Zircons from Eclogite-Associated Rocks of the Marun–Keu Complex, the Polar Urals: Trace Elements and U–Pb Dating

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Abstract: The Marun–Keu complex plays a significant role in our understanding of the geological evolution of the Ural orogen; however, it remains poorly understood. This study aims to provide insights into the complex’s age, protolith composition, rock formation conditions, and its position in the geological history. The zircons from the host granitic gneiss are characterized by magmatic cores with an age of 473 Ma and metamorphic rims with an age of approximately 370 Ma. We suggest that the metamorphic rims were formed during eclogite metamorphism and that the metagranitoids hosting the eclogites experienced eclogite metamorphism simultaneously with the basic and ultrabasic rocks that are common in this area. Heterogeneous zircons were also isolated from the selvage of a pegmatite vein, in which four domains are distinguished, two to three of which can be identified within single grains, as follows: (1) igneous cores with an age of approximately 470 Ma and the geochemical characteristics of zircon crystallized in basic rocks; (2) zircons recrystallized during eclogite metamorphism with geochemical characteristics intermediate between those of the magmatic cores and true eclogitic zircon; (3) pegmatitic zircon, exhibiting the most sharply differentiated REE spectra of all four domains, characterized by a prominent positive Ce anomaly and a weakly expressed negative Eu anomaly; and (4) eclogitic zircon, observed in the form of veins and rims, superimposed in relation to the other three domains. The age of the latter three domains is within the error range and is estimated to be approximately 370 Ma. This indicates that the processes of eclogite metamorphism and the formation of pegmatites occurred at approximately the same time in the studied area.

Keywords: zircon; trace elements; rare earth elements; U–Pb zircon geochronology; eclogites; pegmatites; the Marun–Keu complex; the Polar Urals

1. Introduction

Eclogites and the metamorphic processes associated with them cover a wide range of pressure and temperature conditions, extending from deep crust to the mantle. Various types and occurrences of eclogites reflect different geological settings and environments [1]; however, the origin of eclogites within gneisses is still not completely clear. One of the main problems is the relationship of these eclogites to surrounding gneisses, which often lack evidence of eclogite-facies metamorphism. To date, several explanations have been
suggested for the coexisting of eclogites and gneisses, including the rejection of the high-pressure origin of the eclogites; formation of the eclogites at mantle depths and their subsequent emplacement in gneisses during tectonic event; formation of the eclogites in situ in their host gneisses, followed by a late obliteration of the eclogite-facies parageneses in the surrounding gneisses [2].

The Urals region is a classic example of a fold belt that has undergone a complete geodynamic evolution cycle and represents one of the most significant structural elements of the Eurasian continent [3]. Metamorphic complexes containing eclogites are extensively developed in this region and serve as important markers for understanding the geodynamic settings and reconstructing the history of this fold belt. The Urals contain globally renowned examples of eclogite-containing complexes, including the Maksyutov and Marun–Keu complexes [4].

The Marun–Keu complex is an important study area for understanding the geological history of the Ural orogen. A significant contribution to the understanding of this complex was made by N.G. Udovkina through her monograph “Eclogites of the Polar Urals”, published in 1971 [5]. This work was based on detailed geological and petrographic investigations conducted in 1956 and 1962. However, despite its tectonic significance, the Marun–Keu complex remains poorly studied due to its challenging accessibility and complex geological structure. The age of the complex, the nature of the eclogite protoliths, the rock formation conditions, and its position in the region’s geological history remain subjects of debate ([6–11], etc.).

In terms of the ages of the rocks forming this complex, two clusters of probable ages for eclogite metamorphism have been identified in the area: Mesoproterozoic [12,13] and Paleozoic [5,13–17]. However, there are limited data available regarding the age of the host rocks [5,13,15,16]. The Rb–Sr and Sm–Nd systems have yielded uncertain results, with significant date scatter requiring further interpretation [12,14,15]. Although U–Pb dating studies have produced similar dates [16,17], these results lack analysis of zircon trace element composition and mineral inclusions, both of which are crucial for accurate geochronological interpretation [18–22]. Therefore, a comprehensive study of zircons from rocks associated with eclogites in the Marun–Keu complex is necessary to gain an improved understanding of the regional geological history.

2. Geological Setting and Sample Description

The Ural Fold Belt, spanning a length of 2500 km, represents the northwestern segment of the extensive Paleozoic Ural–Mongolian mobile belt. Structurally, the Ural Fold Belt is divided into distinct zones from west to east, including the Cis-Ural foredeep, the West Ural megazone, the Central Ural megazone, the Tagil–Magnitogorsk megazone, the East Ural megazone, and the Trans-Ural megazone (Figure 1a) [3]. The Cis-Ural foredeep and the West Ural and Central Ural megazones form the paleocontinental sector of the Urals, i.e., the former passive margin of the paleocontinent Baltica/Laurussia. The Tagil–Magnitogorsk, East Ural, and Trans-Ural megazones form the paleo-island-arc sector, which is a collage of ophiolites, island-arc, and, possibly, microcontinental terranes. The boundary between the paleocontinental and paleo-island arc sectors within the Urals is demarcated by the Main Ural Fault, a significant suture zone also referred to as the ophiolite suture [3].

