F granite or apogranites [9] (Ta > Nb, also Sn, Be, Li), related pegmatites and also subvolcanic equivalents-ongonites (topaz-bearing albite-rich peraluminous microleucogranites) (Ta > Nb, also Sn, W).
3. Carbonatites and associated alkaline silicate rocks (Nb > Ta, also REE, Zr, P).

2.1. Alkaline and Peralkaline Granites and Syenites

Alkaline igneous rocks refer to alkali-rich rocks that contain certain sodium- or potassium rich minerals (feldspathoids, alkali amphiboles or pyroxenes). Peralkaline rocks are alkaline rocks with molecular $(Na_2O + K_2O) > Al_2O_3$ (i.e., agpaitic index >1). Alkaline igneous rocks occur in intraplate environments, such as continental rifts but also in post-collisional to post-orogenic settings. Evolved alkaline rocks, especially peralkaline syenites and granites, contain high concentrations of several incompatible trace elements and halogens including fluorine and chlorine. As a result, the rocks could host mineral deposits of Zr, Nb, Y and REE. An enrichment of these elements in peralkaline rocks clearly distinguishes them from mineralized peraluminous equivalents. Their high concentrations are, in part, due to their high solubility in peralkaline melts, which delays crystallization of respective minerals until the last stages of magma evolution [10,11]. Thus, in many localities, ore minerals are disseminated throughout highly evolved rocks. Additionally, deposits in peralkaline rocks have undergone further concentrations of trace elements including HFSE and REE through late/post-magmatic metasomatic/hydrothermal processes [10,12]. These elements are mobile in fluids that are enriched in F and Cl, such as those of accompanying peralkaline magmas. The mineralized peralkaline rocks are characterized by the development of pervasive post-magmatic alteration suggesting that hydrothermal processes play an important role in the origin of the HFSE and REE deposits [13,14].

Peralkaline granitic intrusions with Nb-Ta mineralization occur in northwestern (Khalzan Buregtei, Ulaan Tolgoi, Ulaan Del) and southern (Khanbogd) Mongolia (Figure 1) and are described below. In addition to the mineralization described here, there are several other promising rare metal occurrences associated with peralkaline granites in northwestern and northern Mongolia. They include Tsakhir, Shar Tolgoi and Maihan Uul in northwestern Mongolia and Altan Boom and Dargia Uul in northern Mongolia (Figure 1).

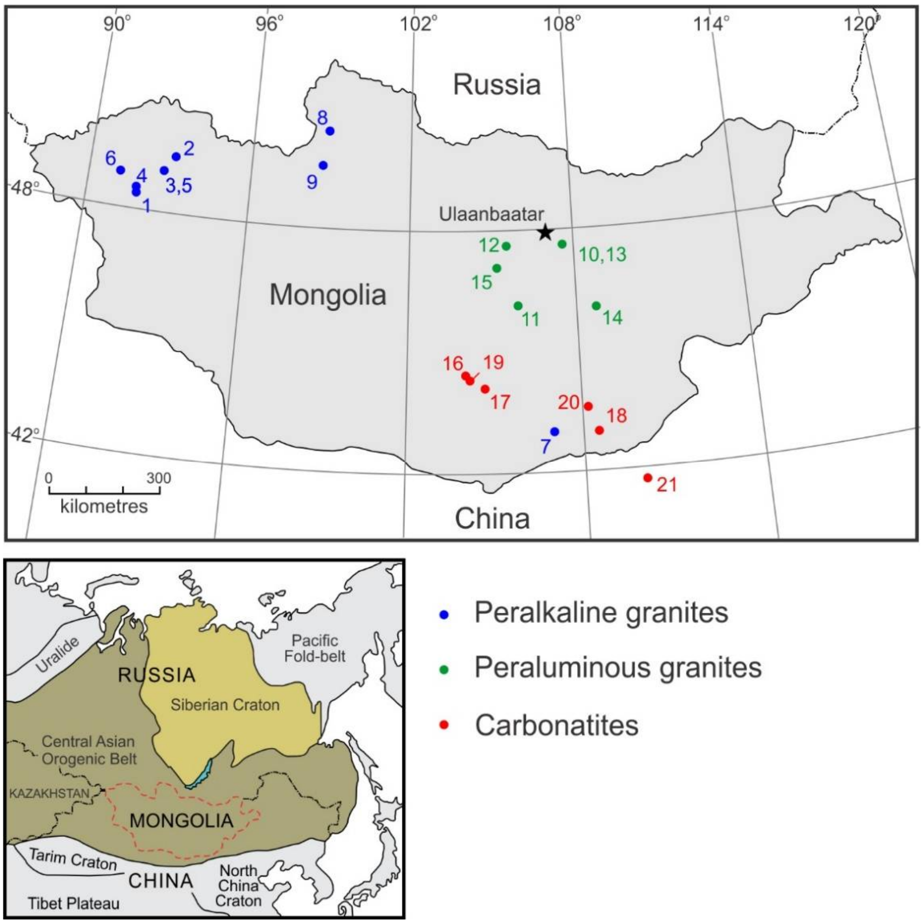

Figure 1. Map of Mongolia showing the location of the significant Nb and Ta occurrences hosted by peralkaline granites (1–9) and peraluminous granites (10–15) and the location of carbonatites (16–21). Number 21 is a giant Bayan Obo deposit in China. Inset map shows a geologic sketch of northeastern Asia and the location of Mongolia. Host rocks -Peralkaline granites: 1—Khalzan Buregtei; 2—Ulaan Tolgoi; 3—Ulaan Del; 4-Tsakhir; 5—Shar Tolgoi; 6—Maihan Uul; 7—Khanbogd; 8—Altan Boom; 9—Dargia Uul; Peraluminous granites: 10—Janchivlan; 11—Baga-Gazar; 12—Avdar; 13—Urt Gozgor; 14—Khukh Del Uul; 15—Ongon Khairkhan; Carbonatites: 16—Mushgai Khudag; 17—Khotgor; 18—Lugiin Gol; 19—Bayan Khoshuu; 20—Ulgii Khiid; 21—Bayan Obo.

2.1.1. Khalzan Buregtei

The Khalzan Buregtei deposit (Figure 1) is located in the Mongolian Altai of northwestern Mongolia, about 45 km northeast from the town of Khovd. It is hosted in a composite oval shaped intrusion (Figure 2; 48°24′ N, 91°57′ E), which is a part of the north–south trending Paleozoic belt of alkaline rocks emplaced within the prominent Tsagaan-Shiveetin fault zone (Paleozoic-Mesozoic intracontinental rift zone). The pluton intruded Vendian to Lower Cambrian sedimentary rocks and Ordovician biotite-amphibole granitoid rocks. The post-tectonic intrusion consists of several phases of peralkaline granitoid rocks, which yielded U-Pb zircon ages of 390–392 Ma [15,16]. Peralkaline syenite forms the outer rim of the complex while younger peralkaline granite is in the core. In the southern part of complex, these rocks were intruded by dikes of peralkaline granites as well as by two small ore-bearing stocks. Although all these rocks are comagmatic and derived from the same mantle-related source [15–17] only two late stocks are mineralized (Figure 2). The rocks of the two mineralized stocks are highly fractionated aegirine- and arfvedsonite- bearing peralkaline granite and pegmatite that were modified and enriched by post-magmatic hydrothermal/metasomatic processes [8,18–20]. In addition to quartz and K-feldspar both mineralized stocks contain about 0.5 vol.% of arfvedsonite, ~9 vol.% of aegirine and ~20 vol.% of ore and accessory minerals [21].

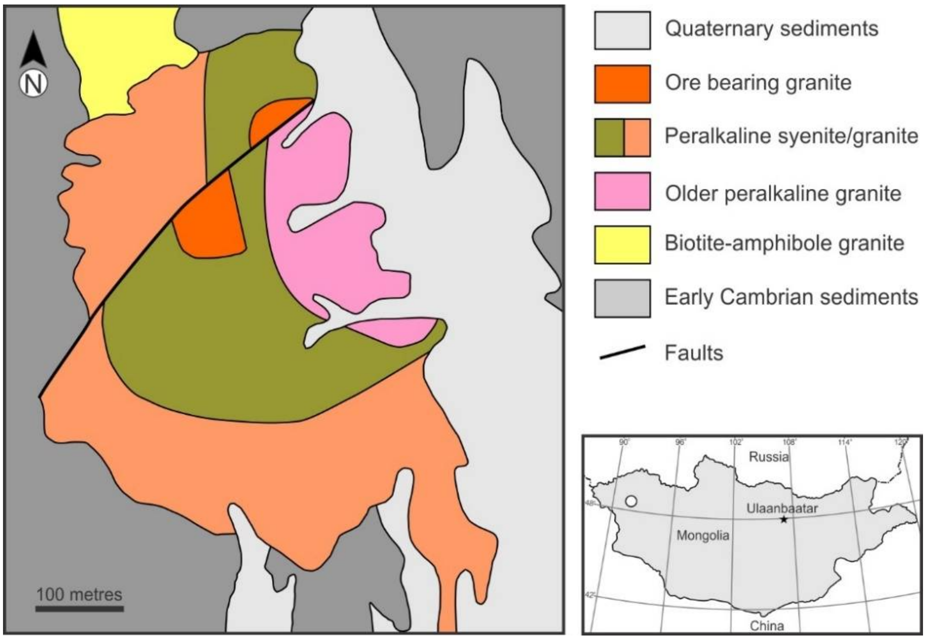

Figure 2. Generalized geological map of a part of the Khalzan Buregtei complex with two ore-bearing peralkaline granitic stocks; modified after Kovalenko et al. [15], Andreeva [18] and Gronen et al. [20]. Inset map shows the location of the Khalzan Buregtei complex (white dot).

