Mineralogy and Geochemistry Variation of Igneous Rocks from Ungaran and Muria Volcano and Its Processes related to Subduction Zone Magmatism of Sunda Arc

Jenian Marin, Tri Winarno, Dewi Mindasari
Departemen Teknik Geologi Fakultas Teknik Universitas Diponegoro
jenianmarin@gmail.com

Abstract. Sunda Arc represent Quaternary magmatism as one of the most significantly active volcanic arc in Indonesia resulted from subduction of oceanic plate beneath continental plate. Along this subduction system, there are systematic variations in subduction angle, depth, crust thickness, and composition contribute to geochemical characteristic of igneous rocks along and across the arc. This study compared mineralogy and geochemistry characteristics from two volcanoes which represent across-arc variation. Petrographic analysis have been conducted on rocks’ thin section samples from Ungaran and Muria Volcano to characterize mineralogy of rocks. Selected samples were analyzed using X-Ray Fluorescence (XRF) for geochemistry of major and trace elements. Mineralogy of Ungaran rocks are dominated by plagioclase, clinopyroxene, and hornblende phenocrysts with composition range from andesite to basaltic andesite of high-K calc alkaline series. Samples from Muria Volcano are from alkaline series characterized by feldspathoid and alkali feldspar rich rocks with calcic plagioclase and pyroxene phenocrysts. This mineral assemblages, supported by major elements data suggest fractionation process in magma. Geochemical trend is systematically consistent with other island arc setting, where there is significant increase of total alkali from Ungaran to Muria. Trace element data shows decreasing in LILE/HFSE ratio further from arc. This suggests that Ungaran has more crustal and subducted slab influence, while Muria has higher degree of partial melting from deeper Benioff Zone.

Keywords: across-arc geochemistry, Sunda Arc, Muria, Ungaran

1. Introduction
Volcanic formation in subduction zones is created from complex magmatic processes, ranging from partial melting of the mantle and its associated crusts, magma rising to the earth's crust, and contamination with country rocks. This process of magmatic differentiation will produce variations in magma series and its igneous rocks. These variations can be observed based on mineralogical and geochemical composition of rocks. There have been widely reported that there is systematic geochemical variations in subduction setting such as the Izu-Oshima Islands Arc, Japan [1], the Southern Volcanic Zone, Chile [2], and the Andean Central Volcanic Zone [3].

Quaternary Java volcanic arc is formed due to the subduction of the Indo Australia Oceanic Plate to the Eurasian Continental Plate. There are variations in the composition of magma formed along the Sunda Arc due to the influence of the subducting plate and contamination of the crustal wall when the magma moves to the surface [4]. A study of lava in the volcanic arc of West Java showed similar variations in rock composition, but different from isotope parameters [5]. Rocks from the back-side arc are enriched by some trace elements compared to rocks from the front-side arc.
Ungaran Volcano and Muria Volcano are two Quaternary volcanoes that located at the back side of the volcanic arc in Central Java. The relationship between the two in the same volcanic arc can be seen from petrogenetic indicators, especially rock geochemistry. To be able to better explain the comparison of its characteristics; further mineralogy and geochemistry studies are needed.

2. Geological Setting
Sunda Arc is one of the most prominent Quaternary volcanic arc in Indonesia, consist of 80% of the total volcanoes in Indonesia. This arc extends from the northern tip of Sumatra to the southeast, continues eastward to Java, Bali, Lombok, Sumbawa and Timor. In north and west Sumatra, this arc is characterized by the emergence of small islands in the Indian Ocean; such as Nias Islands and Mentawai Islands. Although the tectonic setting is nearly the same, geochemical differences between the rocks from Sumatra and Java showing difference in the depth of Benioff Zone. Geophysical and geochemical data indicate the depletion of the crust to the east, where the thickness of the crust on Java is around 20-25 km which thinned to Flores around 15 km [6]. The Benioff Zone tilts north to a depth of 100 km as far as a horizontal distance of 200 km from the Java Trench. Under Java and the Java Sea, the slope increases by about 65° and reaches depths of up to 650 km (figure 1).