The Marun–Keu complex is a tectonic block located in the Urals region, whose dimensions are approximately 14 by 70 km, and it is related to the Central Ural megazone (Figure 1a). It is elongated in a roughly NE–SW direction and is confined to the zone west of the Main Uralian Fault (Figure 1). The complex is bounded to the west by metavolcanic rocks, local granite and diorite intrusions, and metasedimentary complexes of late Neoproterozoic to early Paleozoic age. These rocks underwent low-grade metamorphism of greenschist facies or below [5,10]. They belong to the Nyarovey series and represent a recumbent block beneath the Marun–Keu complex. To the east, the complex borders the Syum–Keu ophiolite massif and metagabbroids, which form the hanging wall of the Main Uralian Fault [5,10].
Syum–Keu ophiolite massif and metagabbroids, which form the hanging wall of the Main Uralian Fault [5,10]. The southern part of the Marun–Keu complex, especially the area known as Mica Hill, contains the most complete eclogites and relics of their protoliths. Previous research ([5–17], etc.) has primarily focused on this part of the complex. The eclogite outcrops are confined to the axial part of the Marun–Keu structure. The eclogites and their protoliths form lenticular blocks embedded in a granitic gneiss matrix. Three main groups of eclogite protoliths have been identified based on geological observations: peridotites, leucogabbros, and dolerite porphyrites, among which the peridotite-derived eclogites are the most common. The eclogite blocks and their associated rocks are elongated in a strip consistent with the strike direction of their host rocks; however, the primary contacts between these bodies have not yet been established. The orientations of linear elements within the eclogite blocks from different protoliths are not consistent. Combined with the above observations, this may imply the tectonic origin of these bodies. Based on geological observations, the age of the eclogite facies metamorphism is interpreted to be the same as or greater than that of

Figure 1. (a) Simplified tectonic scheme of the Urals after [3]. MUF—Main Uralian Fault. 1—the Cis-Ural foredeep; 2—the Central Ural megazone; 3—the East Ural megazone; 4—the West Ural megazone; 5—the Tagil–Magnitogorsk megazone; 6—the Trans-Ural megazone. (b) The inset shows the overall geographic location of the Marun–Keu complex. (c) Geological map of the Marun–Keu complex [5]. Key: 1—Quaternary; 2—Ordovician (?); 3—greenschists of the Nyarovey formation; 4—Marun–Keu series: gneisses, eclogites; 5—gneisses, granite gneisses; 6—granites with fluorite; 7—meta-rhyolites; 8—diorites, 9—gabbroids; 10—ultramafic rocks (Syum–Keu complex); 11—predominately eclogites; 12—glaucophane-hosted rocks; 13—quartz–graphite schists; 14—faults.

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their host rocks. The muscovite pegmatite veins observed cross-cutting the eclogite bodies provide a constraint for the latest possible date of eclogite formation.

This study focuses on an analysis of zircons derived from the host granitic gneisses and the selvage of a pegmatite vein within the peridotites. The samples were collected from an area called “the hill with peak 1040” (67°28′17″ N, 66°29′24″ E), which forms a protrusion of ultramafic rocks, elongated in a roughly NE-SW direction, measuring approximately 200 × 400 m (Figure 2a,b). This protrusion consists primarily of massive peridotites with a local shear zone containing eclogite lenses conformal to its orientation. This shear zone is around 10 m thick with a strike of 5° (magnetic declination +25° was considered) and a subvertical dip (Figure 2a).

Figure 2. (a) Schematic sampling map. (b) General view of the peak 1040 area. (c) Selvage of a pegmatite vein at the contact with its host peridotites; white circle with sample number indicates the location from which sample 2209 was collected. (d) Contact between granitic gneisses and peridotites, cross-cut by a 1.5 m-wide pegmatite vein; white circle with sample number indicates the location from which sample 2218 was collected. The pegmatite vein was previously excavated for exploration purposes. (e) Migmatization zone in granitic gneisses indicated by a blue dashed line.

A sample from the selvage of a pegmatite vein (2209) was collected from a ditch on the eastern slope of the hill (67°28′16″ N, 66°29′28.3″ E). This ditch has a strike orien-
tation of 300° (magnetic declination +25° was considered) and measures approximately 3 × 10 m. The selvage material is a coarsely crystalline rock predominantly composed of muscovite and amphibole. The composition of the selvage is interpreted as host rock material (peridotite) that was reworked by fluids during pegmatite intrusion (Figure 2a,c).

The granitic gneiss sample (2218) was collected from the southern foot of the hill in an exploration ditch in which a pegmatite vein was excavated (67°28′03″ N, 66°29′20.5″ E). This ditch cuts through both host rocks (granitic gneisses) and peridotites (Figure 2a,d). Isolated occurrences of migmatization are observed in the granitic gneisses (Figure 2a,e). The granitic gneiss is a fine-grained leucocratic rock with a weakly expressed schistose texture. The main rock-forming minerals are quartz, potassium feldspar, plagioclase, and micas. Epidote, apatite, rutile, and rare small garnet grains are present as accessory minerals (Figure 3a–d).

Figure 3. Microphotographs of thin section of granitic gneiss (sample 2218): (a,c) transmitted polarized light; (b,d) birefringence.

3. Methods

Zircons were recovered from rocks using magnetic separation and heavy liquids. The selected zircon grains were mounted in epoxy together with TEMORA II [23] and 91500 [24] zircon standard. The spots for in situ analyses were selected based on both transmitted and reflected light images to avoid cracks and inclusions. Cathodoluminescence (CL) images were obtained at the Centre of Isotopic Research of the All-Russian Geological Research Institute (CIR). Back-scattered electron (BSE) images of the zircons and chemical analyses of mineral inclusions were obtained at the Institute of Precambrian Geology and Geochronology of the Russian Academy of Sciences using a JEOL JSM-6510 LA scanning electron microscope with a JED-2200 (JEOL) energy dispersive system. The mineral abbreviations are given according to Warr [25].