The rare metal minerals are disseminated through the mineralized zones within both mineralized stocks. They include pyrochlore and columbite-tantalite, which are the main carriers of Nb and Ta. Other important ore minerals in the stocks are zircon, elpidite (zirconosilicate), xenotime, monazite and fluorocarbonates (bastnäsite and synchysite) and are accompanied by widespread fluorite. The U-Pb zircon dating of the two mineralized stocks yielded overlapping ages (392.2 ± 2.3 Ma and 390.8 ± 1.2 Ma, respectively [21]). The continental crust normalized plots of the averages of the incompatible elements of the mineralized zones (Figure 3A) show distinct enrichments of HFSE including Nb, Ta, Zr and Hf and of REE, particularly heavy REE accompanied by depletion of Ba, Sr and Ti. These features are consistent with the post-magmatic enrichment of highly fractionated granitic rocks. The reserves of the deposit have not yet been calculated but the Mongolian Geological Information Centre [22] reported earlier estimates of ore to the depth of 250 m as 160 Mt containing 1.46 wt.% ZrO_2, 0.2 wt.% Nb_2O_5, 0.011 wt.% Ta_2O_5. Muff and Tamiraa [22] also reported recent estimates of the REE reserves as 49 Mt of ore containing 0.6 wt.% TREO (total REE + Y as oxides).

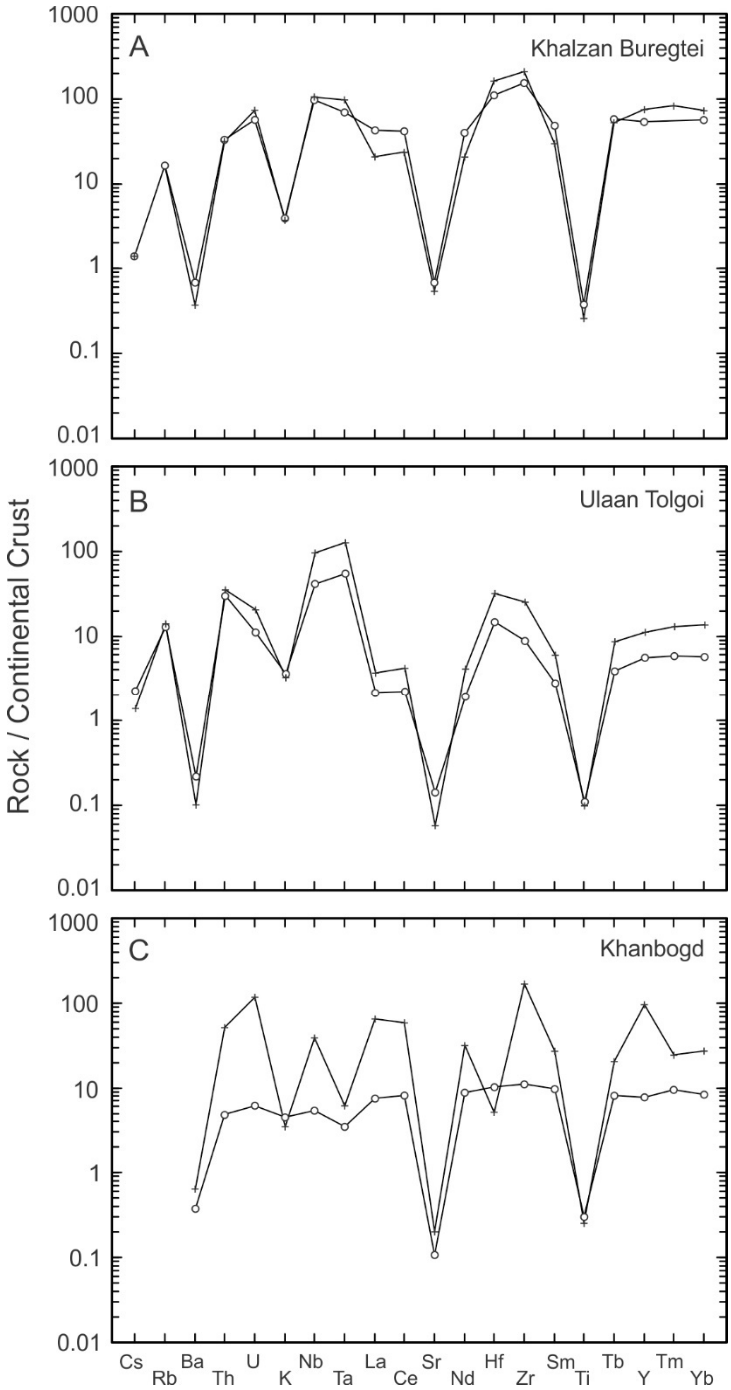

Figure 3. Bulk continental crust-normalized incompatible element abundances of peralkaline granitic rocks of the Khalzan-Buregtei complex (**A**), Ulaan Tolgoi pluton (**B**) and Khanbogd pluton (**C**). Normalizing values after [23]. (**A**)—Average of the mineralized peralkaline granites from the Khalzan-Buregtei complex of Kovalenko et al. [24] (o); average of mineralized granitic rocks from the Khalzan-Burtegei complex of Kempe et al. [19] (+). (**B**)—Average of "barren" peralkaline granites of the Ulaan-Tolgoi pluton (o); average of mineralized peralkaline granites of the Ulaan-Tolgoi pluton (+) [25]. (**C**)—Average of main granitic phase of the Khanbogd pluton (o); average of mineralized pegmatites of the Khanbogd pluton (+) [26].

2.1.2. Ulaan Tolgoi

Ulaan Tolgoi rare-metal (Ta, Nb, Zr) mineralization [25,27] occurs in northwestern Mongolia (Figure 1), at the SW end of the East Sayany rift zone with a belt of granitic intrusions extending across the Mongolia-Russia borders. The northern part of the belt outcropping in Russia (southeastern part of the Tuva Republic) hosts prominent Ulug-Tanzek and Zashikha Nb-Ta-REE deposits [28]. The Ulaan Tolgoi mineralization is hosted in an elongated rift-related intrusion (Figure 4), which is composed of peralkaline granites and syenites dated at ~298 Ma. The stock (49°27′ N, 93°02′ E) intruded Ordovician (~495 Ma) biotite granites [27]. Peralkaline felsic rocks contain minor amounts of arfvedsonite as the main mafic mineral. Lykhin et al. [25] inferred the deposit resembles that of the Khalzan-Buregtei. Both magmatic and post-magmatic processes played a role during the genesis of the mineralization. The rare metal mineralization includes pyrochlore, columbite-tantalite, zircon, bastnäsite, monazite, thorite and Nb-rutile (with ~8 wt.% Nb_2O_5; [25]) and is hosted in granites. The continental crust-normalized patterns of incompatible elements in the barren and mineralized granites of the Ulaan Tolgoi intrusion (Figure 3B) show that "barren" granites (<100 ppm Ta [25]) were highly fractionated felsic rocks with high contents of rare metals. Mineralized granites were subsequently enriched by post-magmatic processes. Mineralized granites contain 830–1260 ppm Nb, 100–166 ppm Ta and 1700–3200 ppm Zr. Total REE ranges from 380 to 535 ppm.

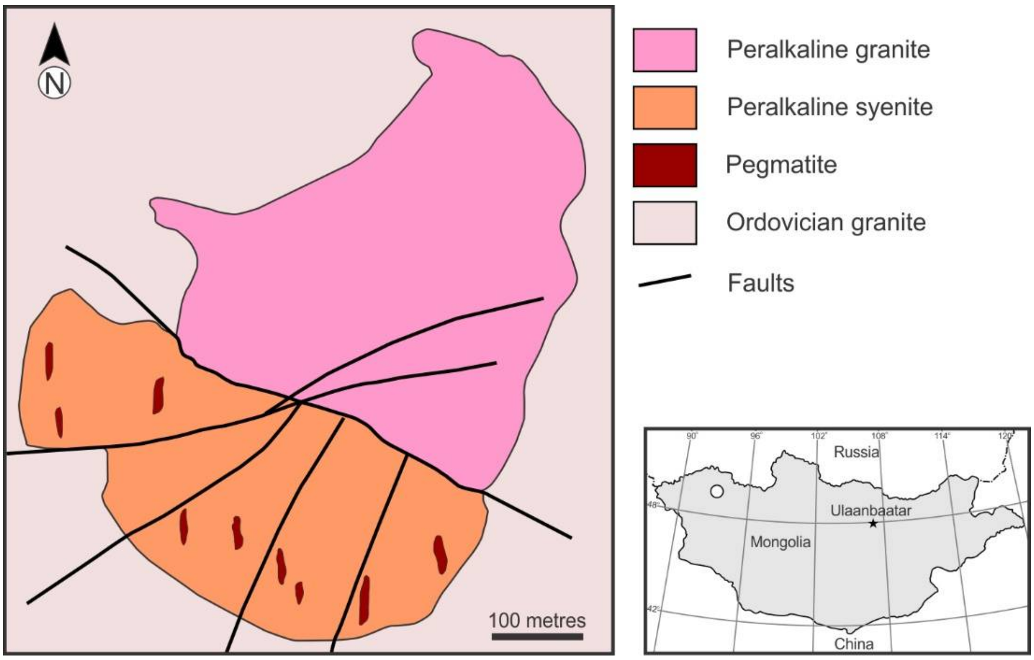

Figure 4. Generalized geological map of the Ulaan Tolgoi intrusion modified after Lykhin et al. [25]. Inset map shows the location of the Ulaan Tolgoi intrusion (white dot).

