The Geochronology and Geochemistry of Zircon as Evidence for the Reconcentration of REE in the Triassic Period in the Chungju Area, South Korea

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Abstract: The Chungju rare-earth element (REE) deposit is located in the central part of the Okcheon Metamorphic Belt (OMB) in the Southern Korean Peninsula and research on REE mineralization in the Gyemyeongsan Formation has been continuous since the first report in 1989. The genesis of the REE mineralization that occurred in the Gyemyeongsan Formation has been reported by previous researchers; theories include the fractional crystallization of alkali magma, magmatic hydrothermal alteration, and recurrent mineralization during metamorphism. In the Gyemyeongsan Formation, we discovered an allanite-rich vein that displays the paragenetic relationship of quartz, allanite, and zircon, and we investigated the chemistry and chronology of zircon obtained from this vein. We analyzed the zircon’s chemistry with an electron probe X-ray micro analyzer (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The grain size of the zircon is as large as 50 µm and has an inherited core (up to 15 µm) and micrometer-sized sector zoning (up to several micrometers in size). In a previous study, the zircon ages were not obtained because the grain size was too small to analyze. In this study, we analyzed the zircon with laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) for dating purposes. The REE patterns and occurrence of zircon in the quartz–allanite vein match well with previous reported recrystallized zircon, while the behavior of the trace elements shows differences with magmatic and hydrothermal zircon. The $^{206}\text{Pb}/^{238}\text{U}$ ages obtained from the zircon in the quartz–allanite vein are from 240.1 ± 2.9 to 257.1 ± 3.5 Ma and this age is included in the tectonic evolution period of the study area. Therefore, we suggest that the quartz–allanite veins in the Gyemyeongsan Formation were formed during the late Permian to early Triassic metamorphic period and the zircon was recrystallized at that time. The Triassic age is the first reported age with zircon dating in the Gyemyeongsan Formation and will be an important data-point for the study of the tectonic evolution of the OMB.

Keywords: allanite-rich vein; LA-MC-ICP-MS; recrystallized zircon; Triassic metamorphism; tectonic evolution of the OMB

1. Introduction

Rare-earth elements (REE) are of great importance and are used in a wide range of applications, especially in high-tech consumer products, such as cellular telephones, computer hard drives, lasers, magnets, batteries, radar and sonar systems, electric and hybrid vehicles, and flat-screen monitors and televisions. However, global REE production has been dominated by China. The United States of America (USA) was a significant producer through the 1990s, but the sale of low-priced materials by China forced mines in the USA and other countries out of operation. As a result of China limiting...
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exports and the dramatic increase in prices in 2009 and 2010, mines in worldwide exploration became active again.

Since REE and high-field-strength element (HFSE) mineralization was first reported in 1989 in the Chungju area in the central part of the Southern Korean Peninsula [1], a steady stream of studies has been carried out [2–10]. The genesis of REE and HFSE mineralization [2,3], the chemical compositions of alkali granite [4], the chemistry of REE-bearing minerals [5,6], and the associated uranium and thorium mineralization [7] have been studied. Constraining the age of the REE and HFSE mineralization at the Chungju area is important to understand the genesis and complicated history of mineralization.

Recently, dating of zircon that is too small (10–20 µm) for sensitive high-resolution ion microprobe (SHRIMP) analysis was conducted with laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) [10]. This analysis revealed that Paleozoic granite (331 ± 1.5 Ma), which intruded into the Gyemyeongsan Formation, is involved in REE and HFSE mineralization [10].

We discovered a quartz–allanite vein containing REE minerals and aggregates of zircon in the Gyemyeongsan Formation. In this study, we focus on zircon geochronology and chemistry with an electron probe X-ray micro analyzer (EPMA), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and LA-MC-ICP-MS in the quartz–allanite vein to clarify the mineralization history and the origin of the REE and HFSE mineralization in the Gyemyeongsan Formation.