U–Pb local dating was performed on the SIMS SHRIMP-IIe instrument at the Centre of Isotopic Research of the All-Russian Geological Research Institute using the method of Williams [26], adopted for CIR according to Schuth et al. [27]. The intensity of the primary O2 beam was 4 nA, and the analytical crater was 20 µm wide and 2 µm deep. The data obtained were processed using the SQUID program, according to Ludwig [28]. Differential
fractionation between U and Pb was monitored using a reference Pb/U ratio of 0.0668 for the TEMORA II zircon standard (416.8 ± 0.3 Ma), according to Black et al. [29]. The 91500 zircon standard with a uranium content of 81.2 ppm and a $^{206\text{Pb}}/^{238\text{U}}$ age of 1062 Ma was used as a concentration standard [24]. The 1σ level was used for uncertainty in the single analyses of U/Pb ratios and ages, whereas the 2σ level was used for uncertainties in the calculated concordia ages and intercepts with the concordia. The Isoplot/Ex program was used to construct the concordia plots according to the method outlined in [30].

Zircon trace element measurements were performed using a Cameca IMS-4f ion microprobe at the Yaroslavl branch of the Institute of Physics and Technology of the Russian Academy of Sciences. We mainly followed the analytical procedure described in [31,32]. The primary O$_2^-$ ion beam spot size was around 20 µm. Each analysis was averaged from three measurement cycles. The precision of the trace element measurements was up to 10% for concentrations exceeding 1 ppm and up to 20% for concentrations between 0.1 and 1 ppm. To construct REE distribution spectra, the zircon compositions were normalized to that of CI chondrite [33]. The term “ppm” in the text and tables means “weight-ppm”. The Ce and Eu anomalies were calculated using the following formulas:

$$\text{Eu/Eu}^* = \frac{\text{Eu}_N}{\sqrt{([\text{Sm}_N]^* * [\text{Gd}_N])}}$$  \hspace{1cm} (1)

$$\text{Ce/Ce}^* = \frac{\text{Ce}_N}{\sqrt{([\text{La}_N]^* * [\text{Pr}_N])}}.$$  \hspace{1cm} (2)

The zircon crystallization temperature was determined using a Ti-in-Zrn thermometer [34].

4. Results
4.1. Zircon Characterization

A total of 120 zircon grains were separated from sample 2218. Most of these grains are prismatic, although bipyramidal forms were occasionally observed. The aspect (i.e., length-to-width) ratio of the grains ranges from two to three (Figure 4a). The grain diameter typically ranges from 30 to 100 µm, with some grains reaching up to 150 µm. In the CL images, the central parts of the grains show dark gray coloring and pronounced oscillation zoning typical of magmatic zircon. These can be readily distinguished from the light gray inhomogeneous rims with thicknesses ranging from a few microns to 50 µm (Figure 4a). The rims are characterized by the development of cracks perpendicular to the grain boundaries, which are visible on BSE images (Figure 4b). Zircons also contain a significant number of inclusions in the cores and rims, both primary and secondary, associated with the fracturing. The mineral inclusions are quartz, potassium feldspar, and less commonly apatite, phengite, and epidote. In one case, a clinopyroxene inclusion with a jadeite end member content of 19% was found in the grain rim (Figure 4b). Chemical compositions of mineral inclusions are given in Table S1.

More than 50 zircon grains were separated from sample 2209. These grains are highly heterogeneous in both size and shape, and many are fragments of crystals. The grain diameter is typically between 200 and 400 µm, and the whole grains have aspect ratios of 3–4.

In the CL images, four distinct zircon domains can be identified based on their color and internal structure (Figure 5a). The first domain is represented by zircon cores with pronounced, fine-banded oscillatory zoning, characteristic of igneous zircons. The second domain (two measurements; points 7 and 19 in Figure 5a) includes gray cores with very weakly expressed or practically absent oscillatory zoning. In the BSE images, these two domains are characterized by numerous irregularly distributed cracks, as well as mineral inclusions comprising mainly phlogopite, phengite, amphibole, and less commonly garnet, rutile, chlorite, quartz, and potassium feldspar (Figure 5b,c). The third domain is composed of dark, monotonous zones, which may comprise almost the entire grain. In one case these zones form thick borders (up to 150 µm thick) with embayed boundaries around the core of the first domain. The fourth domain is characterized by light gray monochromatic rims.
of variable thickness (up to 200 μm) and veinlets, which are present in almost all the grains (Figure 5a). In the BSE images, the third and fourth domains are distinguished by the absence of cracks and inclusions (Figure 5c).

Figure 4. (a) CL images of zircons from granitic gneiss (sample 2218). Colored circles indicate the SIMS analytical spots, the numbers of which correspond to those in Table S2 and Figure 6. Blue circles indicate magmatic cores, while green circles indicate metamorphic rims. (b) BSE images of zircons from granitic gneiss (sample 2218) with labeled mineral inclusions. Png—phengite.

