Comagmatic Andesite and Dacite in Mount Ijo, Kulonprogo: A Geochemistry Perspective

Komagmatic Andesit dan Dasit di Gunung Ijo, Kulonprogo: Suatu Perspektif Geokimia

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Abstract - Mount Ijo is a Tertiary volcano located in Kulonprogo, Yogyakarta Province. Andesite and dacite are the two volcanic rock units in Mount Ijo and around Kulonprogo. Dacite intruded andesite unit in Middle Miocene period. The two volcanic rock units are tried to be correlated based on geochemistry perspective. XRF was applied on major oxides measurements of selected eight samples while ICP-MS on trace and rare earth elements. Major oxides data of volcanic rocks around Kulonprogo from previous studies are selected for additional data. The studied rocks are classified as basalt, basaltic andesite, andesite, and dacite based on their geochemistry contents. The studied samples show high degree of correlation in the Harker's Diagrams. Olivine and pyroxene fractionation together with ilmenite oxidation are most probably took place along magma differentiation. Alike patterns were also shown both in extended REE and REE spider diagrams. The comagmatic andesite and dacite is evidenced more by constant Rb/Sr ratio escalation through differentiation.

Keyword: andesite, dacite, geochemistry, magma differentiation, Kulonprogo


Katakunci: andesit, dasit, geokimia, diferensiasi magma, Kulonprogo
INTRODUCTION

Java Island, on which Kulonprogo is located, is a part of the Sunda Arc and extends north of the contact between Indian and Eurasian plates. At the plate boundaries, Indian plate subducts beneath the other plate. Calc-alkaline and alkaline rocks occupy geographic position with respect to the subduction. Tertiary magmatism in Java in 40-19 Ma (Late Eocene to Early Miocene) emplaced andesitic rocks with majorly calc-alkaline and minor tholeiitic affinities whilst andesitic rocks with totally calc-alkaline affinity was set in the second magmatism about 11-2 Ma (Late Miocene to Pliocene; Harjanto, 2011). Volcanic rocks in Mout Ijo and around Kulonprogo may be emplaced in relation to the subduction. Mount Ijo (+815 m) is a Tertiary volcano in Kulonprogo, Yogyakarta. On lithological and base metal distribution, a mineral deposit in Mount Ijo experienced hydrothermal alteration with Fe, Cu, Zn, and Pb compositions of 41.2%, 167 ppm, 67 ppm, and 35 ppm respectively (Abdissalam et al., 2009). Geological structure of the mountain is controlled of both magmatism and volcanism processes (Bronto, 2006). Many geological studies were conducted around Yogyakarta and Kulonprogo region. The geology of Yogyakarta is controlled by active plate tectonic phenomena such as the active volcano and active subduction of the Indo-Australia oceanic plate below the Euro-Asian continental plate since the middle Eocene to the present-day (Karnawati et al., 2006; Nurwidianto et al., 2014). Petrophysical parameters of igneous rocks and limestone in Kulonprogo was the main topic of Maryanto and Hasan (2011) investigation, whilst Irzon and Permanadewi (2010) focused on trace and REE standard operating procedure analysis for igneous rocks using ICP-MS. The volcanic rocks study around in Kali Wader, Purworejo (+15 km north of study area), revealed that the basaltic andesite was set in two volcanoes: Mount Gajah and Mount Manoreh (Wijaya and Hendratno, 2015). Moreover, lower SiO2-rocks were erupted from Mount Gajah whilst Mount Manoreh with higher SiO2 is an important conclusion of the latest study.

Andesite and dacite are the two igneous rock units around Mount Ijo (Rahardjo et al., 2012). This study tries to correlate the two extrusive igneous rock units based on their geochemical characters. Previous geochemistry results from Godean (Verdiansyah, 2016) and Kokap-Jering (Subiyanto, 1989) was selected for additional data to learn more deeper about magma differentiation in studied location. Moreover, no study is related to the trace and rare earth elements composition in both andesite and dacite units in Kulonprogo which are discussed here.