2.1.3. Ulaan Del

The Ulaan Del mineralization (49°03′ N, 92°46′ E) is located in northwestern Mongolia (Figure 1), in the belt of the granitic intrusions emplaced in the same rift zone as the Ulaan Tolgoi. The mineralization is hosted in a swarm of stockwork-like mineralized dikes that intruded Early Paleozoic granitoid rocks of the Togtokhynshil complex. The dikes are of Devonian age, probably of the same age as the Khalzan Buregtei [29]. The dikes outcropping in an area of about 2 × 2 km, are 0.5 to 2 m wide and up to 500 m long. They are composed of peralkaline syenites and granites. The rocks are extensively albitized (complete replacement of primary textures [21,29]). Mineralization occurs mainly in syenitic rocks and is composed of zircon, elpidite, xenotime, pyrochlore, columbite-tantalite, apatite and fluorocarbonates. Oyunbat [29] and Gerel et al. [21] noted that the Ulaan Del mineralization is similar to that of Khalzan Buregtei and inferred that the magmatic, metasomatic and hydrothermal processes played a role during the ore genesis. Reserves of the mineralization were estimated to be 6.1 Mt of ore containing 0.16 wt.% TREO, 0.33 wt.% ZrO_2 and 0.05 wt.% Nb_2O_5 [8,21,29]. Oyunbat [29] also noted that the concentrations of Nb_2O_5 and Ta_2O_5 at this site are about the same.

2.1.4. Khanbogd

The Khanbogd complex lies in the southern Gobi Desert of southern Mongolia close to the giant Oyu Tolgoi Cu-Mo-Au porphyry deposit. The complex was emplaced in the Southern Gobi-Tien Shan belt in the Late Paleozoic-Mesozoic rift zone. The complex intruded Carboniferous continental sedimentary and volcanic rocks of the Tsokhiot Formation and in turn, is overlain by Cretaceous sedimentary rocks. The Khanbogd complex is a composite intrusion [30], which consists of two circular bodies—the western and the eastern parts (Figure 5). The larger western part shows the circular (ring) structure accentuated by numerous well-exposed ring dikes. The complex consists of several phases. The first phase, which constitutes most of the western part of the intrusion, is composed of elpidite-bearing aegirine-arfvedsonite peralkaline granite. The second phase made up by aegirine-arfvedsonite granite forms the eastern part of the intrusion. The complex, particularly its western part, was subsequently invaded by several generations of peralkaline granitic and pegmatitic dikes, which are typically 5 to 100 m long. All these rocks were dated at 290–292 Ma [30]. They all are genetically related, derived from a common parent magma by fractional crystallization [26]. The peralkaline granites have high contents of alkalis, Zr, Nb, Y and REE; the pegmatites, which are more fractionated, have even higher contents of these elements (Figure 3C). The initial mineralization related to magmatic processes was enriched by hydrothermal/metasomatic activities. The mineralization is present mainly in pegmatitic dikes occurring in the apical part of the intrusion, where hydrothermal alteration was intense. The main rare metal-bearing minerals are elpidite, zircon, fluorocarbonates (bastnäsite, synchysite, parasite) and armstrongite ($CaZrSi_6O_{15}x3H_2O$). In addition, pegmatites host some unusual minerals such as gittinsite ($CaZrSi_{12}O_7$), mongolite and kovalenkoite (hydrated Ca-Nb silicates). In fact, the Khanbogd pegmatites are the original discovery site for armstrongite (named after US astronaut Neil Armstrong), mongolite and kovalenkoite. Vladykin [31] reported that pegmatites contain up to 0.5 wt.% Nb, 7 wt.% Zr, 1 wt.% REE and 0.5 wt.% Y. The continental crust-normalized distribution patterns of the averages of the main granitic phase of the intrusion and of the mineralized pegmatite (Figure 3C) display distinct enrichment of Zr-Hf and Nb-Ta pairs as well as of REE in pegmatite. The plot also records preferential enrichment of Zr relative to Hf and that of Nb relative to Ta leading to an increase of Zr/Hf and Nb/Ta ratios. This is in contrast to the enrichment processes in peraluminous granites where late magmatic/postmagmatic hydrothermal fluids lead to the decrease of these ratios.

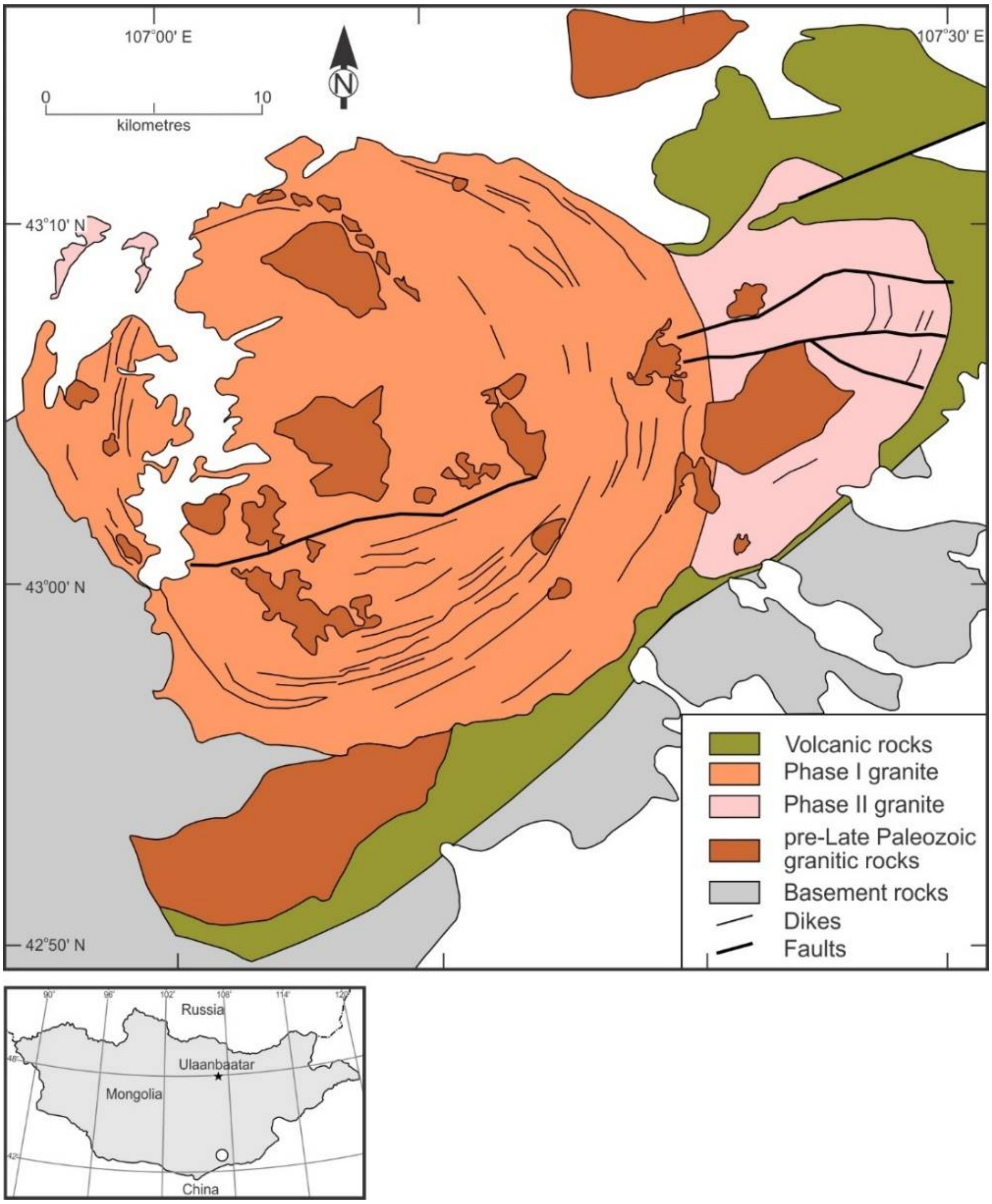

Figure 5. Generalized geological map of the Khanbogd complex modified after Kynicky et al. [26] and Vladykin [31]. Inset map shows the location of the Khanbogd complex (white dot).