4.2. Zircon Trace Element Composition
4.2.1. Zircon from Granitic Gneiss (Sample 2218)

The cores of the zircon grains from granitic gneiss are characterized by a strongly fractionated REE distribution with a regular increase observed from light to heavy REE (LuN/LaN ratios from 33.1 to 11,905; LuN/GdN ratios from 10.0 to 22.1) (Figure 6a). The total REE content varies between 835 and 4210 ppm. A pronounced positive Ce anomaly (average Ce/Ce* of 20.3) and negative Eu anomaly (average Eu/Eu* of 0.18) are observed.
Furthermore, the cores of zircon grains from granitic gneiss are characterized by increased contents of certain elements, including P (272–1014 ppm), Y (1168–9591 ppm), and Li (0.24–13.4 ppm). Based on the Ti-in-zircon thermometer [34], the average calculated formation temperature for the zircon cores was approximately 770 °C (Table S2).

**Figure 5.** (a) CL images of zircons from the selvage of a pegmatite vein (sample 2209). The colored circles indicate the SIMS analytical spots, the numbers of which correspond to those in Table S3 and Figure 7. Blue circles indicate magmatic cores (first domain), green circles indicate recrystallized cores (second domain), navy blue circles indicate pegmatite zircon (third domain), and yellow circles indicate eclogite rims and veinlets (fourth domain). (b,c) BSE images of zircons from the selvage of a pegmatite vein (sample 2209) with labeled mineral inclusions. *Png*—phengite.

The REE distribution patterns of the rims of the zircon grains from granitic gneiss (Figure 6) are also differentiated; however, the spectra are flatter relative to those from the grain cores in the range from Gd to Lu (Lu\(_N\)/La\(_N\) ratio varies from 9.1 to 130, while the Lu\(_N\)/Gd\(_N\) ratio ranges from 4.38 to 42.1). The total REE content in the rims is lower than that in the cores and varies in the range of 99.0–644 ppm. The Ce anomaly remains positive in the grain rims, but its values are lower (Ce/Ce* average of 3.9). In most cases, the Eu anomaly remains negative and decreases in magnitude, with values in the range of 0.14 to 0.58 (with an average of 0.38). However, in two instances, the sign of the Eu anomaly changes...
to positive, with corresponding Eu/Eu* values of 1.66 and 3.71. The rims of the grains also exhibit lower contents of elements such as P (25.5–155 ppm), Y (124–814 ppm), and Li (0.9–2.6 ppm). The temperature value for the rims was calculated using the Ti-in-zircon thermometer approach [34], which yielded an average of approximately 740 °C (Table S2).

Figure 6. Trace element compositions of zircons from granitic gneiss (sample 2218). (a) REE distribution patterns normalized to CI chondrite [33]. (b–d) Co-variation diagrams of element pairs. The position of the analytical spots in different zircon domains is shown in Figure 4 by circles of the corresponding colors.

4.2.2. Zircon from the Selvage of a Pegmatite Vein (Sample 2209)

The first domain within the zircon grains (i.e., zircon cores with pronounced oscillatory zoning) is characterized by differentiated REE spectra, with an increase in the content from light to heavy REE. The LuN/LaN ratio varies from 3955 to 15,027, while the LuN/GdN ratio varies from 10.4 to 18.3 (Figure 7a). The total REE content is lower than in the zircon cores from granitic gneiss, with values ranging from 467 to 1342 ppm. A prominent positive Ce anomaly (Ce/Ce* average of 53.3) and negative Eu anomaly (Eu/Eu* average of 0.22) are observed. The contents of Y (655–2117 ppm), P (185–338 ppm), and Li (0.02–0.42 ppm) are lower than those recorded in the zircon cores from granitic gneiss (Figure 7b,c). Geochemical discriminant diagrams [35] indicate that these zircons fall within the region of overlap between the oceanic and continental crust (Figure 8).
Figure 7. Trace element compositions of zircons from the selvage of a pegmatite vein (sample 2209). (a) REE distribution patterns normalized to CI chondrite [33]. (b–d) Co-variation diagrams of element pairs. The position of the analytical spots in different zircon domains is shown in Figure 5 by circles of the corresponding colors.

In the case of zircon from the second domain, a positive Ce anomaly (Ce/Ce* of 19.0 and 57.3) and a negative Eu anomaly (Eu/Eu* of 0.48 and 0.50) are observed. The total REE content values are lower than that recorded in the cores of the first domain, with values of 40.2 and 288 ppm. Furthermore, this zircon domain is distinguished by an increase in the Li content (0.28 and 0.66 ppm) and a decrease in the Y content (85.4 and 336 ppm) and P content (39.0 and 73.0 ppm) relative to the first domain (Figure 7b,c).

The third zircon domain (i.e., dark, unzoned zircons when viewed in CL) is distinguished by the most sharply differentiated REE spectra of all four domains, with LuN/LaN ratios ranging from 13,926 to 125,367 and LuN/GdN ratios ranging from 185 to 532 (Figure 7a). The total REE content is also high, ranging from 1019 to 2082 ppm. Furthermore, the REE spectra exhibit a prominent positive Ce anomaly (average Ce/Ce* of 12.3) and a weakly negative Eu anomaly (average Eu/Eu* of 0.43). The content of Y varies between 806 and 1374 ppm, P between 112 and 189 ppm, and Li between 0.04 and 1.47 ppm (with an average of 0.42 ppm). The temperature value for this domain was calculated using the Ti-in-zircon thermometer [34], which yielded an average of approximately 700 °C (Table S3).
Figure 8. Geochemical discriminant diagrams for zircon after [35]. Blue markers indicate the positions of zircon cores from the selvage of the pegmatite vein (sample 2209).