REGIONAL GEOLOGY

Study area is in the Old Ijo Mountain southern part of the Menoreh Mountains, Kulonprogo, Yogyakarta Province, in the southwestern part of Yogyakarta Quadrangle (Rahardjo et al., 2012). Kulonprogo comprises four sedimentary formations, from the oldest to the youngest: the Nanggulan Formation, Kebobutak Formation, Jonggrangan Formation, and Sentolo Formation. The Nanggulan Formation is the oldest rock formation in Kulonprogo which consist of sandstone with intercalated lignite, sandy marl, claystone with having limonite concretion, sandstone, and tuff. The Nanggulan Formation was assigned to be deposited at Eocene to Early Oligocene using planktonic foraminifera analyses (Harjanto, 2011). The Kebobutak Formation is the other name of van Bemmelen’s Old Andesite Formation and surrounds the intrusive andesite unit. The Kebobutak Formation is composed successively of conglomerate, sandstone, tuffaceous shale and silt, which is Late Oligocene-Lower Miocene in age, and deposited over the Nanggulan Formation. Conglomerate, tuffaceous marl, calcareous sandstone, limestone, and coralline limestone built the Jonggrangan Formation which was emplaced in Lower Miocene. The Jonggrangan Formation interfingers with the lower part of the Sentolo Formation. The Early Miocene to Pliocene Sentolo Formation consists of conglomerate and tuffs.

Kulonprogo experienced at least two phase of tectonic activities. The Kebobutak Formation was uplift in Late Oligocene to Lower Miocene on the peak tectonic activity in the central of Java. Southwest-northeast and north-south cross-sections produced horizontal faults, foldings and fractures in the Kebobutak Formation and filled with andesite, dacite and quartz veins. The next tectonic activity occurred in Late Miocene to Quaternary era which reoriented the north-south force to northeast-southwest. Faultings, brecciations, and fracture formations were dominant in the second tectonic activity. Andesite was emplaced earlier and was intruded by dacite in Miocene (Rahardjo et al., 2012). Previous andesite study in Bener area (about 20 kms north from study location) concluded that the rock was originated from basaltic magma and undergone differentiation to become more felsic basaltic andesite with number of series (Wijaya and Hendratno, 2015). Geotectonic study of Kulonprogo stated that the basaltic andesite intrusions presumably representing the late phase magmatic activities were observed (Syafri et al., 2013). Previous investigations around the area also used here as additional data. Young Volcanic Deposits of Merapi Volcano, Colluvium and Alluvium are the three nearest Quaternary units from research area. Geological map with sampling locations is shown in Figure 1.
SAMPLE AND ANALYTICAL METHODS

Eight samples of the andesite and dacite units from Mount Ijo were analyzed for XRF and ICP-MS at Center for Geological Survey's Laboratory in Bandung. RK 22 is greyish, porphyritic, medium grained plus phenocrysts andesitic rock in Ngaseman Village. Feldspars, olivines and hornblende were detected megascopically in the hard and massive outcrop. Both multi-component breccia and intrusive rock were located in Sangon River, Sangon Village. The porphyritic and medium grained intrusive rock (RK 54) from this river looked more mafic because of the dark color. Sangon River consists of few confluent and flows south down to the Kukusan Mountain. A dark greyish, fine grained, hard, and massive rock outcropped in one of a Sangon River's confluent (RK 57) about 1.5 km southwest of RK 54. RK 63 was described as fresh, greyish, porphyritic, fine grained andesitic rock from a flow near Telogolego.

RK 68 was taken in the river's wall with high counts of mafic minerals megascopically. Greyish, medium to coarse grained, andesitic rock samples was taken near Bendungan's flow in Krendetan Village (RK 92). Exfoliation joints could be observed at the rock bodies of both RK 68 and RK 92 resulted from contraction and expansion due to cooling and decompression respectively. Two medium grain, hard, and massive intrusive rocks containing relatively minimum mafic minerals were located in Hargorojo Village: RK 94 and RK 96. The RK 94 was found just beside the pathway about 1 km heading to river of RK 96 location. Some field conditions are presented in Figure 2.