2. Geological Setting

The Korean Peninsula comprises three major Precambrian massifs: the Nangrim, Gyeonggi, and Yeongnam massifs (Figure 1). The Gyeonggi and Yeongnam massifs are separated by the Okcheon Belt, which comprises the weakly metamorphosed Paleozoic Taebaeksan Basin and the Okcheon Metamorphic Belt (OMB). The OMB is a notoriously complicated polymetamorphic terrane in the Korean Peninsula.

The OMB mainly consists of metavolcanic and metasedimentary sequences that range in metamorphic grade up to amphibolite facies conditions [11].

Oh (2006) [12] suggests that the OMB can be correlated with the suture zone between the Yangtze and Cathaysia blocks because the suture zone in the South China Block was reactivated as a rift at 820–750 Ma during the breakup of the supercontinent Rodinia [13], which caused rift-related bimodal volcanism (756 Ma) in the OMB [14]. The OMB has been interpreted to represent a stack of syn-metamorphic nappes that comprise, from bottom to top, the Chungju, Turungsan, Pinbanryeong, Iwharyeong, and Poeun structural units [15,16] (Figure 1).

The Gyemyeongsan Formation in the Chungju unit (Figure 1) is mainly composed of metavolcanic rocks [17] and iron-bearing metaquartzites [2]. Schistose rocks are the dominant rock type of the Gyemyeongsan Formation and are derived from lava and tuffs [17]. The quartz–feldspar schist, which is one of the schistose rocks, contains substantial amounts of REE-bearing minerals, such as allanite, sphene, pyrochlore, and zircon [2]. Magnetite and hematite bearing quartzite is commonly intercalated with schistose rocks [2]. The granitic rocks that intruded into the Gyemyeongsan Formation occur as plutons, stocks, and dikes (Figure 1). These granitic rocks include Paleozoic alkali granite [10] and Mesozoic granite [9].
**Figure 1.** The location of the Chungju deposit and its geological setting. (a) A simplified map showing the tectonic provinces of East Asia, including the Korean Peninsula. (b) A geological map showing the stratigraphic/lithotectonic units of the Okcheon Metamorphic Belt and the Taebaeksan Basin. (c) A geological map of the study area. The figures are modified from reference [9].
3. Methods

3.1. EPMA

The chemical compositions of the zircons collected from the hydrothermal vein were analyzed by wavelength dispersive spectrometry using an electron microprobe (EPMA; JEOL JXA-8100) at Gyeongsang National University (Jinju, Korea). Quantitative analyses were carried out using instrumental settings, including an accelerating voltage of 15 kV, a beam diameter of 5 µm, and a counting time of 20–40 s for peak measurements. In-house standards were used for the analysis.

3.2. LA-ICP-MS

Analyses were carried out at the Korea Basic Science Institute, Ochang (Cheongju, Korea), using a NewWave UP 213 Nd:YAG laser coupled to a Thermo X2 series ICP-MS. The samples were then analyzed for about 30 s using a spot size of 30 µm for zircon at a 10 Hz repetition rate and with a fluence of 15 J/cm². Data reduction was carried out with the Glitter program [18]. The ablated aerosol was carried to the ICP source with He gas. The plasma was operated at 1300 W and the Ar carrier gas flow rate was 0.73 L/min. The certified reference glass NIST 612 was used to tune the instrument, to monitor drift, and as the primary standard for calibration. ²⁹Si was used as the internal standard, with the Si concentrations having been previously determined by EMPA.