2.2. Peraluminous Granites

The rare metal granites are frequently peraluminous (have molecular Al_2O_3 > [CaO + Na_2O + K_2O]), muscovite- and albite-rich granites that display high degrees of chemical fractionation. They represent the last stages of felsic magma evolution in upwardly differentiated granitic intrusions [32]. Tantalum and niobium mineralization is associated with the peraluminous granites that are characterized by a fluorine enrichment and extensive post-magmatic alteration. In Mongolia and the neighboring part of Russia (Transbaikalia), most promising among these rocks are so-called lithium-fluorine Li-F) granites. They are highly evolved post-orogenic granites associated with Sn, W, Li and Ta-Nb mineralization [2,8,9,21,33–35]. In Transbaikalia, there are economically significant rare metal (mainly Ta-Li) deposits associated with the Li-F granites including Orlovka and Etyka, e.g., [35–38]. The Li-F granites are characterized by high Al_2O_3, F, Li, Rb, Sn, W, Ta and Ta/Nb but low Ba, Sr, Eu, Zr and REE. These rocks include microcline-albite, amazonite-albite and lepidolite-albite types [33]. In Mongolia, Ta-Nb mineralization is generally associated with lepidolite-albite granites. These rocks are typically made up of quartz, albite, K-feldspar, lepidolite and topaz with rounded phenocrysts of quartz surrounded by fine-grained sugar-like groundmass composed mainly of albite [33]. In addition, pervasive post-magmatic alteration of the rare metal granites generated greisens with dark mica, quartz-lepidolite greisens and albitites. Thus, the mineralogical and geochemical features of the rare metal-bearing Li-F granites are the results of their source compositions, as well as magmatic evolution and post-magmatic alteration processes. They can be parts of the large multiphase plutons (e.g., Janchivlan and Baga Gazar intrusions) or form small intrusions (e.g., Avdar). In Mongolia and Transbaikalia, they were emplaced over a time interval from about 320 Ma to 135 Ma [35]. The Li-F granites usually represent the youngest phase of the late/post-orogenic granitic intrusions related to the tectonic evolution of the Mongol-Okhotsk orogen. They are compositionally different from the Early Paleozoic collisional granitoids.

2.2.1. Janchivlan

The Janchivlan pluton occurs at the southwestern margin of the post-orogenic Early Mesozoic Khentei batholith dated at 227–207 Ma [39,40], in the NW-trending Kharkhorin Permian-Early Cretaceous rift zone (Figure 6). The Janchivlan pluton is an unfoliated discordant intrusion surrounded by contact metamorphic aureole or tectonic contacts. This shallow seated intrusion (Figure 7) consists of four intrusive phases [33]. The first and main phase is composed of porphyritic coarse-grained biotite granite with miarolitic pegmatite while the second phase is represented by eqiugranular medium grained biotite and biotite-muscovite granite, dated (U-Pb zircon age; [39]) at 217 $\pm$ 52 Ma and 227 $\pm$ 8 Ma, respectively. They are considered distinct intrusive phases although they have similar compositions [34,41]. The third phase corresponds to leucogranites (biotite alaskite of Kovalenko et al. [33]), which are associated with lithium-fluorine granites and albitites of the fourth phase. The Li-F granites yielded a whole-rock Rb-Sr age of 195 $\pm$ 0.6 Ma [39]. Leucogranites contain, in addition to quartz, K-feldspar and plagioclase ($An_{5\text{-}15}$), also biotite (3–4%) and accessory minerals—topaz, fluorite, monazite, Fe-Ti oxides [34]. Li-F granites are composed of microcline (or amazonite)-albite-quartz with variable amounts of Li-mica (lepidolite, Li-phengite or zinwaldite). The accessory and ore minerals include topaz, fluorite, zircon, columbite-tantalite, pyrochlore, monazite and cassiterite [41]. The rocks are commonly greisenized, producing quartz-tourmaline, quartz-topaz, quartz-lepidolite and quartz-muscovite greisens, which are accompanied by quartz veins. Some of these veins contain the Sn-W mineralization (cassiterite and wolframite). Albitites contain up to ~90 vol.% albite and minor amounts of microcline, quartz, lepidolite and topaz. Accessory minerals include fluorite, zircon, monazite, columbite, pyrochlore and cassiterite [41]. A similar multiphase Mesozoic intrusion with Li-F granites is the Baga-Gazar pluton in Central Mongolia [35].

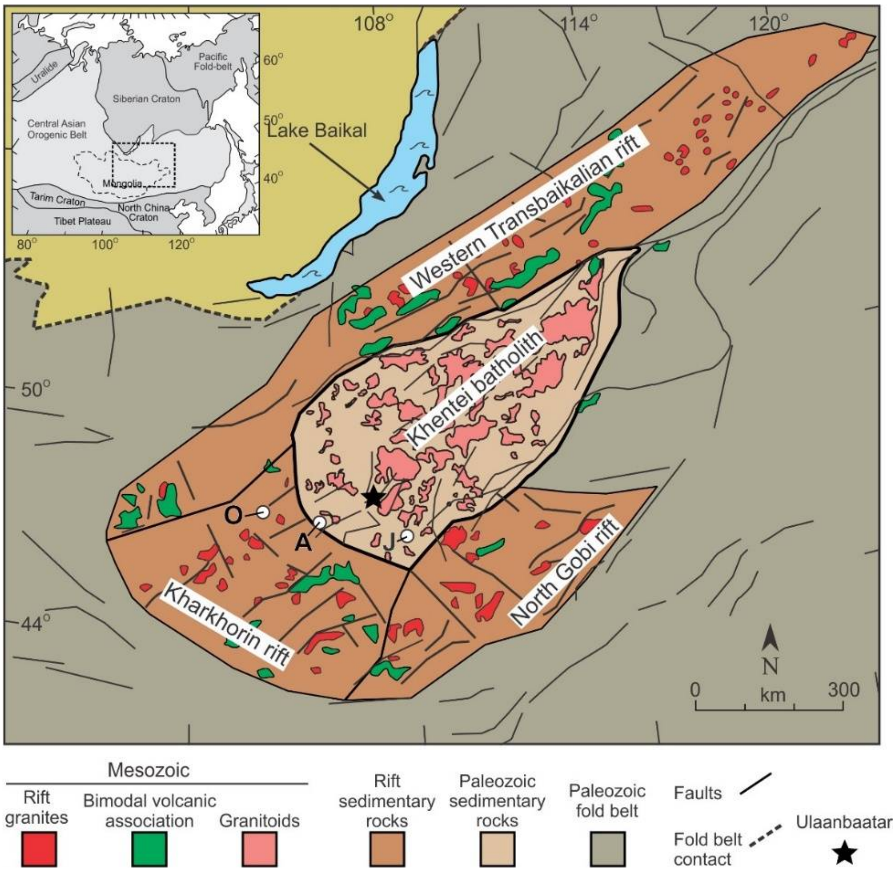

Figure 6. Simplified geological map of a part of the Central Asian Orogenic Belt showing of the Daurian-Khentei megadome or uplift composed of the Early Mesozoic Khentei batholith, North Gobi, Kharkhorin, and Western Transbaikalian rifts (modified after [42]). J—Janchivlan, A—Avdar, O—Ongon Khairkhan, the type locality of ongonites. Inset map shows a sketch of Central Asian Orogenic Belt, the surrounding provinces, and the location of Figure 6 (rectangle).

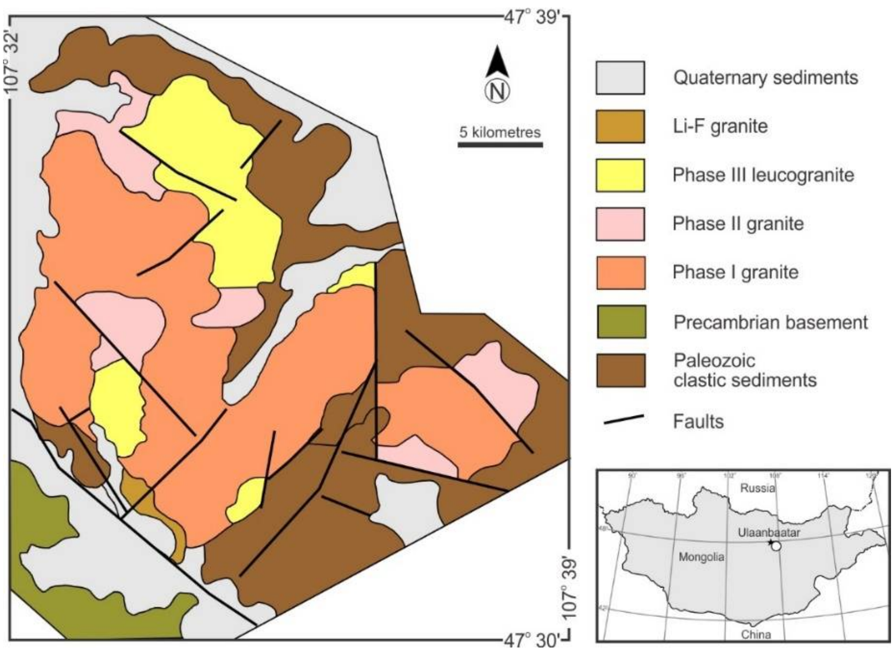

Figure 7. Generalized geological map of Janchivlan complex modified after Kovalenko et al. [33] and Antipin et al. [34]. Inset map shows the location of the Janchivlan complex (white dot).