Two analytical instruments: XRF and ICP-MS of The Center for Geological Survey were applied to study the geochemistry of the selected samples. Before instrument measurements, the rock samples were prepared as in Irzon et al. (2014). Samples were washed and dried outdoor for one day minimum. Whole samples were then crushed with jaw crusher to gain particle size of 200 mesh and were grounded using a ball mill. Basically, there are two main sample preparation techniques for measurement of sample powders with XRF: pressed pellets and fused beads. The excellences of the first technique are that it keeps sample homogenous, minimizes cross contamination, reduces the sample size, and the high sensitivity although the accuracy is not as good as fused beads. Pressed pellets are prepared by pressing loose sample powders filled in a ring or cup using a set of dies and a press machine. Ease of pelletization depends on sample characteristics and grain size, and can be improved by sufficient pulverization (Takahashi, 2015). The pressed pellets technique was applied in XRF preparation of this study. The pressed pellets were analyzed with the Advant XP x-ray fluorescence method (XRF) for major oxides measurement. Loss on Ignition (LOI) analyze is an important factor of geochemistry analyze as a simple method for estimating the content of organic matter and carbonate minerals. LOI represents the weight loss following...
heating to 1000°C and was often used as a good indicator of the degree of weathering (i.e., Regassa et al., 2014; Syafri et al., 2014). The andesite AGV-2 from Guano Valley and the rhyolite GBW 07113 were prepared and analyzed using the same procedure with the studied samples to verify the measurement accuracy.

REE contents of the selected rock samples were analyzed using quadrupole iCAP-Q Thermo Fisher Scientific’s Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Nitric acid (ultra-pure grade), formic acid (ultra-pure grade), and perchloric acid (pro analysis grade) were the solvents in sample digestion. The digestion procedure was done carefully because incomplete dissolution of highly resistant minerals in rock samples may cause biased results for a number of trace and rare earth elements (Bayon et al., 2009). Full suite of rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ro, Er, Tm, Yb, Lu) and as some other trace elements (Sc, V, Rb, Sr, Y, Ba, Zr, Nb, Th, and U) were analyzed. The CPSs (counts per second) of one blank and six levels of calibration solutions (0.1, 1, 5, 10, 25, and 50 ppb) were measured to produce the calibration curves of analyzed elements. Computer program of the ICP-MS device transformed elements’ CPS of samples to concentrations using the previous calibration curves. AGV-2 and GBW 7112 were the two certified reference materials used in this study to certify the quality of measurement results.

**RESULT AND DISCUSSION**

**Whole-rock Composition and Classification**

Eight samples (RK 22, RK 54, RK 57, RK 63, RK 68, RK 92, RK 94, and RK 96) were selected and were analyzed for the geochemical contents. SiO$_2$, Al$_2$O$_3$, CaO, and Fe$_2$O$_3$ are the dominant major oxides of selected volcanic rock from the Mount Ijo with range values of 45.63-62%, 18.5-22.3%, 4.4-15.5%, and 3-9.48% respectively. In other hand, Na$_2$O, K$_2$O, TiO$_2$, MnO, and P$_2$O$_5$ were detected in lower content: 0.87-3.47%, 0.71-2.00%, 0.32-1%, 0.11-0.25%, and 0.1-0.26% respectively. Chemical analysis results of the samples are given in Table 1. Loss on Ignition (LOI) is a good indicator of the degree of weathering based on the physical aspects. The more weathered a rock, it will be more minerals are oxidized (Syafri et al., 2014). Applying a parameter submitted by Regassa et al. (2014), three of the selected samples are categorized into unweathered whilst five others into intermediately weathered rocks. The data were then normalized to 100% without volatiles, including LOI, for later used in geochemistry based diagrams. Previous geochemistry results from Godean (AI and A2) (Verdiansyah, 2016) and Kokap-Jering (K2, K5, K7, and J5) (Subiyanto, 1989) was selected for additional data. Godean is about 15 km east of Mount Ijo with relatively similar andesite and dacite rocks in Yogyakarta Quadrangle (Rahardjo et al., 2012) while Kokap and Jering are located just in Kulonprogo.