3.3. Laser Ablation Multi-Collector (LA-MC)-ICP-MS

Zircons collected for U–Pb isotopic analyses were mounted as rock chips in epoxy resin. We analyzed the zircons with a Nu Plasma II Multi-collector ICP-MS coupled to a NewWave Research 193 nm ArF excimer Laser Ablation system at the Korea Basic Science Institute, Ochang (Cheongju, Korea). This technique is very similar to that published by Paton et al. [19]. Samples were ablated in helium (He) gas (with a flow rate of 970 mL/min). Prior to entering the plasma, the He aerosol was mixed with Ar (flow rate = 600 mL/min). All analyses were completed in the static ablation mode under normal conditions, including a beam diameter of 7 to 15 µm, a pulse frequency of 5 Hz, and a beam energy density of 2.81 J/cm². A single U–Pb measurement included 30 s of on-mass background measurement, followed by 30 s of ablation with a stationary beam. The masses of Pb 202, 204, 206, 207, and 208 were measured in secondary electron multipliers, and masses of 232 and 238 were measured in an extra-high-mass Faraday collector. ²³⁵U was calculated from the signal measured at mass 238, with ²³⁵U/²³³U = 137.88. Mass 204 was used to monitor common ²⁰⁴Pb after discarding the ²⁰⁴Hg background. In ICP-MS analyses, ²⁰⁴Hg mainly originates from the He supply. The background counting rate for a mass of 204 was calculated on the basis of ²⁰²Hg. Age-related common lead correction [20] was used when the analysis revealed common lead contents above the detection limit. Two calibration standards were run in duplicate at the beginning and end of each analytical session, as well as at regular intervals during each session. Raw data were corrected for background, laser-induced elemental fractionation, mass discrimination, and drift in ion counter gains. They were then reduced to U–Pb isotope ratios by their calibration to concordant reference zircons of known ages, with protocols adapted from Andersen et al. [21]. The reference materials zircons 91500 (1065 Ma; [22]) and Plešovice (337 Ma; [23]) were used for this calibration. Data processing and age calculations were performed off-line with the lolite 2.5 [19] and Isoplot 3.71 [24] programs. To minimize the effects of laser-induced elemental fractionation, the depth-to-diameter ratio of the ablation pit was kept low, and isotopically homogeneous segments of time-resolved traces were calibrated against the corresponding time interval for each mass in the reference zircon. To compensate for drift in instrument sensitivity and Faraday versus electron multiplier gain within an analytical session, a correlation of signal versus time was assumed for the reference zircons. All ages were calculated with 2σ uncertainties and without decay constant uncertainty. Data point uncertainty ellipses in all figures are presented at the 2σ level.
4. Results

4.1. Quartz–Allanite Vein and Zircon Occurrence in the Gyemyeongsan Formation

The quartz–allanite (allanite has not yet been defined according to an official nomenclature) veins were emplaced along the foliation in the metavolcanic rocks (Gyemyeongsan Formation) and crosscut the Paleozoic alkali granite [10] (Figure 2). In some areas, these veins appear similar to coarse-grained pegmatite (Figure 2). It has sharp contacts with metavolcanic rocks and alkali granite (Figure 2b). These veins are mainly composed of allanite (up to 80%), quartz, fluorite, microcline, minor chlorite, sericite, and microcrystalline (up to 50 µm in length) zircon (Figure 3). Coarse-grained euhedral allanite grains show various sizes and shapes (Figure 3). Aggregates of microcrystalline zircon (each grain size from 5 to 50 µm in length) have irregular shapes, coprecipitated with allanite and unknown REE-minerals (Figure 3d). The results of EDS analysis (3 points) unknown minerals are composed of O, F, Ca, V, Ag, Cs, Ba, and La.