The rocks of the Janchivlan intrusion have high silica (70–77 wt.%), which increases from the biotite granite of the first phase to the leucogranite and Li-mica- albite granite of the third and fourth phases [34,35,41]. These rocks are peraluminous with mol.% Al_2O_3 > (CaO + Na_2O + K_2O), highly fractionated and have relatively low CaO, MgO and FeO_{tot}. Leucogranites are more fractionated than the granites of the first and second phases and are high in total alkalis (8–9 wt.%). The chondrite-normalized REE patterns of the phases 1 and 2 are enriched in light REE (LREE), have slightly fractionated heavy REE (HREE) and display moderate negative Eu anomalies (Figure 8A). The patterns are generally subparallel. The shapes of the REE patterns of the leucogranites differ (Figure 8B). While the LREE segment shows a decrease from La to Sm, the HREE display an opposite trend, an increase from Gd to Lu. The patterns possess a distinct negative Eu anomaly. The REE patterns of Li-F- granites (Figure 8C) are kinked-shaped, typical of "tetrad REE patterns" of some highly evolved leucogranites and pegmatites (e.g., [43,44]). These shapes are likely the result of interaction of the residual melts with hydrothermal fluids, probably rich in F (e.g., [44]). The distinct differences between the main phases of granites and the leucogranites and Li-F granites are shown on the continental crust-normalized plots (Figure 9C), which are consistent with the tetrad effect of the REE patterns. The leucogranites and Li-F granites exhibit an enrichment of several strongly incompatible elements particularly Cs, Rb and Th but are strongly depleted in Ba, Sr, Eu and Ti. Although fractionation of alkali feldspars and Fe-Ti oxides may produce negative anomalies of these elements, Jahn et al. [44] concluded their distinct relative depletion, such as that of the Janchivlan leucogranites and Li-F granites, was enhanced by late stage melt-fluid interaction. Irber [43] and Jahn et al. [44] documented fractional crystallization alone cannot generate "the tetrad effect".

The high concentrations of Rb in the leucogranites and Li-F-granites are accompanied by low K/Rb ratios relative to the upper crustal average of ~250 [45]. The leucogranites have low K/Rb ratios (~50; [34]) indicating a role of fluids in their genesis [46]. In addition, the leucogranites and Li-F granites show an enrichment of Ta relative to Nb and Hf relative to Zr as reflected by the unusual values of the Zr/Hf and Nb/Ta ratios, which are commonly constant during various geological processes [47]. Zirconium and Hf are nearly identical geochemically, and most of the crust maintains near-chondritic Zr/Hf ratios of ~35–40 e.g., [48]). Ballouard et al. [49] and Zaraisky et al. [50] inferred that the Zr/Hf ratio is a geochemical indicator of the fertility of granitic rocks and a low Zr/Hf ratio (< ~18–25) is characteristic of mineralized granites. Similarly, whereas the average crustal ratio of Nb/Ta is ~11 [3], Ballouard et al. [49] argued that a Nb/Ta ratio of ~5 is a good marker to discriminate mineralized (<5) from barren (>5) peraluminous granites. The Zr/Hf and Nb/Ta ratios in the leucogranites are low (8–20 and 2–12, respectively). The greisens and Li-F granites have even lower ratios with values of ~2 for both ratios, suggesting that all these rocks have characteristics of mineralized granites.

Most of the tantalum and niobium mineralization is associated with lepidolite-albite granites and albitites. Lepidolite-albite granites of the Janchivlan pluton form bodies up to 3.5 km long and 800 m thick [34]. Gerel [8] also reported that an average Nb/Ta ratio of the lepidolite-albite granite from a drill core to the depth of 100 m is <1 with 60–110 ppm Ta. An enrichment of Ta and Nb in some leucogranites, greisens and Li-F granites reaches a level of economic significance [34]. The rocks also have low Nb/Ta ratios, characteristic of mineralization. In addition, some of these rocks contain >1000 ppm Li [8]. The alluvial deposits around the Janchivlan pluton also carry the Nb, Ta and Li minerals [8]. In the immediate vicinity of the Janchivlan intrusion, there are about 20 placer deposits, which host mainly cassiterite but also have wolframite, topaz, monazite, fluorite, zircon and Nb-Ta oxides. Some of the placers extend up to 5–10 km in length and their width reaches up to 500 m; the heavy mineral-bearing horizon is 0.5 to 15 m thick [8]. In the 1950's, several of these tin-tungsten placer deposits were mined. One of the promising placers is a tin-tantalum placer deposit Urt Gozgor, which is about 2–2.5 km long and 60–300 m wide. The heavy mineral-bearing layer is 0.5 to 2.5 m thick [8]. In addition to cassiterite, its heavy mineral concentrates hold elevated amounts of columbite-tantalite.

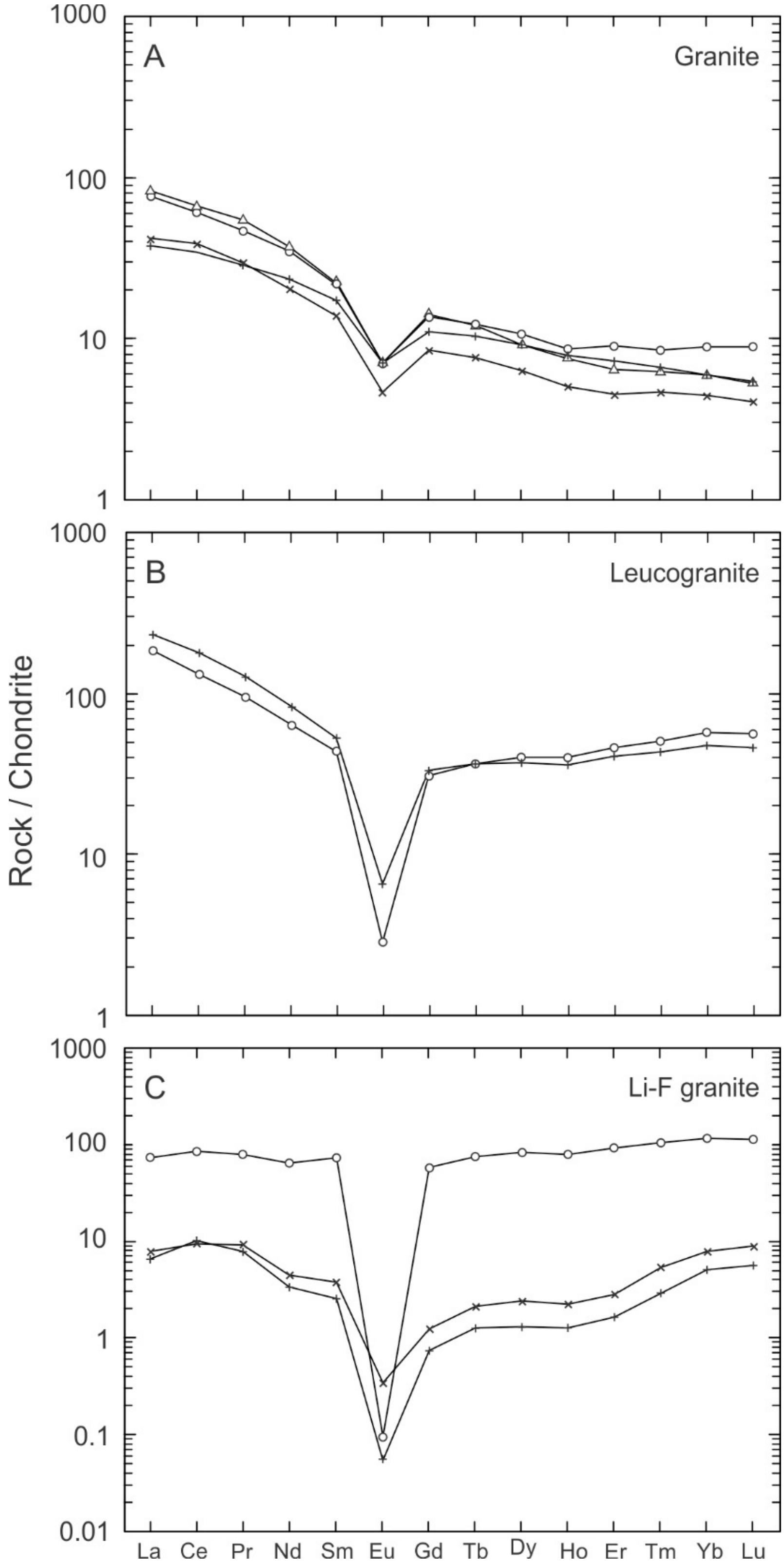

Figure 8. Chondrite-normalized REE abundances of the Janchivlan granites (**A**): phase 1 and 2 Phase 1: JA-1 (o), J-1 (Δ); Phase 2: JA-3 (+), J-2 (x); (**B**)—Phase 3—Leucogranite: JA-4 (o); JA-5 (+); (**C**)—Li-F granites: lepidolite-albite JA-7 (o), amazonite-albite JA-8 (+), JA-9 (x). Data are from Supplementary Table S1. Except J-1 and J-2, which are from Antipin et al. [34]. Normalizing values after Boynton [51].