The fourth zircon domain, which forms the late rims and veinlets, is characterized by weakly differentiated REE spectra. In most cases, the slope of the HREE distribution is less steep than samples from the other domains, with the Lu\(_N\)/La\(_N\) ratio varying from 108 to 5182 and the Lu\(_N\)/Gd\(_N\) ratio varying from 2.90 to 119. The total REE content is lower than in all the other domains, with values ranging from 11.9 to 158 ppm. The REE spectra are characterized by the presence of a positive Ce anomaly (average Ce/Ce\(^*\) of 7.96) and a weak negative Eu anomaly (average Eu/Eu\(^*\) of 0.46). The values of the Ce and Eu anomalies are lower than those in first domain (Figure 7a). Zircon from this domain exhibits a lower P (12.7–86.7 ppm) and Y (19.5–174 ppm) content relative to the first domain (Figure 7b,c), whereas the Li content in the fourth domain is higher (Li = 0.426–1.26 ppm) (Table S3).
4.3. Zircon U–Pb Geochronology
4.3.1. Zircon from Granitic Gneisses (Sample 2218)

A concordia age value of 473 ± 2 Ma was determined for magmatic cores in zircon from granitic gneiss at six points (MSWD = 0.12, Figure 9). To exclude the problem of Pb-loss, we used not all measured points to calculate age. Chosen points are marked in Table S4. The U content varies between 71.3 and 3538 ppm, while the Th content ranges from 94.7 to 5120 ppm. The Th/U ratio varies within the range of 0.64–2.49.

![Concordia plot for zircons (a) from granitic gneiss (sample 2218) and (b) from the selvage of a pegmatite vein (sample 2209). Error ellipses are at 2σ confidence. The blue ellipses represent the concordia age and error. Decay constant errors are included.](image)

A concordia age was established from the metamorphic zircon rims at seven points, with an age of 370 ± 4 Ma (MSWD = 0.16, Figure 9). The U and Th contents were lower in
the rims relative to the cores, with values of 51.6–105 ppm and 0.48–6.90 ppm, respectively. The Th/U ratio falls within the range of 0.01–0.10 (Table S4).

4.3.2. Zircon from the Selvage of a Pegmatite Vein (Sample 2209)

For the first domain of the zircons from the pegmatite vein selvage, a concordia age of 470 ± 6 Ma was determined based on six points (MSWD = 0.36, Figure 9a). The U and Th contents are lower than those recorded in the magmatic zircon cores from sample 2218 (U = 31.7–94.8 ppm; Th = 48.1–187 ppm). The Th/U ratio varies within the range of 0.01–0.10 (Table S4).

The remaining three zircon domains, collectively comprising 16 points, yield a concordia age of 367 ± 2 Ma (MSWD = 0.21, Figure 9b). There is a considerable disparity in the U and Th contents observed across the different zircon domains. Zircons of the second domain exhibit an elevated U content (170 and 254 ppm) and a reduced Th content (7.16 and 13.8 ppm) compared to the first domain. Zircon of the third domain displays the highest U content (73.6–542 ppm), while the Th content varies within the range of 2.07–7.98 ppm. Zircon of the fourth domain is characterized by a lower Th content relative to the magmatic cores of the first domain (1.63–6.17 ppm), while the U content is higher (U = 60.7–281 ppm). The Th/U ratio is notably low in this domain (0.02–0.03) (Table S5).

5. Discussion

5.1. Trace Elements Behavior in Zircon through the Geological Processes

5.1.1. Zircon from Granitic Gneiss

The cores of zircon grains from granitic gneiss show the presence of a paired positive Ce anomaly and negative Eu anomaly, which is typical for zircons of magmatic origin. Positive Ce anomalies are associated with high oxygen fugacity in the system, while negative Eu anomalies are associated with simultaneous crystallization of plagioclase in the melt [36,37]. The elevated concentrations of P and Y (Figure 6a) and the strongly fractionated distribution of HREE also indicate a magmatic origin for these zircons [38]. The Th/U ratio > 0.1 in all cases, which indirectly indicates the magmatic genesis of this zircon [39]. The observed Li content > 0.1 ppm and elevated P content may suggest that the zircon cores crystallized in granitoids [40,41]. The average calculated formation temperature for the zircon cores (~770 °C) is broadly consistent with the temperature of granite formation [42].

The rims of zircon grains show a decrease in the value of Ce anomaly and an increase in the value of Eu anomaly relative to the zircons’ cores, which may indicate recrystallization of zircon in the presence of fluid [36,38]. The flattening of REE spectra in the range from Gd to Lu is also characteristic of metamorphic zircon [38,43]. The Th/U ratio falls within the range of 0.01–0.10, which provides further evidence for the metamorphic genesis of this zircon [39]. A decrease in the content of Y and P (Figure 6b,c) in the rims of the grains may be associated with the redistribution of these elements into accessory minerals such as allanite and apatite.

The uniformity of the zircon grains’ morphology from granitic gneiss and the presence of a significant number of mineral inclusions of the zircon host rock (i.e., quartz, potassium feldspar, white mica, and apatite) support the interpretation that the studied rocks are indeed orthogneisses and not metasediments.