Figure 2. Allanite vein intrusion in the Gyemyeongsan Formation and in alkali granite. (a) The allanite vein consists of allanite aggregates and felsic minerals. (b) The sharp contact between the alkali granite and allanite vein composed of allanite aggregates, fragments of alkali granite, and the latest quartz vein.
4.2. Geochronology

In previous studies, the zircon ages associated with REE mineralization from metavolcanic rock (Gyemyeongsan Formation) were not obtained because the grain size was too small to analyze. In this study, we analyzed U–Th–Pb isotope systematics (Table 1) in zircon from the quartz–allanite vein that occurred in metavolcanic rock via LA-MC-ICP-MS. Analysis of the cathodoluminescence images (Figure 4) revealed that the zircons from the quartz–allanite veins comprised aggregated microcrystalline grains. The zircon grains were euhedral and short-prismatic. Most of grains were less than 30 µm in length and several exceeded 50 µm. In the CL (cathodoluminescence) images (Figure 4b), the zircon grains showed overgrowth rim (up to several micrometers in size) or weak zoning. Some zircon grains (50 µm size in length) have inherited cores with very small sizes (<20 µm) (Figure 4b). We tried to analyze of parts of the zircon grains except the inherited cores.

Forty U–Th–Pb isotopic analyses of zircon in quartz–allanite vein are reported in Table 1. 15 spots on zircon yield concordant to near-concordant $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from 240.1 ± 2.9 to 257.1 ± 3.5 Ma, with a weighted mean age of 247.9 ± 2.8 Ma (2σ, MSWD = 15, Figure 4e,f). The zircons had Th/U ratios of 0.21 to 0.68. The other twenty-five spots yielded discordant ages. The age versus Th/U ratio was presented with Paleozoic magmatic zircon from alkali granite [10] in Figure 4d.
Figure 4. U–Pb isotope analyses. (a) Back-scattered electron (BSE) image of zircon from the zircon–allanite vein. (b) Cathodoluminescence (CL) image of the euhedral microcrystalline zircon. Note that some zircons have an inherited core and oscillatory zoning. (c) Tera–Wasserburg Concordia diagram (all data). (d) Age versus Th/U ratio scatter plot (all data; forty). (e) Tera–Wasserburg Concordia diagram (selected data; fifteen). (f) Weighted average zircon U–Pb ages of the quartz–allanite vein.
Table 1. Laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) U–Pb–Th isotopic analytical data for zircon from the quartz–allanite vein.

| No. | U (ppm) | Th (ppm) | Pb (ppm) | Th/U | 208Pb/206Pb | 2σ | 207Pb/206Pb | 2σ | 206Pb/238U | 2σ |
|-----|---------|----------|----------|------|-------------|----|-------------|----|-------------|----|
| 1   | 462     | 715      | 232      | 1.43 | 14.938750   | 0.071413 | 0.082570 | 0.000810 | 412.6 | 2.3 |
| 2   | 407     | 145      | 14       | 0.36 | 32.000000   | 0.39360  | 0.052200 | 0.001400 | 196.4 | 2.7 |
| 3   | 434     | 238      | 66       | 0.53 | 20.833333   | 0.520833 | 0.065000 | 0.001700 | 299.2 | 8.0 |
| 4   | 116     | 80       | 9        | 0.68 | 24.740230   | 0.232590 | 0.050900 | 0.002250 | 254.1 | 2.4 |
| 5   | 113     | 57       | 6        | 0.51 | 25.214320   | 0.292451 | 0.050600 | 0.003100 | 250.9 | 2.9 |
| 6   | 286     | 126      | 29       | 0.42 | 22.558900   | 0.432537 | 0.052200 | 0.001400 | 275.1 | 5.4 |
| 7   | 411     | 596      | 223      | 1.40 | 16.528930   | 0.273205 | 0.089000 | 0.001200 | 362.2 | 6.3 |

4.3. Zircon Composition

The chemical compositions of the zircon grains from the quartz–allanite vein have 32.3 to 33.1 wt% SiO₂, 63.7 to 66.4 wt% ZrO₂, and 1.6 to 1.9 wt% HfO₂ (Table 2). They have similar chondrite-normalized REE patterns (Figure 5). Light REEs vary from 62 to 165 ppm, and total REEs range from 564 to 808 ppm, with light REE (LREE)/heavy REE (HREE) ratios of 0.11 to 0.26 (Table 3). They display positive Ce anomalies and negative Eu anomalies with Ce/Ce* ratios ranging from 1.53 to 4.89 and an Eu/Eu* ratio from 0.14 to 0.17, respectively (Figure 5). The zircon grains have La concentrations ranging from 5.2 to 20.5 ppm, with (Sm/La)₅ ratios ranging from 0.18 to 0.89.
Table 2. Electron microprobe analyses (wt%) of the zircon from the quartz–allanite vein.

