



Fluid-Rock Interaction During Hydrothermal Alteration at Parangtritis Geothermal Area, Yogyakarta, Indonesia

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Abstract - Parangtritis Volcano is part of the Tertiary magmatic belt in Java, which was tectonically formed by collisions between the Eurasian Continental Plate and Indo-Australian Oceanic Plate. The collisions have taken place since Late Cretaceous and still continue until today. In that period, the magmatic belt in Java Island was formed and produced mineralization and geothermal. The characterization of geothermal in Tertiary volcanoes differs from the geothermal system that is on Quaternary volcano alignment in the middle of Java, such as: Awibengkok, Wayang Windu, Darajat, and Kamojang which have a high temperature. The purpose of this research is to study the mobilization elements due to interaction of hydrothermal fluids with wall rocks in low enthalpy geothermal regions of the Tertiary magmatic arc in Parangtritis. Identification of minerals and chemical element changes is approached by methods of petrographic and scanning electron microscope (SEM) analyses. As for knowing the composition and the origin of hydrothermal fluids, it used analyses of cations, anions, and isotope $\delta^{18}\text{O}$ and δD of hot water manifestation. The occurrence of geothermal manifestations in Parangtritis, such as hot water and rock alteration, reflects the interaction of hydrothermal fluids with wall rocks which generates an argillic zone with mineral alteration such as quartz, calcite, montmorillonite, and hematite. The presence of alteration mineral montmorillonite replacing pyroxene provides an evidence that there have been interactions between the fluids and rocks. This interaction is as a process of element mobilization. Decrease in elements Si, Ca, Mg, and Fe is accompanied by an increase of Al during the replacement of pyroxene into montmorillonite. The mobility of this element occurs due to acid fluids. However, the hydrothermal fluid composition of the current hot water manifestation is neutral chloride water type composition, and the origin of the fluids is meteoric water ($\delta^{18}\text{O}$: -4.20 ‰ and δD : 23.43 ‰).

Keywords: rocks, hydrothermal fluid, alteration mineral, mobilization element

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INTRODUCTION

Parangtritis is located in the Kretek Subregency, Bantul Regency, Yogyakarta Province, which is about 20 km to the south of the Yogyakarta City (Figure 1). This area lies in the southern coastal region that has the historical value, and tourist ob-

jects, and occurs as a natural laboratory of geology. Parangtritis region is bounded by the landscape of wide sand dunes, which extend until the estuary of Opak River in the west. The northern part is the landscape of Tertiary volcano fossil that is overlain by Wonosari limestones stretching from west to east. The limestones lengthwise into the eastern

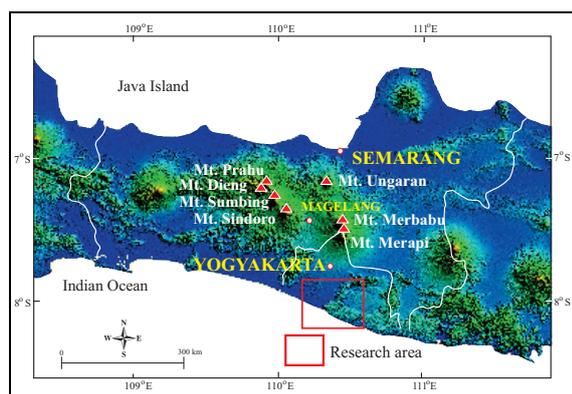


Figure 1. Location of the researched area.

part forming steep escarpment that just into the sea. The southern part of the area is situated close to the Indian Ocean with the rhythm of big waves.