There are four possible types of metamorphic zircon: solid-state, replacement and dissolution recrystallizations of protolith zircons, and new growth from the aqueous fluid [44,45]. The rims are contrastingly different from the central parts of zircon grains by their geochemical features and appearance in CL; they cut the zoning of the central zones and their thickness is distributed unevenly within the grain. Based on these observations, we suggest that the metamorphic rims of the zircons from the granitic gneiss were formed during the solid-state recrystallization of igneous zircon in combination with the process of dissolution–reprecipitation of zircon [46,47].

Based on these findings, we interpret that the cores of the zircon grains from granitic gneiss reflect the igneous stage of their formation, while the compositions of their rims reflect the metamorphic stage.
5.1.2. Zircon from the Selvage of a Pegmatite Vein

The first domain of zircon grains from the selvage of a pegmatite vein reveals the differentiated REE spectra, positive Ce anomalies, and negative Eu anomalies, as discussed above, in the cores of zircon grains from granitic gneisses, which likely indicate the magmatic genesis of these zircons. The lower contents of HFSE and P relative to zircon cores from granitic gneiss, in addition to the Li content of < 0.1 ppm in all grains except one, may indicate that the first-domain cores were crystallized in basic rocks of the oceanic crust [40,42]. The Th/U ratio values exceed 0.1, which may imply the magmatic genesis of these zircons [46]. In one case, third-domain zones form thick borders (up to 150 µm thick) with embayed boundaries around the core of the first domain, indicating that the grain has undergone partial melting. It is assumed that the zircons from the first domain belong to the igneous protolith of the eclogites and were captured by the pegmatite melt.

Based on geochemical features of the second zircon domain, we suggest that it corresponds to the solid-state recrystallization of igneous zircon in combination with the process of dissolution–reprecipitation [46–49], with the preservation of some of their geochemical characteristics.

The overall character of the REE distribution, along with the high observed Y and P values (Figure 7b,c), indicates that the third zircon domain was formed during crystallization of the pegmatite [49–51], i.e., that this zircon is true pegmatitic zircon. The temperature value for this domain (~700 ºC) is broadly consistent with the typical formation temperature of pegmatites [52]. A decrease in the total REE content, particularly HREE, as well as a decrease in the magnitudes of the Ce and Eu anomalies, suggests that zircon from the fourth domain formed during the recrystallization of magmatic zircon under eclogite facies metamorphism under significant influence of metamorphic fluid [38,43]. The reduced Y and P contents are also indicative of eclogitic zircon [38]. The notably low Th/U ratio in this domain is typical of metamorphic zircon [48].

5.2. Metamorphic Rims of Zircon from Granitic Gneiss: A Result of Eclogite Metamorphism?

Our studies have shown that the age of metamorphic zircon rims extracted from granitic gneiss and that of eclogite zircon rims from pegmatite veins are almost the same. Based on this fact, we considered the question of whether eclogite metamorphism is superimposed on granitic gneiss or whether the Marun–Keu complex represents a more recent tectonic collage of rocks that were in different pressure-temperature (P-T) conditions.

Metagranitoids and quartzo-feldspathic gneisses frequently serve as the host rocks for eclogites within various high-pressure (HP) and ultrahigh-pressure (UHP) complexes, as evidenced in studies from regions such as the Western Gneiss Region [53], the Belomorian Mobile Belt [54], the Muya block eclogites [55], and the Tso Morari massif [56]. The Marun–Keu is also an example of this type of complex [5]; however, a significant challenge remains in determining the pressure–temperature (P–T) conditions of these supposedly HP acidic rocks, which raises questions about their involvement in HP and UHP metamorphic processes. Researchers frequently focus on eclogites that originate from mafic and ultramafic rocks because the formation of eclogite parageneses and eclogite index minerals is typically hindered in granitoids due to their composition and fluid imbalance [52,56,57]. Furthermore, in certain instances, eclogite parageneses may be obliterated during subsequent retrograde metamorphism associated with rock dehydration, which occurs in metagranitoids [58].

The identification of isolated small garnet grains within the granitic gneiss, as well as the observation of Na–pyroxene inclusions in the metamorphic rim of their zircons (with a jadeite mineral content of 19%), suggests that the metamorphic evolution of the studied granitic gneiss may have occurred under eclogite facies conditions, albeit at a relatively modest P–T configuration. This scenario suggests that omphacite may have crystallized within the granitic gneiss during eclogite metamorphism; however, subsequent retrograde metamorphism has likely led to its dissolution or alteration, resulting in the absence of omphacite in the rock’s current mineral assemblage. The presence of a significant number
of phengite inclusions in zircon grains may also be an argument that granitic gneisses experienced eclogite metamorphism.

The observed flattening of the REE spectra in the HREE range in the rims of zircons from granitic gneiss compared to their magmatic cores, and the variations in trace element composition, including decreases in Th, P, Y, and Li content in the rims, are consistent with the known behavior of these elements during zircon recrystallization in response to eclogite metamorphism in basic rocks [38,43]. Based on these observations, we interpret that the metamorphic rims of the zircons from the granitic gneiss were formed during the recrystallization of igneous zircon during eclogite metamorphism. We also interpret that the rock itself was involved in eclogite metamorphism, along with the mafic and ultramafic rocks common in this area.

5.3. Discussion of Geochronological Data

As previously stated, the dating of eclogites and related rocks from the Marun–Keu area has been conducted by various authors [5,12,14–17]. The data obtained by all the listed authors are summarized in Table 1.

Table 1. Summary of published rock age estimates from the Marun–Keu complex.