| Spots | SiO₂  | HfO₂  | UO₂  | Al₂O₃ | Ce₂O₃ | ThO₂  | La₂O₃ | PbO  | TiO₂  | ZrO₂  | Y₂O₃  | Total |
|-------|-------|-------|------|-------|-------|-------|-------|------|-------|-------|-------|-------|
| 1     | 32.5  | 1.8   | <0.1 | <0.1  | 0.3   | <0.1  | <0.1  | <0.1 | 63.7  | <0.1  | <0.1  | 98.6  |
| 2     | 32.6  | 1.7   | <0.1 | 0.2   | 0.2   | <0.1  | <0.1  | <0.1 | 64.4  | <0.1  | <0.1  | 99.3  |
| 3     | 33.1  | 1.8   | <0.1 | <0.1  | <0.1  | <0.1  | <0.1  | <0.1 | 65.0  | <0.1  | <0.1  | 100.1 |
| 4     | 32.6  | 1.7   | <0.1 | <0.1  | <0.1  | <0.1  | <0.1  | <0.1 | 66.4  | <0.1  | <0.1  | 100.9 |
| 5     | 32.3  | 1.6   | <0.1 | <0.1  | <0.1  | <0.1  | <0.1  | <0.1 | 64.3  | <0.1  | <0.1  | 98.4  |
| 6     | 32.5  | 1.9   | <0.1 | <0.1  | <0.1  | <0.1  | <0.1  | <0.1 | 66.2  | <0.1  | <0.1  | 100.9 |
| 7     | 32.4  | 1.8   | <0.1 | <0.1  | <0.1  | <0.1  | <0.1  | <0.1 | 65.6  | <0.1  | <0.1  | 100.0 |
| 8     | 32.6  | 1.6   | <0.1 | <0.1  | <0.1  | <0.1  | <0.1  | <0.1 | 65.5  | <0.1  | <0.1  | 99.8  |
| 9     | 32.7  | 1.6   | <0.1 | <0.1  | <0.1  | <0.1  | <0.1  | <0.1 | 65.5  | <0.1  | <0.1  | 99.9  |
| 10    | 32.5  | 1.6   | <0.1 | <0.1  | <0.1  | <0.1  | <0.1  | <0.1 | 65.6  | <0.1  | <0.1  | 99.9  |
| 11    | 32.6  | 1.8   | <0.1 | <0.1  | <0.1  | <0.1  | <0.1  | <0.1 | 65.5  | <0.1  | <0.1  | 100.2 |
| 12    | 32.8  | 1.9   | <0.1 | <0.1  | <0.1  | <0.1  | <0.1  | <0.1 | 65.0  | <0.1  | <0.1  | 99.8  |

Table 3. Laser ablation ICP-MS analyses (in parts per million) of zircon from the quartz–allanite vein.