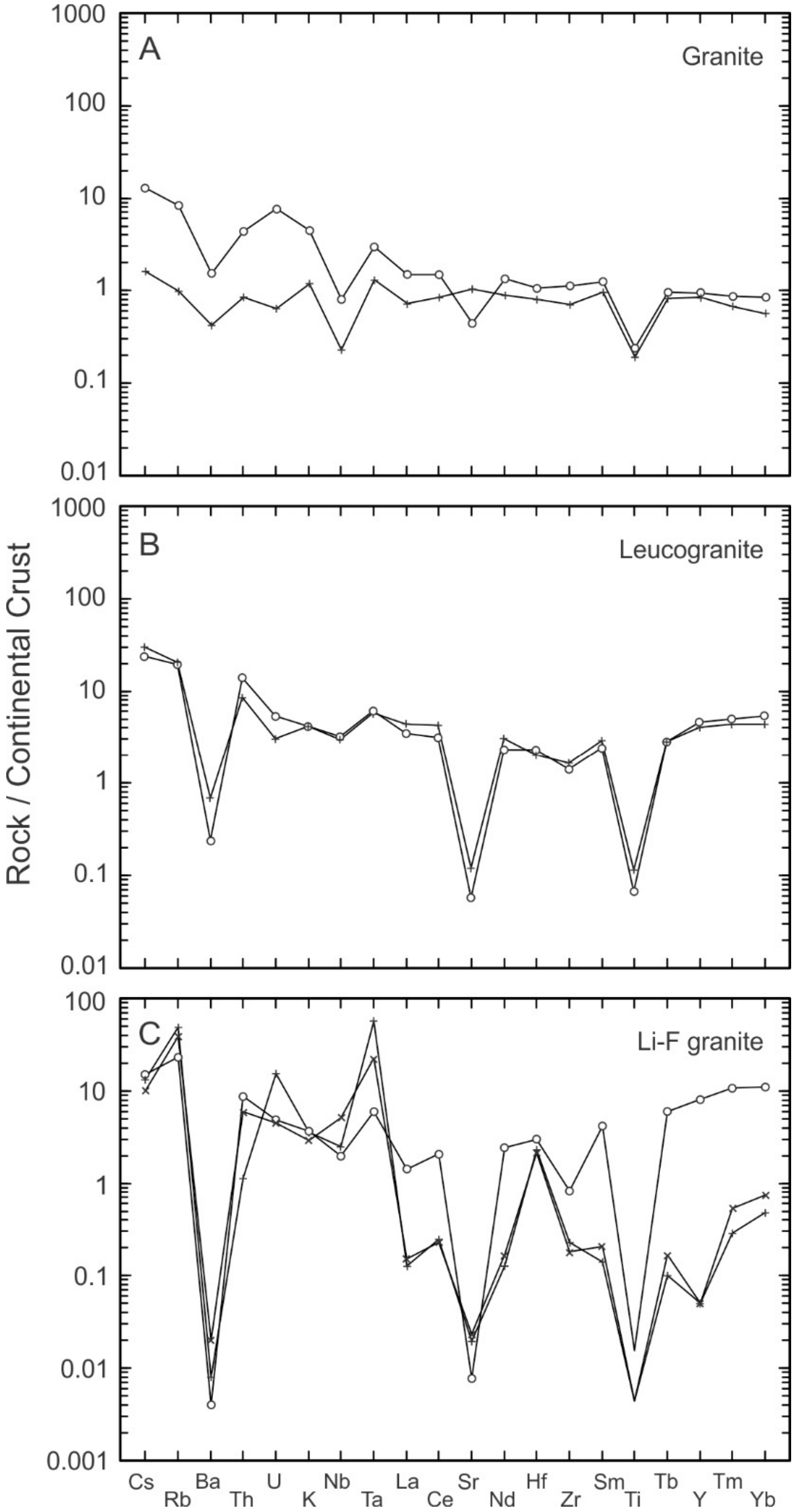

Figure 9. Bulk continental crust-normalized incompatible element abundances of the Janchivlan granites. Normalizing values after [23]. (**A**)—Phases 1&2- phase 1: JA-1 (o) and phase 2: JA-3 (+); (**B**)—Phase 3—Leucogranite JA-4 (o), JA-5 (+); (**C**)—Li-F granites: lepidolite-albite JA-7 (o); amazonite-albite JA-8 (+), JA-9 (x). Data are from Supplementary Table S1.

The alluvial deposits around the Janchivlan pluton also carry the Nb, Ta and Li minerals [8]. In the immediate vicinity of the Janchivlan intrusion, there are about 20 placer deposits, which host mainly cassiterite but also have wolframite, topaz, monazite, fluorite, zircon and Nb-Ta oxides. Some of the placers extend up to 5–10 km in length and their width reaches up to 500 m; the heavy mineral-bearing horizon is 0.5 to 15 m thick [8]. In the 1950's, several of these tin-tungsten placer deposits were mined. One of the promising placers is a tin-tantalum placer deposit Urt Gozgor, which is about 2–2.5 km long and 60–300 m wide. The heavy mineral-bearing layer is 0.5 to 2.5 m thick [8]. In addition to cassiterite, its heavy mineral concentrates hold elevated amounts of columbite-tantalite.

2.2.2. Avdar

The Avdar pluton is a shallow seated dome-shaped intrusion, elongated in an N-S direction for about 6 km while its width is 2–2.5 km (Figure 10). It intruded the weakly metamorphosed Devonian clastic sediments and superimposed a contact metamorphic aureole, which is 1–1.5 km wide. The intrusion is a composite body with the dominant core formed mainly by medium-grained biotite granite. The core is surrounded in part by a zone of amazonite-albite granites, which also occur in the apical parts. The amazonite-albite granite is quarried as a decorative stone. The contacts between the granitic rocks are gradational [34,35], although Kovalenko et al. [33] observed the amazonite granite crosscutting biotite granite. Kovalenko et al. [33] reported a K-Ar age of 207 Ma for the biotite from the Avdar pluton. The results agreed well with the Rb-Sr age (209–212 Ma) later obtained by Kovalenko et al. [52].

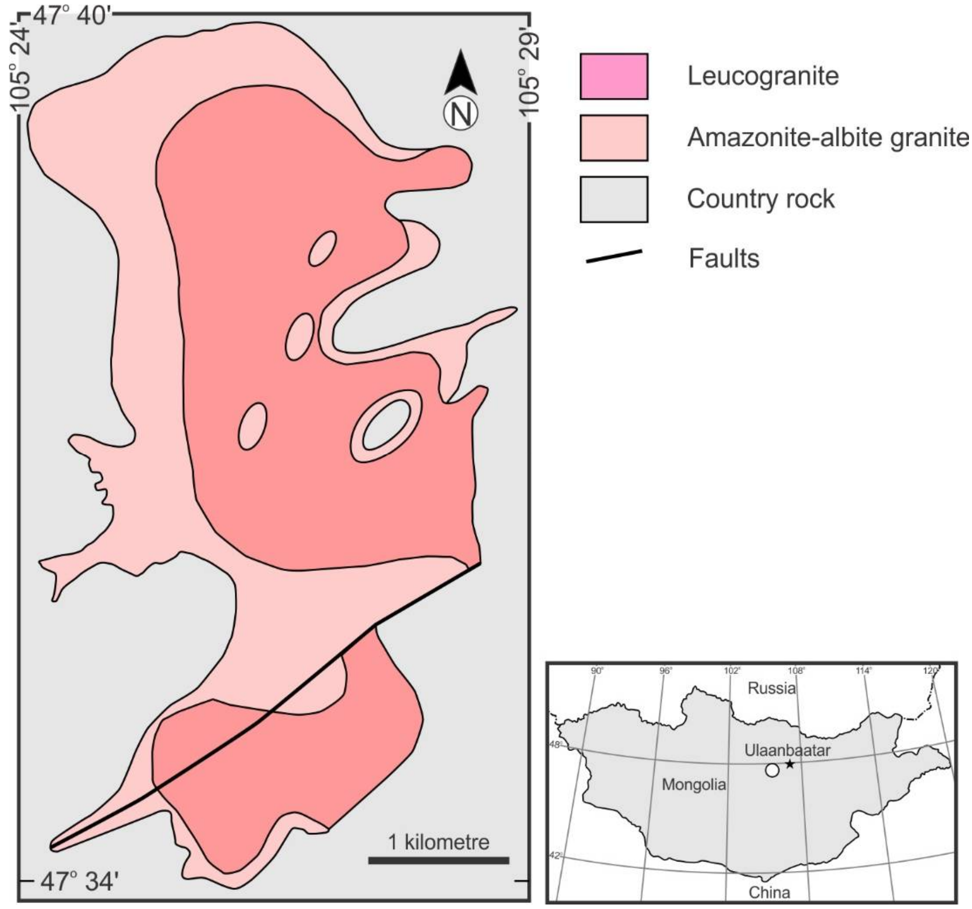

Figure 10. Generalized geological map of Avdar pluton modified after Kovalenko et al. [33] and Antipin et al. [34]. Inset map shows the location of the Avdar intrusion (white dot).