<table>
<thead>
<tr>
<th>Type of Rock</th>
<th>Targeted Object</th>
<th>Dating Method</th>
<th>Age</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granitic gneisses</td>
<td>Whole rock, muscovite, biotite, amphiboles</td>
<td>K–Ar</td>
<td>250–417 Ma</td>
<td>[5,13]</td>
</tr>
<tr>
<td>Eclogites</td>
<td>Whole rock, mica, amphiboles, clinopyroxenes, garnets</td>
<td>Sm–Nd</td>
<td>338–366 Ma</td>
<td>[14]</td>
</tr>
<tr>
<td>Kyanite eclogites</td>
<td>Zircon</td>
<td>U–Pb</td>
<td>351–385 Ma</td>
<td>[17]</td>
</tr>
<tr>
<td>Eclogites</td>
<td>Whole rock, amphiboles, kyanite, garnets, omphacite</td>
<td>Rb–Sr/Sm–Nd</td>
<td>1.54–1.69 Ga</td>
<td>[12]</td>
</tr>
<tr>
<td>Eclogites, metagranitoids, garnet amphibolites, etc.</td>
<td>White mica, apatite, amphiboles, whole rock, omphacite</td>
<td>Rb–Sr</td>
<td>352–360 Ma</td>
<td>[15]</td>
</tr>
<tr>
<td>Metagranites, metamorphic rim in eclogite facies vein</td>
<td>Zircon</td>
<td>U–Pb</td>
<td>353–375 Ma</td>
<td>[16]</td>
</tr>
<tr>
<td>Eclogites (after gabbro and peridotites); formation of garnet peridotites</td>
<td>Amphiboles, micas</td>
<td>K–Ar</td>
<td>439–650 Ma</td>
<td>[5,13]</td>
</tr>
<tr>
<td>Rutile eclogite</td>
<td>Zircon</td>
<td>U–Pb</td>
<td>750–1700 Ma</td>
<td>[13]</td>
</tr>
<tr>
<td>Eclogite protoliths</td>
<td>Phlogopite, amphiboles</td>
<td>K–Ar</td>
<td>600–800 Ma</td>
<td>[5,13]</td>
</tr>
<tr>
<td>Gabbro, troctolites</td>
<td>Zircon</td>
<td>U–Pb</td>
<td>420–508 Ma</td>
<td>[17]</td>
</tr>
<tr>
<td>Gabbro</td>
<td>Amphibole, clinopyroxene, plagioclase, whole rock</td>
<td>Rb–Sr</td>
<td>467 Ma</td>
<td>[15]</td>
</tr>
<tr>
<td>Basic rocks</td>
<td>Zircon</td>
<td>U–Pb</td>
<td>481–542 Ma</td>
<td>[16]</td>
</tr>
<tr>
<td>Metagranitoid’s protoliths (granitic gneiss)</td>
<td>Zircon</td>
<td>U–Pb</td>
<td>470–670 Ma</td>
<td>[16]</td>
</tr>
<tr>
<td>Granitoids</td>
<td>Whole rock, muscovite, biotite, amphiboles/zircon</td>
<td>K–Ar/U–Pb</td>
<td>525–780 Ma</td>
<td>[5,13]</td>
</tr>
<tr>
<td>Pegmatites cutting eclogite bodies</td>
<td>Muscovite, feldspar</td>
<td>K–Ar</td>
<td>271–500 Ma</td>
<td>[5,13]</td>
</tr>
<tr>
<td>Quarz-plagioclase-muscovite veins</td>
<td>Plagioclase, white mica, apatite, epidote, whole rock, titanite</td>
<td>Rb–Sr</td>
<td>356–358 Ma</td>
<td>[15]</td>
</tr>
</tbody>
</table>
5.3.1. Age of the Eclogite Protolith

Using the K–Ar method for olivine gabbros, gabbro-norites, and peridotites, Udvokina [5,13] obtained age values ranging from 800 to 600 Ma (Table 1) for the protoliths of eclogites. Additionally, the Rb–Sr dating method applied to relict gabbro samples yielded an age of approximately 467 Ma [15]. An analysis of magmatic zircon cores within kyanite eclogites using the U–Pb system revealed ages spanning 508–420 Ma, which were interpreted by the authors as representing the time of formation of the original gabbro/troctolite [17]. In addition, individual igneous zircon grains extracted from a mafic eclogite specimen exhibited ages falling within the range of 542–481 Ma [16].

In the present study, the age of the magmatic zircon cores retrieved from the selvage of a pegmatite vein (470 Ma) is interpreted as representative of the eclogite protolith’s age. This finding is consistent with previous dating results reported by Glodny et al. [15] and Meng et al. [17]. But the observed variability in the ages attributed to the eclogite protoliths may also relate to the tectonic juxtaposition of protoliths originating from distinct temporal periods.

5.3.2. Age of the Host Rock Protolith (Granitic Magmatism)

Using the U–Pb system, age values of 670–470 Ma were obtained for a heterogeneous population of igneous zircons from metagranitoids [16]. The authors linked a cluster of zircon grains with an age of ~490 Ma to the tectonic rifting phase associated with the development of the Paleo-Ural Ocean and the Early Paleozoic East European passive margin. It was assumed that the source of these granitoids could be an island-arc-type crust [16].