![Figure 2](image-url) Some outcrops and field activities in this study. a) Greyish andesite from Ngaseman Village (RK 22); b) Andesit from Sangon Village, Kokap (RK 57); c) Precious metals prospecting in Bendungan River, near RK 92; and d) Brighter igneous extrusive rock of dacite’s location (RK 94).
Table 1. Geochemical contents of volcanic rock samples from Mount Ijo, Kulonprogo. Before plotting on geochemistry diagrams, the major elements composition has been normalized to 100% on the basis of LOI free.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO2 (%)</th>
<th>A12O3</th>
<th>CaO</th>
<th>Fe2O3</th>
<th>MgO</th>
<th>K2O</th>
<th>Na2O</th>
<th>TiO2</th>
<th>MnO</th>
<th>P2O5</th>
<th>LOI</th>
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<tbody>
<tr>
<td>RK22</td>
<td>50.80</td>
<td>45.63</td>
<td>46.38</td>
<td>55.71</td>
<td>47.15</td>
<td>59.13</td>
<td>62.01</td>
<td>59.07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RK54</td>
<td>53.73</td>
<td>45.63</td>
<td>46.38</td>
<td>55.71</td>
<td>47.15</td>
<td>59.13</td>
<td>62.01</td>
<td>59.07</td>
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<tr>
<td>RK57</td>
<td>50.80</td>
<td>45.63</td>
<td>46.38</td>
<td>55.71</td>
<td>47.15</td>
<td>59.13</td>
<td>62.01</td>
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<tr>
<td>RK63</td>
<td>50.80</td>
<td>45.63</td>
<td>46.38</td>
<td>55.71</td>
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<td>62.01</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>RK68</td>
<td>50.80</td>
<td>45.63</td>
<td>46.38</td>
<td>55.71</td>
<td>47.15</td>
<td>59.13</td>
<td>62.01</td>
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</table>

The data has been normalized to 100% free volatile base before it was used in geochemistry diagrams. The igneous extrusive rocks around Kulonprogo are classified into broad group: Three basalts (RK 54, RK 57, and RK 68), four basaltic-andesites (RK 22, RK 56, A1, and A2), four andesites (RK 92, RK 96, K2, and K5), and three dacites (RK 94, K7, and J5) after plotted in TAS diagram of Middlemost (1994) (Figure 3). Felsic character of RK 92, RK 96 and RK 94 confirms the geology map of Rahardjo et al. (2012) as those rocks are located in the dacite unit (Figure 1). The plentiful value of mafic mineral of RK 68 as detected on the field is corresponded on its basaltic composition. The Andesite in Kulonprogo area has passed through differentiation and evolves from the parental magma (Wijaya and Hendratno, 2015) to explain the wide composition of the samples. Variety of the previous research only ranges from basaltic andesite to dacite whilst some more mafic compositions are characterized in this study. Almost all of the samples are plotted in calc-alkaline series, except RK 54 and RK 57 in shoshonite series of potassic-silica diagram in Figure 4 (Peccerillo and Taylor, 1976).

Four of totally eight rocks were selected to be analyzed using ICP-MS for trace and rare earth element contents. The four selected samples represented the four groups in previous TAS diagram: RK 68 which is classified as basalt, RK 22 (basaltic andesite), RK 94 (andesite), and RK 94 (dacite) in Figure 3. Results of trace and rare earth elements analyses are presented in Table 1. However, please note that neither Subiyanto (1989) nor Verdiansyah (2016) presented trace and rare elements contents in their investigations. Ba and V are the two dominant trace element in the range of 226-458 ppm and 51-254 ppm respectively whilst U (1.2-4.4 ppm) and Th (3.5-11 ppm) are minor in the selected samples. Total REE of these rocks is in intermediate counts of 47-60 ppm to reflect that the rocks are not important REE sources.

Ternary plots of Ti/100-Zr-3*Y and Ti/100-Zr/Sr/2 (Pearce and Cann 1973), and binary diagram of Ti versus Zr (Pearce 1982) show the island arc affinity of study area for the rocks from Mount Ijo (Figures 5 a-c). Nevertheless, only RK 68 that may be originated from two sources: island arc lava or mid-ocean ridge basalt according to diagram in Figure 5c. Most of the samples were formed in calc-alkaline arc setting, excluding RK 68 in the border of calc-alkaline and tholeiitic AFM diagram (Irvine and Baragar, 1971; Figure 5d).