Some parts of the Quaternary volcanic arc in Indonesia have two or more volcanoes across the arc's continuity. This phenomenon is called a double volcanic arc, which is divided into front-side arc and the back-side arc. In Java, the volcanic chain on the back-side arc appears on the west side with an orientation of 105° - 110° E at a depth of surface slab subducting of about 200 km [7]. The chemical characteristics of Sunda Arc rocks in Java and Bali, characterize the magma series from toleitic to high-K calc alkaline above the Benioff zone with a depth of 120-250 km. The result is an increase in incompatible trace elements as the Benioff zone deepens. The most prominent parameter is the content of K which is also positively correlated with the depth of the Benioff zone. This change in chemical variation occurs due to the modification of the mantle source associated with the thermal structure of the subducted plate.

The subduction zone on Java Island has undergone periodic changes since Cenozoic Age. Rock age data show that volcanic activity shifted north from Tertiary to Quaternary [8]. Most of the active volcanoes on the Java Island are stratovolcano, which lies extending in the middle of the island. The dominant rock composition is high-alumina basalt and pyroxene andesite. This active volcanic belt rises on older volcanic and volcaniclastic rocks from Oligocene and Neogene sediment formations [9].
3. Methodology
Field activities are needed for sampling fresh rock products of volcanic activity of Mount Ungaran and Mount Muria. The samples will be analyzed petrographically and geochemically as the primary data of the study. Petrographic sampling is carried out on nonfragmental rocks, both derived from lava flows and intrusions to represent the characteristics of rocks in each volcano. For petrographic analysis, fresh rock samples were prepared with a thin section of 30 μm which was attached to a glass plate and covered with thin glass. Preparations are observed under a polarizing microscope to identify mineralogy of rock and its texture. Detailed descriptions are made so that the rock petrogenesis can be determined. The classification used in petrographic observation is the classification of the International Union of Geological Science (IUGS) based on the composition of QAPF (Quartz - Alkali Feldspar - Plagioclase - Feldspathoid). Geochemistry of major and trace elements were analyzed using x-ray fluorescence (XRF) method at BPPTKG Yogyakarta. Before analyzed, LOI (loss on ignition) in all samples were determined using gravimetry method. All elements data were plotted to various diagrams to classify rocks, determine magma affinity, and construct petrogenetic models for the research area.

4. Results

4.1. Mineralogy of Rocks from Ungaran and Muria Volcano
Mineralogy of rocks from both volcanoes are significantly different, which is further explained by geochemistry. Samples were obtained from lavas, intrusions, and lithic fragments of andesitic breccia. Rocks from Ungaran are typical basaltic andesite - andesite with aphanitic - porphyritic texture. The groundmass consist of plagioclase and pyroxene microcrystals and volcanic glass. The most abundant phenocryst is plagioclase (25 – 45%) which composition tends to be more sodic in younger rocks. Other significant phenocrysts are clinopyroxene, hornblende, orthopyroxene, opaque minerals (Fe-Ti oxides). Zoned plagioclase is common in all samples with concentric, patchy, and spongy texture (figure 2). Some igneous textures featured subophitic, intergranular, glomeroporphyritic, reaction rim. Pyroxenes often occur as glomerocryst and have twinning habit. Olivine is rarely showed in the samples, while hornblende is more prominent in younger rocks and show distinctive habit of being altered in the rim (figure 3).

Figure 2. Mineralogy of rocks from Ungaran volcano, the abundant phenocryst of plagioclase, mostly accompanied with clinopyroxene, orthopyroxene (parallel extinction angle), and hornblende (a). Twinning and zoning in plagioclase as microtextural characteristic in basaltic andesite with minor olivine (b)
Figure 3. (a) Hornblende with altered rim is dominant in younger rocks with glassy groundmass (b) glomeroporphyritic texture with crystal aggregate of pyroxene, hornblende, and opaque minerals

Figure 4. Petrographic images of rocks from Muria shows porphyritic texture, with plagioclase, pyroxene, feldspathoid, K-feldspar, olivine phenocryst (a). Abundant plagioclase as phenocryst and groundmass (b)