| Elements | 1  | 2  | 3  | 4  | 5  | 6  | 7  |
|----------|----|----|----|----|----|----|----|
| P        | 167| 155| 149| 113| 117| 74.6| 81.1|
| Y        | 651| 577| 766| 581| 885| 718 | 697|
| Nb       | 118| 105| 152| 122| 112| 109 | 107|
| La       | 11.8| 10.3| 16.3| 11.1| 15.4| 14.3| 20.5|
| Ce       | 51.2| 45.3| 109.4| 31.7| 75.2| 55.9| 71.1|
| Pr       | 2.6 | 2.1 | 4.2 | 2.3 | 3.3 | 3.4 | 4.1 |
| Nd       | 9.4 | 8.2 | 17.9| 8.6 | 17.0| 11.8| 11.9|
| Sm       | 2.6 | 2.1 | 5.3 | 1.9 | 4.1 | 3.5 | 2.3 |
| Eu       | 0.2 | 0.2 | 0.4 | 0.2 | 0.3 | 0.3 | 0.2 |
| Gd       | 7.4 | 6.1 | 11.9| 5.9 | 12.5| 9.6 | 7.3 |
| Tb       | 2.9 | 2.4 | 4.2 | 2.2 | 4.1 | 3.2 | 2.6 |
| Dy       | 42.7| 35.1| 57.2| 34.7| 57.1| 44.7| 39.7|
| Ho       | 16.7| 14.7| 20.4| 14.5| 22.4| 18.1| 15.9|
| Er       | 93.4| 85.0| 110.9| 85.0| 117.9| 98.2| 93.3|
| Tm       | 27.1| 25.1| 31.6| 24.2| 33.0| 28.0| 27.5|
| Yb       | 316| 282| 351| 287| 367| 316| 315|
| Lu       | 62.7| 55.9| 67.9| 55.1| 72.7| 63.4| 64.2|
| Hf       | 8406| 7785| 10086| 7228| 11441| 9380| 11780|
| Ta       | 116| 102| 134| 107| 116| 109| 140|
| Pb       | 4.6 | 2.8 | 6.1 | 2.8 | 6.7 | 4.8 | 4.0 |
| Th       | 149| 114| 190| 121| 184| 170| 157|
| U        | 180| 154| 203| 161| 194| 154| 165|
| Ce/Ce*   | 2.24| 2.33| 3.21| 1.53| 2.56| 1.95| 1.87|
| Eu/Eu*   | 0.15| 0.14| 0.14| 0.17| 0.14| 0.16| 0.17|
| (Sm/La)N | 0.35| 0.32| 0.52| 0.27| 0.43| 0.40| 0.18|
| LREE     | 85 | 74 | 165| 62 | 128 | 99 | 118|
| HREE     | 562| 500| 643| 502| 674| 572| 558|
| TREE     | 647| 574| 808| 564| 802| 671| 676|
within the metamorphism age of 300–220 Ma, as reported by Cheong et al. [9]. And, the most similar quartz–allanite vein has non-formula elements Hf (1.6–1.9 wt % HfO\(_2\); Table 2). Hafnium enrichment shapes—especially small sizes (~50 µm)—and the variation of the Th/U ratio (fifteen concordant to near-concordant grains) from 0.21 to 0.68 for the zircon from the quartz–allanite vein, suggest that the medium age of 247.9 ± 2.8 Ma was obtained. This age has not been reported for intrusive rocks distributed within the metavolcanics (Gyemyeongsan Formation). However, it is included within the metamorphism age of 300–220 Ma, as reported by Cheong et al. [9]. And, the most similar zircon age (257 ± 3.3 Ma) was reported by Kim et al. [27]. The zircon grains separated from the metamorphisms (Gyemyeongsan Formation) and conducted SHRIMP U–Pb spot analyses from the overgrowth rims [27]. It means that the zircon from the quartz–allanite vein was not related with igneous activity, but related with metamorphism.

In addition, the partially to fully crystallization of zircon during metamorphism has been reported over a wide range of temperatures and pressures during prograde, retrograde, and peak metamorphic conditions [28–36]. The Permian–Triassic allanite ages linked with the collision in the OMB have been reported [9,37]. Observations of cathodoluminescence images show that most of the zircons are euhedral and short-prismatic, some of which have inherited cores and overgrowth zoning. This feature is similar to that metamorphic zircon formed in veins (quartz vein or complex vein) that can be formed during recrystallization [38,39].