Continuous magmatic evolution from primitive arc tholeiites to more mature calc-alkaline magmatism is a feature characteristic of many island arc such as in the Shirehama Group, Japan and Umm Nagagat, Egypt (Mohammed and Hassanen, 1996). An Island arc affinity confirms the tectonic setting in Indonesia which is highly controlled by the movement of the Indian-Australian Oceanic Plate in collision with the Eurasian Continental Crust (e.g. Syafri et al., 2013; Wijaya and Hendratno, 2015). The TiO2 range of the selected samples (0.32-1%) confirms the orogenic type of the rocks. Typical characters of orogenic andesite confirm previous conclusion based on mineralogical views such as zoning in plagioclase and pyroxene from West Progo (Subiyanto, 1989).
Figure 3. Total alkali versus silica (TAS) diagram with chemical classification and nomenclature of volcanic rocks according to Middlemost (1994). The presented values are in (%). ● = this study, □ = data from Verdiansyah (2016), △ = data from Subiyanto (1989).

Figure 4. Plot of the chemical analyses of the volcanic rocks around Kulon Progo on the K₂O vs SiO₂ diagram (Peccerillo and Taylor, 1976). ● = this study, □ = data from Verdiansyah (2016), △ = data from Subiyanto (1989).
Magma Evolution

Rahardjo et al (2012) proposed that dacite in Yogyakarta Quadrangle intruded into previous andesite unit. Meanwhile, basaltic andesite to dacite composition in Kulonprogo is the result of differentiation process including: magma assimilation, magma mixing, and fractional crystallization based on a study in Kali Wader (Wijaya and Hendratno, 2015). Moreover, magma mixing characterized on both oscillatory zone and spongy cellular of plagioclase. Fractional crystallization of the source magma was concluded base on Na₂O, K₂O, and incompatible elements data. Geochemical contents of the rock samples around KulonProgo were then study more intensively about magma differentiation of the andesite and dacite units.

In Harker's variation diagrams, Al₂O₃, CaO, Fe₂O₃, TiO₂, and MgO show descending trends with increasing SiO₂ and show very good degree of association with r values of -0.82, -0.92, -0.96, -0.89, and -0.71 respectively (Figure 6a-e). These negative correlations may be attributed to the fractionation of Al-Ca-Fe-Ti-Mg rich phases such as plagioclase, olivine, and pyroxene (Hartono, 1994; Mohamed and Hassanen, 1996; Best, 2003). Negative correlation of Fe and Ti to silica has been attributed to magnetite crystallization in calc-alkaline series. Figure 6h shows that P₂O₅ increases in the basaltic rock and start to decrease in the andesite and continuously until the dacitic composition. It means no crystallization of apatite in basaltic magma and it starts to crystallize in the andesitic magmas. However, MnO depicts scatter in this Harker's diagram (r<0.6l) (Figure 6i).

Trace elements of the four selected samples trends against silica in Harker's diagram are presented in Figure 7. Throughout differentiation Ba, Rb, and Th content were increased whilst Sr, Sc, V, Zr, and Y were decreased. All plots depict -0.91<r<-0.99 and r>0.89 as evidence of high correlation's degree, especially SiO₂ vs Ba and SiO₂ vs Th with r=1 (Figure 7a and 7g). The negative correlation between Sc and SiO₂ is parallel to previous pyroxene (particularly clinopyroxene) fractionation based on major oxides trends (Hartono, 1994; Best, 2003; Figure 7d). Moreover, scandium, vanadium and titanium decrease along differentiation process may suggest titaniferous magnetite or ilmenite oxidation (Best, 2003; Wijaya and Hendratno, 2015; Figures 7d-e; Figure 6d). It has been known that most SiO₂-rich igneous rocks have much higher Rb/Sr than SiO₂-poor igneous rocks and that this ratio can therefore be used as an index of differentiation. This is obviously because Rb is more incompatible than Sr in nearly all magmatic systems (Halliday et al., 1991). The increasing Rb/Sr ratio with SiO₂ rising in convincing correlation coefficient (r=0.9959; Figure 7f) affirms that the long differentiation process of similar originated magma emplaced both namely andesite and dacite in Mount Ijo.
Figure 6. Major oxides (%) versus silica dioxide (%) pattern of volcanic rocks around Kulonprogo. a) Si\(_2\)O\(_3\) vs Al\(_2\)O\(_3\); b) Si\(_2\)O\(_3\) vs CaO; c) Si\(_2\)O\(_3\) vs Fe\(_2\)O\(_3\); d) Si\(_2\)O\(_3\) vs TiO\(_2\); e) Si\(_2\)O\(_3\) vs MgO; f) Si\(_2\)O\(_3\) vs Na\(_2\)O; g) Si\(_2\)O\(_3\) vs K\(_2\)O; h) Si\(_2\)O\(_3\) vs P\(_2\)O\(_5\); and i) Si\(_2\)O\(_3\) vs MnO. ●: volcanic rocks from field work, □: data from Verdiansyah (2016), ▲: data from Subiyanto (1989). ◊: samples that were identified as basalts in TAS diagram (Middlemost, 1994) and shoshonite series in potassium versus silica diagram (Peccerillo and Taylor, 1976) (not used in correlation models). In Table 1 and Figure 4 the K\(_2\)O contents of the two basalts are almost 2%.