Rocks from Muria show different mineralogy than Ungaran based on lava and intrusive samples, which is more of alkali-basalt. Samples have hipocrystalline texture and porphyrophanitic inequigranular. The major phenocryst is plagioclase (30-40%) with composition ranged calcic anorthite to more sodic andesine. Plagioclase also shows twinning and zoning. Nepheline and leucite from feldspathoid group appear at a significant amount (7-14%). Based on the type of twinning, it can distinguish plagioclase from K-feldspar (sanidine and microcline), which abundance is less than 5%. Ferromagnesian minerals dominated by clinopyroxene and orthopyroxene (8-10%), while olivine is just a minor constituent (less than 5%). Pyroxene crystal shows wide range of crystal size and habit, from coarse phenocryst to fine groundmass, and from prismatic-equant to lathlike crystals (figure 4).

4.2. Geochemistry of Rocks from Ungaran and Muria Volcano
Nine volcanic rock samples from Ungaran and two from Muria were analyzed both major and selected trace elements, combined with earlier data for Young Ungaran [10] and Muria [11].

4.2.1. Major elements. Some major elements are plotted on Harker diagram using SiO2 as primary x-axis. The samples from two volcanoes belong to different magma series from calc-alkaline affinity. Based on alkalinity diagram [12], Ungaran rocks fall in the high-K alkaline, while Muria is more alkaline to shoshonitic series (figure 5). Plotting on TAS (Total Alkali Silica) diagram, rocks from Ungaran are
classified predominantly as basaltic andesite and andesite, also trachyandesite. Younger samples tend to be more andesitic than the older and samples from parasitic lavas. Muria which is already has high K composition classified as basaltic trachyandesite and trachyandesite (figure 5). Total alkali for Ungaran is ranged 4.4 – 6.2 wt% and Muria is higher at more than 6 wt%. Other oxide that shows positive correlation is Al₂O₃, although in Muria it does not show clearly because of limited samples. This trend can be seen at Ungaran clearly on Harker diagram (figure 6). Negative correlations are happened with MgO, CaO, TiO₂ (slightly), and Fe₂O₃.

Figure 5. Alkalinity magma diagram (a) and TAS (total alkali silica) diagram (b) of Muria and Ungaran

4.2.2. Trace elements. Selected trace elements have been analyzed, not all are important indicator in petrogenetic aspect, only several incompatible element will be elaborated (table 1). Groups of LILE (large ion lithophile element) includes barium, strontium, rubidium are good petrogenetic indicator. Rare earth elements are better indicator because of their stable phase. Niobium, zircon, mercury, and thorium are being used in this research. Some elements must be excellent indicator, if compared to other elements. Ratio of LILE/HFSE and HFSE/LREE will show more about magmatic processes produced the rocks. Based on calculation, Sr/Rb, Ba/Zr, Ba/Th, Pb/Ce ratio is higher in Ungaran than Muria and Nb/Zr is higher in Muria. For general, LILE is higher in Ungaran and HFSE is higher in Muria. Based on this characteristics, subduction and magmatic process can be interpreted.
Figure 6. Harker variation diagram for SiO2 vs major oxides

Table 1. Trace element ratios of Ungaran and Muria samples. MU-01, MU-02 are from [11], UG05-UG12 are from [10]