The biotite granite is composed of plagioclase ($An_{5\text{-}15}$), microcline, which is locally perthitic, quartz and a minor amount of biotite (2–3 vol.%). Common accessory minerals are Fe-Ti oxides, fluorite, zircon and monazite. The amazonite-bearing granite is equigranular, medium-grained rock mostly with hypidiomorphic texture. It is composed of quartz (~45 vol.%), albite (~30 vol.%), microcline/amazonite (~20 vol.%) and Li-Fe-rich mica. Common accessory minerals include fluorite, zircon, Fe-Ti oxides, cassiterite and columbite-tantalite. Antipin et al. [35] reported that the Li-Fe-rich mica has high concentrations of Nb (553–725 ppm), Ta (91–107 ppm) and Sn (440–750 ppm), the values similar to those of mica from Janchivlan.

Both rock types of the Avdar pluton are peraluminous granites high in alkalis (Na_2O + K_2O ~8–10 wt.%) but low in Ca, Mg and Fe [34,35]. Compared to biotite granite, amazonite-albite granite is more fractionated with higher silica but lower Ca and Mg. Amazonite-albite granite has a composition typical of Li-F granites, with high contents of Cs, Rb, Ta, Hf and HREE but low Ba, Eu, Sr and Ti (Figures 11 and 12). Their chondrite-normalized REE patterns display a strong negative Eu anomaly and enrichment of HREE (Figure 11A). These rocks have also significantly lower K/Rb (~30) and La/Yb (<1) ratios relative to the biotite granites suggesting that they were affected by fluid interaction. The interaction took place prior to their emplacement, possible at their source. Amazonite granites have low Nb/Ta and Zr/Hf ratios (~4.4 and ~6.2, respectively; [35]), indicating that they are mineralized. Antipin et al. [34] inferred that rare metal mineralization from the amazonite-albite granites of the intrusion is related to the nearby placer (Sn-W-Ta-Nb) deposits, which were mined in the past. The placers are 2–4.5 km long, 10–450 m wide and have a heavy mineral bearing layer 1–2 m thick [8].

2.2.3. Pegmatites

Rare metal pegmatites related to the Late Paleozoic and Mesozoic Li-F leucocratic granites are abundant in Eastern Mongolia and some of them have significant Ta, Nb, Li, Be, Sn and W mineralization [53]. In addition to quartz, albite and microcline, the pegmatites contain Li-mica or muscovite and Ta-Nb oxide minerals (mostly columbite- tantalite and pyrochlore), cassiterite, tourmaline, beryl and wolframite. Rare metal pegmatites commonly form dikes or lenticular bodies ranging in length from few meters to hundreds of meters. The pegmatites are zoned and show a multistage evolution, which involved albitization and greisenization. Greisens are composed of quartz and lepidolite or Li-muscovite and form veins or schlierens. One of such pegmatite sites is Khukh Del Uul (Figure 1), situated about 250 km southeast of Ulaanbaatar, where in the area of about 6 km^2, there are approximately 25 pegmatite bodies, which are 50 to 300 m long and 1 to 10 m wide [8]. Pegmatite contains tantalite-columbite and microlite-pyrochlore.

2.2.4. Ongonites

The promising Mesozoic rare metal mineralization in Mongolia is associated with subvolcanic equivalents of the Li-F granites-ongonites. Ongonite was named after the late Mesozoic Ongon Khairkhan granite pluton and W deposit (quartz-wolframite stockwork) which occur in central Mongolia (Figure 13; 47°04′ N, 105°10′ E). Kovalenko and Kovalenko [54] originally defined it as a topaz-bearing albite-quartz keratophyre, enriched in Li (0.2–0.3 wt.%) and F (up to 4 wt.%). Similar subvolcanic ongonites occur elsewhere in this part of Mongolia (e.g., [8,34,35]. In the type locality, ongonite forms a dike swarm about 1 km long consisting of dikes varying from several cm to about 2 m in thickness, which are shallow seated and dated at ~120 Ma [55]. The larger dikes range in length from tens of meters to 500 m. The dikes have chilled margins and sharp contacts with the surrounding sedimentary country rocks. They represent the youngest phase of the late/post-orogenic magmatism related to Mongol-Okhotsk orogeny.

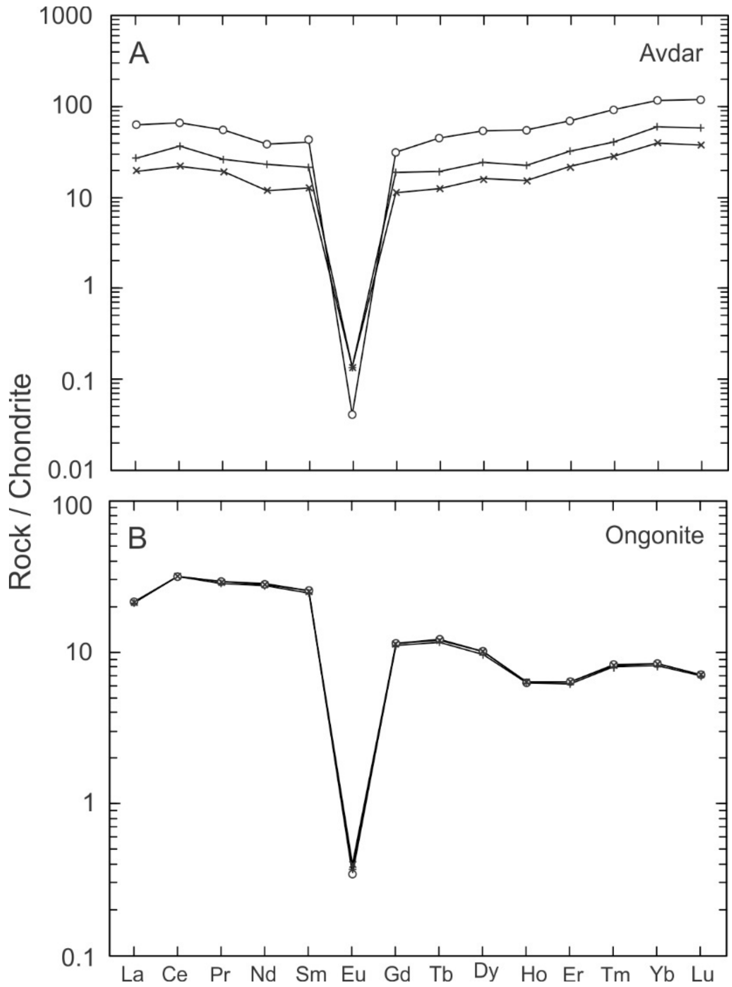

Figure 11. Chondrite-normalized REE abundances of Avdar granites and ongonites (from Ongon Khairkhan, Figure 6) (**A**): amazonite-albite granites-Avdar: A-1 (o) (Supplementary Table S1); + and x—Data from Antipin et al. [34]; (**B**): ongonite: ON-2 (o); ON-1 (+), ON-3 (x) (Supplementary Table S1). Normalizing values after Boynton [51].

Ongonite is made up of microphenocrysts of quartz, albite, orthoclase and minor mica and topaz hosted in groundmass dominated by albite and quartz. Li-Fe-rich mica is mainly zinwaldite, enriched in rare metals (Sn, W, Nb, Ta). The main accessories are zircon and Nb-Ta oxides. Other accessory minerals are monazite, apatite, pyrite and Fe-Ti oxides. The ongonites are peraluminous leucogranites characterized by high Al and alkalis. The chondrite-normalized REE patterns (Figure 11B) are kinked-shaped with a large negative Eu anomaly, typical "tetrad REE patterns" [56]. Compared to average continental crust, the rocks are strongly enriched in Rb, Cs and Ta (Figure 12B) and have anomalous K/Rb (8–15), Zr/Hf (2–5) and Nb/Ta (0.6–2.2) ratios [55]. These low ratios suggest that the rocks are mineralized [49,57]. The ongonites probably represent the highly differentiated F-rich granitic magma, which was modified by the late-to post-magmatic fluids enriched in incompatible elements including Ta, Sn and W [55]. The mineralized zones of ongonite contain about 2800 ppm Li, 2400 ppm Rb and up to 130 ppm Ta [58]. The ongonites are not related to nearby late Mesozoic Ongon Khairkhan granite (Supplementary Table S1), which was emplaced at the same period as the ongonites [59].