According to Hartono (2000) and Delvianus Tae *et al* (2018), the research area was in the Parangtritis paleo-volcano composed of breccia and andesite lavas of Nglanggran Formation. Furthermore Hartono (2000) explained that the andesite breccia fragments were rich in volcanic bombs with intersection of andesitic lavas as strato volcanoes. This formation is intruded by microdiorite intrusion occurring as a heat source rock on the geothermal system. The hot rock can be identified from Bouger's anomalies (Marzuki and Otong, 1991) which shows rising anomaly in the Parangtritis area. This indicates the presence of bedrock with a density of 2.8 g/cm^3 which was interpreted as an igneous intrusion (Bahagiarti and Santoso, 1998). The results of the magnetic field anomaly analysis show a low magnetic value interpreted as the potential zone of a non-volcanic geothermal reservoir at a depth of 580 m (Delvianus Tae *et al*, 2018). This zone is characterized by a hydrothermal alteration of rock that experienced the chloritization and sericitization. The hydrothermal fluid was responsible for chloritization, generally having pH values <6 (Browne, 1978). In general, hydrothermal alteration minerals can be formed due to the chemical composition of fluid and geothermal temperature. Both of these were important factors that control hydrothermal alteration (Steiner, 1968), as the primary mineral plagioclase Ca-Na transformed to a variety of

hydrothermal minerals such as montmorillonite, calcite, albite, and quartz. While ferromagnesian was altered to a chlorite mineral, clay minerals, quartz, calcite, and quartz (Steiner, 1953). Besides this, the presence of hot springs that appear on the surface show as an additional information that the Parangtritis area is a potentially geothermal area.

The composition of the hot water appearing at the surface reflects the end result of a series of chemical element transport and complex chemical reaction process (Evans *et al.*, 2005). Thereby, in this area a process of interaction between hydrothermal fluid-rock has taken place. This condition is necessary for the study of hydrothermal fluid-rock interaction, because it can mobilize elements in the hydrothermal process.

This study aims to analyze the mineral alteration, due to the interaction of hydrothermal fluids against the rocks. By studying the changes of primary minerals into secondary minerals, the mobilization of elements that occurred during the mineral replacement process as the result of the rock interaction with hydrothermal fluids can be explained.

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Geological setting

The researched area is part of the western Indonesian region affected by tectonic activity due to the collisions between the Eurasian Continental Plate, and the Indo-Australian Oceanic Plate which has been occurring since the Late Cretaceous and still continues today. In Java, the collision between the plates is directed perpendicular to subduction that produces magmatic arc lines east-west trending. The formed magmatic arc produces mineralization and geothermal.

Morphologically, Parangtritis area is a Tertiary volcano overlain by limestones and surrounded by beaches and vast stretches of river sediments. The

formation of volcano morphology does not form a cone, as has been eroded and denudation. The lithostratigraphical name of Southern Mountain has been proposed by some researchers, but they are different from each other. This difference is mainly between the western part (Parangtritis-Wonosari) and the eastern part (Wonosari-Pacitan). Proposed sequence stratigraphy of the western part of The Southern Mountain was put forward by Bothe (1929) and Suroño *et al.* (1992). The eastern part stratigraphy was proposed by Sartono (1964) and Nahrowi *et al.* (1979). While Samodra *et al.* (1992) proposed a stratigraphy in the transition area between the western and eastern parts. Geological map of Yogyakarta was compiled by Raharjo *et al.* (1977).

Parangtritis is the western part of the Southern Mountain with the oldest stratigraphy setting is a pre-Tertiary metamorphic rock exposed at Jiwo Mountain, Bayat. Then, on top of pre-Tertiary rocks rest unconformable Tertiary rocks consisting of Kebo-Butak, Semilir, Nglanggran, Sambipitu, Oyo, Wonosari, and Kepek Formations. The lithologies which were the results of volcanic activity include Kebo-Butak, Semilir, Nglanggran, Sambipitu, and Oyo Formations.

The rocks constituting the studied area comprise Nglanggran Formation, Wonosari Formation, and Beach Alluvium. The Nglanggran Formation resulted from volcanic eruption products is part of alignment of Tertiary volcanic complex. The age of the alignment volcanoes according to Soeria-Atmadja *et al.* (1990, 1991) ranges from Paleocene (58.58 ± 3.24 Ma) to Oligo-Miocene (33.15 ± 1.00 Ma - 24.25 ± 0.15 Ma). The affinity of the volcanic rocks includes tholeiitic-calc alkaline volcanic rocks series constituent of basalt, basaltic andesites, andesite, and dacite (Soeria-Atmadja *et al.*, 1990, 1991; and Hartono, 2000). The Wonosari Formation consists of Middle-Late Miocene limestones, while the coastal sediment is in the form of alluvial sands and Quaternary riverine alluvial. Following the stratigraphy of Southern Mountains, Central Java, by Suroño *et al.* (1992), the area of research is composed of rock formations of Nglanggran consisting of breccias, diorite, andesite intrusions, and basaltic and

andesitic lavas. Whereas the Wonosari Formation comprises limestone, as well as coastal sediment consisting of Quaternary alluvial sand and alluvial sediment of Opak River.