Figure 7. Binary plots of silicon oxide (%) and trace elements (ppm). a) Si\(_2\)O\(_3\) vs Ba; b) Si\(_2\)O\(_3\) vs Rb; c) Si\(_2\)O\(_3\) vs Sr; d) Si\(_2\)O\(_3\) vs Sc; e) Si\(_2\)O\(_3\) vs V; f) Si\(_2\)O\(_3\) vs Rb/Sr; g) Si\(_2\)O\(_3\) vs Th; h) Si\(_2\)O\(_3\) vs Zr; and i) Si\(_2\)O\(_3\) vs Y. ●●●●●●●●●●●●●● were classified as basalt, basaltic andesite, andesite, and dacite in TAS diagram (Middlemost, 1984).

Ce, La, and Nd are the three dominant REE with the contents exceed 10 ppm whilst others in much lower values. The basalt, basaltic andesite, andesite and dacite show similar geochemical characteristics in the spider diagram (Figure 8a). Primitive mantle normalized spider diagrams show positive spike in large ion lithophile elements (LILE) (e.g. Sr and Eu) and exhibit distinct negative anomalies in high field strength elements (HFSE; e.g. Nb, Ti, and Y; Figure 8a). Troughs of Ti and P probably reflect the removal of magnetite and apatite. Moreover, a pronounced trough is present at Nb, which is a common feature of arc magmas and often taken to characterize subduction-related magma (Rotolo and Castorina, 1998). Strontium shows a positive spike in the most primitive compositions (RK 68) and becomes progressively depleted in the more evolved compositions (RK 94) while Ti trough intensifies upon differentiation.

The higher LREE content than HREE is common as LREE is more incompatible than HREE as shown in Figure 8b. LREE/HREE ratio of the selected samples range in 4.3 to 9. All four samples indicate positive Eu anomaly and negative Gd anomaly. Ce trough is deepest in basaltic samples (RK 68) and moves up continuously to be relatively flat in the most acid rock (RK 94) to indicate that less Ce’ (III) were oxidized to Ce’ s (IV) in more felsic rock. Refer to low Rb/Sr value (0.03-0.17) the studied rocks did not come from highly evolved magma. The anomalies in Eu are related to the feldspar accumulation during differentiation. The rocks are derived from subduction zone based on Nb and Ti negative anomalies as described in the study about granitoids at Jiru-Tibet (Yang et al., 2015), mafic granulites from Laserman Hills (Tong et al., 2017), eclogites in Monviso (Rubatto and Hermann, 2003), and granitoids in Goalpara (Bhagabaty et al., 2017).

**CONCLUSIONS**

Geochemical characteristics of the andesite and dacite from Mount. Ijo, Kulonprogo, confirm that those two type of rocks are comagmatic. They are related each other by a process of differentiation. The dacite magma is believed to be derived from andesite magma by fractionating olivine, plagioclase, pyroxene, and magnetite. Apatite might has been crystallized in late stage differentiation processes. Olivine and pyroxene fractionation together with ilmenite oxidation were emplaced during magma differentiation based on geochemistry analysis. The comagmatism is strengthened on the identic large ion lithophile elements spikes, high field strength elements negative anomalies, and Eu positive anomaly of the studied samples.

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