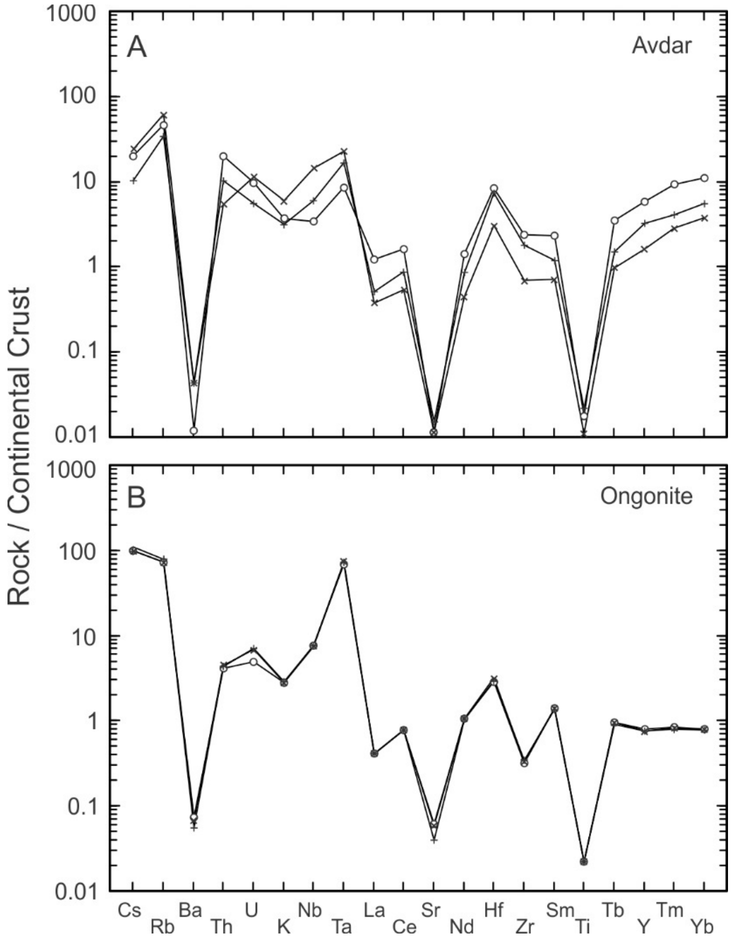

Figure 12. Bulk continental crust-normalized incompatible element abundances of the rocks of Avdar complex and ongonites (from Ongon Khairkhan, Figure 6). (**A**): amazonite–albite granites: A-1 (o) (Supplementary Table S1); (+) and (x)—Data from Antipin et al. [34]; (**B**)—Ongonite: ON-2 (o), ON-1 (+), ON-3 (x) (Supplementary Table S1). Normalizing values after Taylor and McLennan [23].

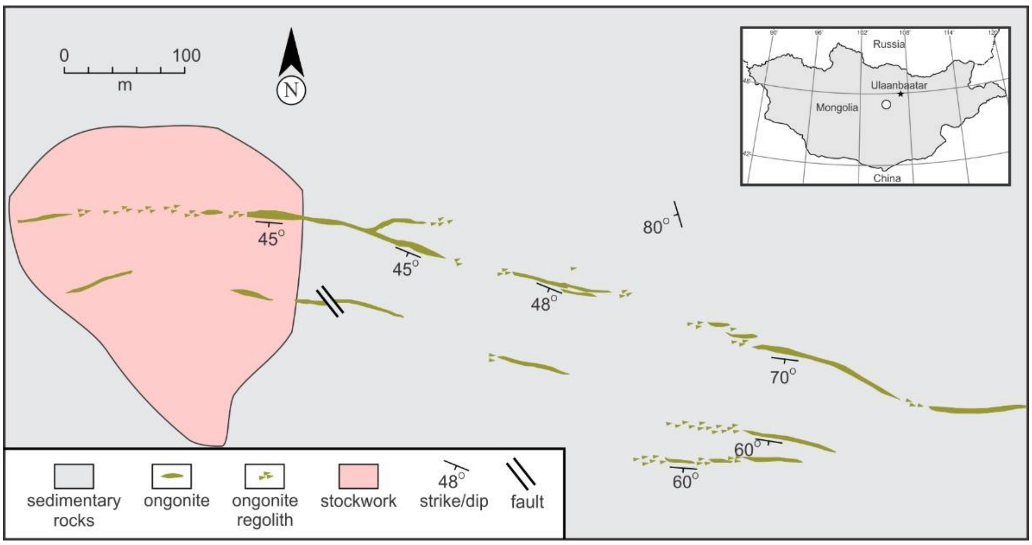

Figure 13. Geological sketch map of the Ongon Khairkhan area showing the type locality of the ongonite dike swarm and the tungsten mineralization (after [33,55]). Inset map shows the location of the Ongon Khairkhan intrusion and the ongonite dike (white dot).

2.3. Carbonatites

Carbonatites are unusual igneous rocks that contain more than 50 vol.% of primary carbonate minerals, mainly calcite and dolomite, reflecting carbonate-rich source magmas. Most carbonatites occur as relatively small intrusions such as dikes, sills and plugs or rarely as volcanic deposits. The carbonatites are commonly associating with alkaline silicate rocks in alkaline igneous provinces. The carbonatites were emplaced in stable areas during periods of continental extension and rifting along major faults or crustal boundaries [60,61].

Carbonatites are typically enriched in a range of elements including the rare earth elements, niobium, fluorine, phosphorus, uranium, thorium and zirconium. Niobium is preferentially enriched relative to tantalum in CO_2-rich melts and thus carbonatites do not generally have high contents of Ta. However, there are differences in the trace element enrichment of carbonatites. Some carbonatites are enriched in REE and Sr, but not niobium, while others are enriched in Nb, P, and Ti but not REE [62]. Common Nb-bearing minerals in carbonatites are members of the perovskite and pyrochlore groups [62].

In southern Mongolia (southern Gobi Desert), there are several carbonatite bodies containing promising REE mineralization (Figure 1). They include the Mesozoic Mushgai Khudag [21,22,31,63,64], Bayan Khoshuu [21,63], Lugiin Gol [21,31,63] and Khotgor [21,22,65] complexes among others associated with the Gobi Rift zones. Although the complexes are rich in REE, Ba and Sr, they do not have high concentrations of Nb, Ta, Zr and Hf. In fact, in trace element distribution plots normalized to the primitive mantle, they show negative HFSE anomalies, e.g., [31,64] suggesting an involvement of metasomatized lithospheric mantle in the genesis of these rocks. However, as some of them are geographically close to the major Bayan Obo REE-Nb carbonatite deposit in China (Figure 1), Vladykin [31] indicated that a search for Nb enrichment during the REE explorations of these carbonatite complexes would be worthwhile.

3. Conclusions

In Mongolia, Nb and Ta mineralization of potential economic significance is related to Late Paleozoic and Mesozoic felsic rocks, in particular either to peralkaline granites, pegmatites and syenites or to peraluminous Li-F-rich granites and related rocks (pegmatites and ongonites). All these rocks were emplaced in a continental intraplate setting, typically associated with rifting, faulting or crustal extension. In both cases, the mineralization is composed of disseminated Nb-Ta-rich minerals, which can reach percentage levels in mineralized sites. Ore minerals, dominantly oxides, mostly belong to the columbite-tantalite and pyrochlore (pyrochlore, microlite) groups and are accompanied by fluorite. Mineralization in these rocks typically records two stages. The first stage produced primary magmatic ore assemblages, which are associated with the extensive fractional crystallization, which was protracted, in part, due to high contents of alkalis and fluorine. Melt inclusion studies (e.g., [18]) indicate that the original magmas were enriched in rare metals. Both assemblages were typically overprinted during the second mineralization stage by the late magmatic to hydrothermal fluids, which remobilized and enriched the original mineralization. The newly formed ore mineral assemblages display complex replacement textures. The primary phases were re-mobilized and re-deposited as secondary phases. In the case of peralkaline felsic rocks, the processes generated mineralization of Zr, Nb, HREE, Y, U, Th and Ta whereas in peraluminous Li-F felsic rocks, the mineralization contains Sn, W, F, Ta, Li, Rb and Nb. Mongolia hosts several promising occurrences of both types of Nb-Ta mineralization. However, they have not yet been sufficiently explored. As Nb and Ta are subordinate commodities of Sn-W and REE deposits, the most perspective occurrences are mineralization associated with significant concentrations of the other rare metals, particularly of REE in northwestern Mongolia. The most promising is the occurrence in the Devonian Khalzan Buregtei peralkaline granites in western Mongolia, where Nb-Ta is associated with significant REE and Zr mineralization. Mesozoic carbonatites of southern Mongolia do not contain significant Nb and Ta mineralization.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12121529/s1, Table S1. Whole-rock major and trace element analyses of peraluminous granites.

Author Contributions: J.D. and O.G. equally developed the idea and wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The authors declare that all analytical data supporting the findings of this study are available within the paper and its supplementary information files or cited peer-review references.

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

Appendix A

Analytical Methods

Whole-rock major and trace elements were analyzed at the Activation Laboratories Ltd. (Ancaster, ON, Canada). An inductively-coupled plasma-optical emission spectrometer was used for the analysis of major elements, whereas trace element contents were determined with the use of an inductively-coupled plasma mass spectrometer. Based on analytical results obtained from international standard rocks, the analytical precision and accuracy were typically better than 5% for major elements and better than 10% for trace elements.

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