| Samples | SiO2 | Sr/Rb | Zr/Y | Ti/Y | Nb/Zr | Ba/Zr | Rb/Sr | Ba/Th | Pb/Ce |
|---------|------|-------|------|------|-------|-------|-------|-------|-------|
| MU-01   | 53.08| 1.87  | 11.00| 194.85| 0.12  | 3.05  | 0.53  | 44.67 | 0.05  |
| MU-02   | 55.2 | 3.38  | 13.67| 303.73| 0.04  | 5.60  | 0.30  | 49.87 | 0.07  |
| MU-03   | 50.99| 4.02  | 9.55 | 220.73| 0.02  | 0.87  | 0.25  | 8.27  | -     |
| MU-04   | 52.96| 1.44  | 8.33 | 462.08| 0.05  | 2.30  | 0.70  | 8.21  | -     |
| UN-01   | 54.30| 8.10  | 5.47 | 196.13| 0.07  | 5.12  | 0.12  | 56.25 | 0.25  |
| UN-02   | 55.84| 6.02  | 5.89 | 209.13| 0.06  | 3.98  | 0.17  | 62.03 | 0.37  |
| UN-03   | 57.04| 5.34  | 6.17 | 210.22| 0.07  | 3.75  | 0.19  | 55.57 | 0.42  |
| UN-04   | 55.64| 6.39  | 5.85 | 217.48| 0.06  | 3.95  | 0.16  | 58.18 | 0.32  |
| UN-05   | 53.25| 6.05  | 5.28 | 210.94| 0.09  | 4.47  | 0.17  | 42.27 | 0.37  |
| UN-06   | 52.04| 6.34  | 5.20 | 207.68| 0.09  | 4.16  | 0.16  | 43.51 | 0.22  |
| UN-07   | 56.32| 9.21  | 5.18 | 160.66| 0.04  | 8.59  | 0.11  | 116.89| 0.35  |
| UN-08   | 52.34| 10.25 | 4.87 | 184.44| 0.05  | 7.61  | 0.10  | 78.76 | 0.38  |
| UN-09   | 52.97| 10.66 | 4.81 | 192.09| 0.05  | 8.81  | 0.09  | 90.16 | 0.43  |
| UG-05   | 57.31| 4.67  | 6.30 | 174.65| 0.07  | 3.31  | 0.21  | 34.29 | -     |
| UG-06   | 59.39| 4.69  | 6.52 | 161.61| 0.06  | 3.42  | 0.21  | 32.06 | -     |
| UG-08   | 55.61| 6.69  | 6.08 | 187.33| 0.06  | 3.64  | 0.15  | 37.93 | -     |
| UG-09   | 59.79| 6.10  | 6.78 | 153.78| 0.06  | 3.46  | 0.16  | 36.00 | -     |
| UG-11   | 59.02| 1.65  | 6.63 | 159.88| 0.06  | 3.45  | 0.61  | 36.60 | -     |
| UG-12   | 56.45| 6.08  | 6.41 | 185.32| 0.06  | 3.37  | 0.16  | 39.58 | -     |

5. Discussion
Geochemistry of rocks is a result of several complex processes, from tectonic setting, magma generation, magma processes and its interaction before igneous rocks crystallization. Magma generates under a specific tectonic setting, which interaction of every crustal component will be recorded in geochemical characteristics. Based on major and trace elements, Ungaran and Muria are product of calc-alkali basalt, which is produced in subduction zone setting (figure 7). As parental magma derives from mantle, in this
setting, mantle wedges interact with two different crusts (oceanic-oceanic or oceanic-continental) and then produce more complex and evolved magma. In this setting, the occurrence of volcano depends on degree of partial melting underneath which controlled by Benioff Zone depth, heat flow, and crustal composition. Ungaran located nearer to the trench than Muria, hence the Benioff Zone depth is shallower at approximately 225 km. Muria located in the back of Sunda Arc approximately 325 km depth of Benioff Zone. While Muria is being one from just a few back arc volcano, the rock geochemistry is significantly different than other abundant front arc volcano. Being the nearest across arc volcano from Muria, Ungaran rock geochemistry slightly overlaps with Muria.

![Figure 7. Tectonic setting discriminant diagram Ti-Zr-Sr and TiO$_2$-MnO-P$_2$O$_5$ [12]](Ungaran and Muria plotted at CAB (calc-alkali basalt))

It has been determined that Ungaran rocks are product of high-K alkaline magma, while Muria rocks are product of alkaline magma. The mineralogy resulted from those product is a different mineral assemblage with slight overlap. Ungaran rocks’ mineral assemblages mostly are silica saturated, with dominance of plagioclase, pyroxene, hornblende, and opaque minerals. Sometimes, an undersaturated melt still contain olivine in it. There are no quartz and little felsic minerals in all samples.

As Muria is product from deeper mantle, it should be expected that an undersaturated or near saturated mineral assemblages will appear in rocks. Mostly undersaturated melts resulted in such mineral assemblage: calcic to sodic plagioclase, pyroxene, feldspathoid, a little amount of K-feldspar and olivine, and opaque minerals. Leucite and nepheline are the most common feldspathoid here, which is much depleted in silica that has been used in K-feldspar.