The Th/U ratio in zircon has been reported to decrease during recrystallization [38]. The Th/U ratio in zircon has been reported to decrease during recrystallization [38]. The Th/U ratio in zircon has been reported to decrease during recrystallization [38]. The Th/U ratio in zircon has been reported to decrease during recrystallization [38]. The shapes—especially small sizes (~50 µm)—and the variation of the Th/U ratio (fifteen concordant to near–concordant grains) from 0.21 to 0.68 for the zircon from the quartz–allanite vein, suggest that the zircon recrystallized from microcrystalline Paleozoic magmatic zircon from alkali granite [10], which has a Th/U ratio from 0.69 to 0.75.

Zircon is zirconium orthosilicate, ZrSiO\(_4\) and has a stoichiometric composition (ideally) of 67.2 wt % ZrO\(_2\) and 32.8 wt % SiO\(_2\). Zircon from the quartz–allanite vein in the study area, however, ranges from 63.7 to 66.4 wt % ZrO\(_2\) and from 32.3 to 33.1 wt % SiO\(_2\) (Table 2). In addition, the zircon from the quartz–allanite vein has non-formula elements Hf (1.6–1.9 wt % HfO\(_2\); Table 2). Hafnium enrichment

5. Discussion and Conclusions

The results of dating have been reported for REE mineralization in the Gyemyeongsan Formation, located in the Chungju area: Park and Kim [2,3] and No and Park [10] reported the REE mineralization ages associated with Paleozone alkali granite, and Cheong et al. [9] reported data for allanite from metavolcanics (Gyemyeongsan Formation) and suggested that REE was reconcentrated during metamorphism (446 ± 8.0, 300–220, 199–183 Ma).

In this study, we investigated the zircon from the quartz–allanite vein which emplaced in the metavolcanics (Gyemyeongsan Formation), and the ages ranging from 240.1 ± 2.9 to 257.1 ± 3.5 Ma, with a weighted mean age of 247.9 ± 2.8 Ma was obtained. This age has not been reported for intrusive rocks distributed within the metavolcanics (Gyemyeongsan Formation). However, it is included within the metamorphism age of 300–220 Ma, as reported by Cheong et al. [9]. And, the most similar zircon age (257 ± 3.3 Ma) was reported by Kim et al. [27]. The zircon grains separated from the metavolcanics (Gyemyeongsan Formation) and conducted SHRIMP U–Pb spot analyses from the overgrowth rims [27]. It means that the zircon from the quartz–allanite vein was not related with igneous activity, but related with metamorphism.

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Figure 5. Chondrite-normalized rare earth element (REE) patterns for zircon from the quartz–allanite vein from study area and the partially to fully recrystallized zircon from high-grade metagranitoids from Queensland, Australia [26].

5. Discussion and Conclusions

The results of dating have been reported for REE mineralization in the Gyemyeongsan Formation, located in the Chungju area: Park and Kim [2,3] and No and Park [10] reported the REE mineralization ages associated with Paleozone alkali granite, and Cheong et al. [9] reported data for allanite from metavolcanics (Gyemyeongsan Formation) and suggested that REE was reconcentrated during metamorphism (446 ± 8.0, 300–220, 199–183 Ma).

In this study, we investigated the zircon from the quartz–allanite vein which emplaced in the metavolcanics (Gyemyeongsan Formation), and the ages ranging from 240.1 ± 2.9 to 257.1 ± 3.5 Ma, with a weighted mean age of 247.9 ± 2.8 Ma was obtained. This age has not been reported for intrusive rocks distributed within the metavolcanics (Gyemyeongsan Formation). However, it is included within the metamorphism age of 300–220 Ma, as reported by Cheong et al. [9]. And, the most similar zircon age (257 ± 3.3 Ma) was reported by Kim et al. [27]. The zircon grains separated from the metavolcanics (Gyemyeongsan Formation) and conducted SHRIMP U–Pb spot analyses from the overgrowth rims [27]. It means that the zircon from the quartz–allanite vein was not related with igneous activity, but related with metamorphism.