In the Urals region, Udoratina et al. [59] delineated two significant categories of granitoids: the pre-Uralids, which were formed prior to the fold belt’s formation, with ages ranging from 735 to 480 Ma, and the Uralids, characterized by ages ranging from 460 to 249 Ma. The formation of A-type granitoids within the Marun–Keu complex is attributed to rift-related magmatism of 520–480 Ma age, which coincides with the age of the pre-Uralid granitoids, a conclusion that is consistent with the findings of Glodny et al. [16].

The age obtained in this work for magmatic zircon cores from granitic gneiss (473 Ma) may be ascribed to the transitional period marking a shift in tectonic conditions from a rift-related setting to an island-arc environment.

5.3.3. Age of Eclogite Metamorphism

The studies by Udvokina in 1971 and 1985 provide insights into the age determination of eclogites through the application of the K–Ar method, yielding ages ranging from 650 to 439 Ma. In a subsequent study [12], the Rb–Sr and Sm–Nd methods were employed to determine the age of eclogites, resulting in an age range of 1.69–1.54 Ga. This suggests that this timeframe is the probable period of “primary crystallization of eclogites” [12]. Precambrian ages were also obtained using the U–Pb method on zircons from a sample of a rutile eclogite (1700–750 Ma) [13]. Highly consistent age estimates of eclogites were also obtained from the Sm–Nd method (366–338 Ma) [14], the U–Pb method (385–351 Ma) [16,17], and the Rb–Sr method (360–352 Ma) [15]. The age of metamorphic zircon is interpreted as the time of arc-continental collision due to the eastward subduction of the East European passive margin [16].

The age determination of host rocks using the K–Ar method yielded dates with marked variability, ranging from 417 to 250 Ma [5,13]. This variation in age estimates likely relates to the complex nature of multiphase granitization and migmatization processes affecting the host rocks, as highlighted by Udvokina and the authors of the present study. These processes can potentially lead to disturbances in the K–Ar isotopic system. The metamorphic ages of the metagranitoids, as determined using the Rb–Sr and U–Pb systems, demonstrate close agreement within the range of 375–353 Ma [15,16].

In the present study, we obtained an eclogitisation age close to those described above (ca 370 Ma); thus, it is assumed that eclogite metamorphism was reflected not only in the tectonic blocks composed of basic and ultrabasic rocks but also in the acidic host rocks.
5.3.4. Age of Pegmatites

The ages of the pegmatites and quartz–muscovite veins that cut the eclogite bodies were estimated using the K–Ar method, yielding age values ranging from 500 to 271 Ma [5,13]. In a more recent study, Glodny et al. [15] used the Rb–Sr method to analyse samples from veins comprising primarily quartz, muscovite, and feldspars, resulting in estimated ages of 358–356 Ma.

Based on field observations, the pegmatites are the youngest formations in the study area; however, our date estimates (ca 370 Ma), in turn, indicate that the processes of eclogitisation and the intrusion of pegmatite veins were approximately simultaneous, which is also confirmed by the data obtained in [15]. The question regarding the source material for the formation of the pegmatites remains open. The near-simultaneous eclogite metamorphism and crystallization of pegmatites do not exclude partial melting of some areas of the host granitoids during metamorphism. The pegmatitic zircon described in this work, with the exception of one crystal, does show no evidence of magmatic cores that would indicate granitoid magmatism with an age of 470 Ma. The only crystal identified in this study with a magmatic core of 470 Ma age may have been captured from the host acid rocks rather than a relic left from the melting of the rocks. Consequently, the question of the source of the material for the pegmatites remains unresolved and requires further investigation.

6. Conclusions

In this study, zircons from the Marun–Keu complex were investigated to determine the timing and nature of igneous and metamorphic processes in the study area. The zircons separated from the granitic gneiss exhibited magmatic cores with an age of 473 Ma, in addition to metamorphic rims with an age of around 370 Ma. We identified four distinct domains of heterogeneous zircon separated from the selvage of the pegmatite vein: (1) magmatic cores of approximately 470 Ma age exhibiting geochemical features typical of zircons crystallized in basic rocks; (2) zircons that recrystallized during eclogite metamorphism; (3) pegmatitic zircon; and (4) eclogitic zircon in the form of veinlets and rims that overlay the three aforementioned domains. The ages of the last three domains coincide within the error limits, indicating that the eclogite metamorphism and pegmatite formation processes that occurred at around 370 Ma were synchronous. It is shown that the granitic gneisses hosting the eclogites could also have experienced eclogite metamorphism, which brings some clarity to the understanding of the geodynamic history of the studied object.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/geosciences14080206/s1, Table S1: Composition of mineral inclusions in zircons from granitic gneiss (sample 2218) by SEM–EDS; Table S2: Trace elements composition of representative zircons from granitic gneiss (sample 2218) by SIMS (in ppm); Table S3: Trace elements composition of representative zircons from selvage of pegmatite vein (sample 2209) by SIMS (in ppm); Table S4: Zircon U–Pb SIMS data (sample 2218); Table S5: Zircon U–Pb SIMS data (sample 2209).

Author Contributions: Conceptualization, L.S. and A.B.; methodology, S.S. (Sergey Sergeev); field works, L.S., A.B., N.G. and S.S. (Sergey Skublov); writing—original draft preparation, L.S.; writing—review and editing, A.B., N.G., S.S. (Sergey Skublov) and E.S.; visualization, E.S.; supervision, S.S. (Sergey Skublov); funding acquisition, N.G. All authors have read and agreed to the published version of the manuscript.

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


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