Analytical Methods

This research is to analyze the identification of minerals in surficial altered rock samples as much as eight samples by carrying out a petrographic analysis. While mineral chemistry from primary minerals and alteration was studied using SEM (Scanning Electron Microscope) and EDX (Energy Dispersive X-ray Spectroscopy) analysis. SEM-EDX analysis was conducted in the BPPTKG Laboratory of the Geological Agency, in Yogyakarta. This analysis was carried out on one alteration rock sample with five observation points. While the geochemical analysis of hot spring (hydrothermal fluid) was conducted on one sample which included analyses of cations and anions as well as isotopes $\delta^{18}\text{O}$ and δD . Analyses of isotopes $\delta^{18}\text{O}$, δD , cations, and anions were conducted at the Center for Mineral, Coal, and Geothermal Resources. The analyses of cations and anions were conducted using Atomic Absorption Spectroscopy (AAS). The isotope analyses $\delta^{18}\text{O}$ and δD were done using Isotope Ratio Mass Spectrometer (IRMS) or isotope mass spectrometer.

RESULTS AND DISCUSSIONS

Geology of Parangtritis

The studied areas are included in the Nglanggran Formation and Wonosari Formation (Figure 2). Early-Middle Miocene aged Nglanggran Formation has an unconformable contact with Wonosari Formation (Middle Miocene-Pliocene). The Nglanggran Formation consists of volcanic rocks, namely: Volcanic Breccia Nglanggran Formation (VBNF), Andesite Lava (ALNF), Basaltic Lava (BLNF), and Andesite Intrusion (AI). The Nglanggran Formation is overlain unconformably by the Wonosari Formation consisting of clastic limestones (CWF). Then the Miocene rock underlies Quaternary sediment comprising Sand Dune Deposits (SD) and Alluvial Deposits (AD).

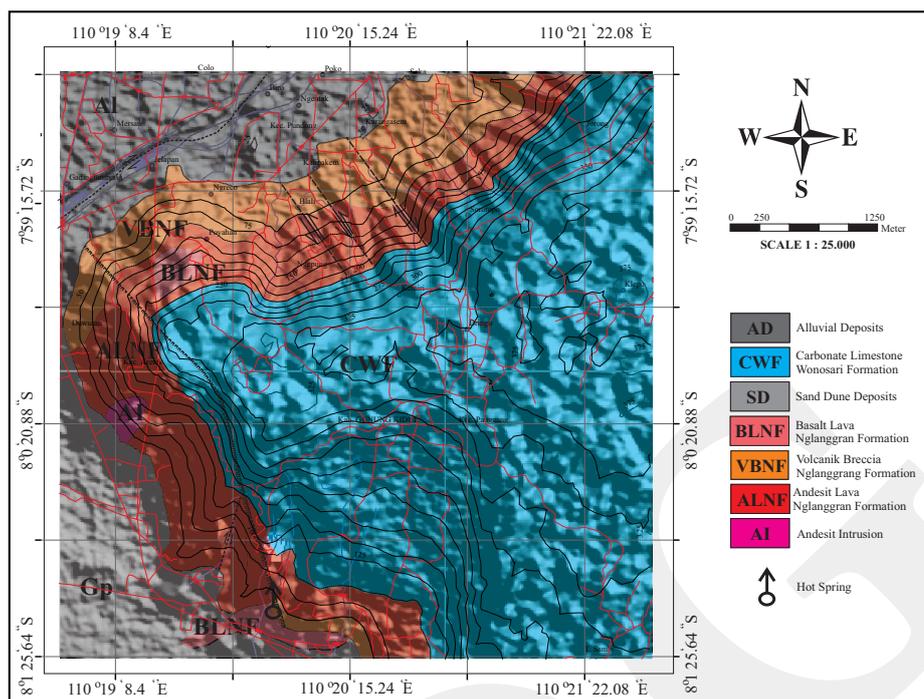


Figure 2. Geological map of Parangtritis.