In addition, the partially to fully crystallization of zircon during metamorphism has been reported over a wide range of temperatures and pressures during prograde, retrograde, and peak metamorphic conditions [28–36]. The Permian–Triassic allanite ages linked with the collision in the OMB have been reported [9,37]. Observations of cathodoluminescence images show that most of the zircons are euhedral and short-prismatic, some of which have inherited cores and overgrowth zoning. This feature is similar to that metamorphic zircon formed in veins (quartz vein or complex vein) that can be formed during metamorphism (446 ± 8.0, 300–220, 199–183 Ma).

The Th/U ratio in zircon has been reported to decrease during recrystallization [38]. The shapes—especially small sizes (~50 µm)—and the variation of the Th/U ratio (fifteen concordant to near–concordant grains) from 0.21 to 0.68 for the zircon from the quartz–allanite vein, suggest that the zircon recrystallized from microcrystalline Paleozoic magmatic zircon from alkali granite [10], which has a Th/U ratio from 0.69 to 0.75.

Zircon is zirconium orthosilicate, ZrSiO\(_4\) and has a stoichiometric composition (ideally) of 67.2 wt % ZrO\(_2\) and 32.8 wt % SiO\(_2\). Zircon from the quartz–allanite vein in the study area, however, ranges from 63.7 to 66.4 wt % ZrO\(_2\) and from 32.3 to 33.1 wt % SiO\(_2\) (Table 2). In addition, the zircon from the quartz–allanite vein has non-formula elements Hf (1.6–1.9 wt % HfO\(_2\); Table 2). Hafnium enrichment
is a feature of recrystallized zircon [38], however metamorphic zircons that have formed under low temperature have low Ti (<2 ppm; [36]).

As can be seen from Figure 6, the Ce/Ce* vs. (Sm/La)_N and (Sm/La)_N vs. La (ppm) for the zircons from the quartz–allanite vein are not magmatic or hydrothermal zircons [40]. While the values of Ce/Ce* and (Sm/La)_N are slightly higher than those of the Baerzhe hydrothermal zircon, the values of (Sm/La)_N and La (ppm) are slightly lower than those of the Baerzhe hydrothermal zircon due to the medium-REEs (MREE) that have relatively low values compared to LREE and HREE. Moreover, the steep REE patterns from La to Lu with positive Ce and Negative Eu anomalies of metamorphic zircon was reported [26]. They show clear differences with magmatic and hydrothermal zircon (Figure 6), while the REE patterns are well matched with the recrystallization front of the zircon (Figure 5), as reported by Hoskin and Black [26].

![Discriminant diagrams for zircons. (a) Ce/Ce* vs. (Sm/La)_N (b) (Sm/La)_N vs. La (ppm) for zircons from the quartz–allanite vein compared to the magmatic and hydrothermal zircons from other areas such as the Boggy Plain Zoned Pluton (BPZP) aplite and Jack Hills Hadean zircon data are taken from Hoskin, 2005 [40]; the Baerzhe alkali granite, Inner Mongolia, NE China, data are taken from Yang et al., 2014 [41].](image-url)
In conclusion, the Gyemyeongsan Formation in the OMB was metamorphosed during the late Permian to early Triassic period (240.1 ± 2.9 to 257.1 ± 3.5 Ma). As reported by previous studies [9,10], the REEs that existed in the Gyemyeongsan Formation were mobilized and reconcentrated during metamorphism. The previously reported Pb–Pb whole-rock and U–Pb mineral ages indicate that the OMB experienced peak metamorphism during the Permian (290–260 Ma) age [27,42]. It means the quartz–allanite vein emplaced in the metavolcanics (Gyemyeongsan Formation) after the peak metamorphism. The Triassic age is the first reported through zircon dating from the Gyemyeongsan Formation. This first reported Triassic age is considered to offer important data to reveal the metamorphic evolution of the OMB.

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