It is also possible to configure magmatic processes (crystal fractionation, magma mixing, and assimilation) based on interpretation of geochemistry and mineralogy. Harker diagram using MgO as x-axis can be used to identify crystal fractionation in magmas correlating with geochemistry pattern. Normal differentiation will deplete MgO as it fractionate into ferromagnesian minerals. SiO$_2$ and Al$_2$O$_3$ are negatively correlated with MgO, while Fe$_2$O$_3$ and CaO are positively correlated. Samples contain olivine are from Muria, Old Ungaran, and its parasitic lava (figure 8). Those samples represent a lower degree of fractionation, with less silica content. Olivine is accompanied by abundant clinopyroxene and more calcic plagioclase. This process occurs when melts is high in MgO and lower silica content. Petrographic evidence showed mineral aggregates of pyroxenes, plagioclase, and opaque mineral which settled during magmatic processes. Thus, make fractionation process more effective as the ascending magma will be more evolved. Products from younger activity of Ungaran tend to have more hornblende/amphibole group and also still abundant plagioclase. Therefore, the petrogenetic model for fractionation can be interpret. Diagram MgO vs Fe$_2$O$_3$ and MgO vs CaO display amphibole and pyroxene fractionation as MgO content decreases. Sometimes, fractionation in magma did not happened normally because of changes in physical condition (pressure and temperature fluctuation) and chemical condition,
in this case is change in magma composition because of mixing or assimilation. Zoned plagioclase is evident in suggesting these processes, although the exact changes cannot be determined without chemical analysis of single mineral.

Figure 8. Harker diagram using MgO as x-axis, plotted with other major elements to identify correlation between mineralogy and rock chemistry.

Trace elements data provided more excellent evidence about magmatic processes. For this research, a comparison is needed to determine which influence is more prominent in one over another. LILE to HFSE ratios are decreases from Ungaran to Muria (Ba/Zr, Pb/Ce, Ba/Th, Nb/Zr). Those ratios indicate subducted slab derived fluid. The melting of subducted crust and sea sediment add LILE constituent to magma, and the amount will be decreased further away from trench. Diagram Ba/Zr vs Nb/Zr discriminate a mantle zone [4], where increasing in Ba content is enriched from subducted slab (figure 9). Crust contamination other than slab is the overlying crust and host rock surrounds magma chamber. Lower Sr/Rb in Muria suggests lower crustal contamination during magmatic process. Ratios of LILE/HFSE can be further confirmed by HFSE/LREE ratios [3]. For example, Ungaran Pb/Ce ratio is also higher than Muria, also indicates higher slab fluid.

Figure 9. (a) Diagram Ba/Zr vs Nb/Zr ratio and (b) diagram SiO₂ vs Sr/Rb and the petrogenetic interpretation
Modification of magma composition or also mentioned as magma differentiation involves several processes. Even in the same tectonic setting and in the same arc, the degree of partial melting, subducted slab, and crustal contamination will contribute at different level. Therefore, systematic geochemical trend in a volcanic arc is a manifestation of those components. These trend can be observed in Muria and Ungaran too as part of Sunda Arc, along with other adjacent volcanoes. More detailed rare earth elements and isotopic data from whole rock or mineral geochemistry will be needed in the future to unravel more about this subduction magmatism in Java Island.

6. Conclusions

Geochemical and mineralogical evidence of igneous rocks from Ungaran and Muria volcano represent two different characteristics of subduction magmatism. Ungaran, which is located nearer from volcanic front, displays typical basaltic andesite – andesite with mostly silica saturated mineral assemblages. Plagioclase as main phenocryst, followed by pyroxene and hornblende. Less evolved magma also near saturated, with olivine occurrence. Meanwhile, Muria rocks composed by under saturated magma with plagioclase, pyroxene, feldspathoid minerals, and lesser K-feldspar and olivine. Magma series change from high-K calc alkaline to alkaline magma. Geochemical trend is systematically consistent with other island arc setting, where there is significant increase of total alkali from Ungaran to Muria. Trace element data shows decreasing in LILE/HFSE ratio further from arc. This suggests that Ungaran has more crustal and subducted slab influence, while Muria has higher degree of partial melting from deeper Benioff Zone.

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