Volcanic Breccia of Nglanggran Formation is brown, massive, 2 - 64 mm grain size, angular shape, and unsorted. The rock component consists of andesite fragments embedded in the volcanic ash matrix. Andesite Lava of Nglanggran Formation showing sheeting joint structure have gray, hypocrySTALLINE, moderate-aphanitic, inequigranular, and subhedral-anhedral crystals. The rock consists of plagioclase, pyroxene, and hornblende embedded in the groundmass of volcanic glasses. Basaltic Lava of Nglanggran Formation is the most widely spread. This basaltic lava shows the sheeting joint structure, gray, hypocrySTALLINE, moderate-aphanitic, inequigranular, and subhedral-anhedral crystals. Andesite Intrusion unit intruding volcanic breccia has the features of gray, hypocrySTALLINE, moderate-aphanitic, inequigranular crystal, and subhedral-anhedral form. Mineralogically, the intrusion is composed of plagioclase, pyroxene, and hornblende embedded in volcanic glass groundmass. Limestone of Wonosari Formation consists of boundstone, wackestone, and crystalline carbonates. These limestones are yellowish brown, massive structure, grain size of arenite-rudite, subrounded, well sorted, and open fabric. The fragment composition consists of al-

lochem, interclast, quartz, micrite, and the sparite is carbonate. The youngest sediment in the studied area is the surface sediment that lies in the north and west parts of the studied area. This sediment is unconformably deposited above the Wonosari Formation. The youngest sediments are the Quaternary sediments consisting of aeolian sediment or sand dunes and alluvial deposits. The studied area is cut by some strike-slip and normal faults with the relative direction of southeast-northwest.

Geochemistry of Hydrothermal Fluids

In the researched area, there are surface manifestations including hot spring and hydrothermal alteration rocks. The manifestation was a sign of the presence of geothermal system. Manifestations of hot spring having temperature of about 41.8°C, pH 6.55, salty, no smell, the electrical conductivity of 1722 $\mu\text{S}/\text{cm}$, gas bubbles appear and hot water accumulated in the pond. The hot water in Parangwedang Parangtritis has been studied by several researchers, including Idral *et al.* (2003) (Table 1).

The hot water chemistry elements were then plotted in $\text{SO}_4\text{-Cl-HCO}_3$, Na-K-Mg, and Cl-Li-B triangle diagrams (Giggenbach, 1988). From the $\text{SO}_4\text{-Cl-HCO}_3$ diagram, the hot water type was

Table 1. Chemical Analysis of Parangtritis Hot Water

| | Samples | | |
|-------------------|----------|-----------|-----------|
| | PS | Psr 1* | Psr 2* |
| T (°C) | 41.80 | 43.00 | 28.20 |
| pH | 6.65 | 7.5-7.7 | 7.49 |
| DHL/EC | 17.22 | 17,750.00 | 18,110.00 |
| TDS | | | |
| SiO ₂ | 36.83 | 62.25 | 67.68 |
| B | 9.29 | 7.71 | 8.25 |
| Al ³⁺ | 0.09 | | |
| Fe ³⁺ | 0.14 | | 0.04 |
| Ca ²⁺ | 2,286.00 | 2,450.98 | 2,433.55 |
| Mg ²⁺ | 2.85 | 11.62 | 15.10 |
| Na | 1,894.70 | 2,470.59 | 2,117.65 |
| K | 29.10 | | |
| Li | 0.20 | | |
| As ³⁺ | 0.20 | | |
| Nh ⁴⁺ | 0.01 | 5.10 | 5.27 |
| F | 0.64 | 2.00 | 2.00 |
| Cl | 6,068.66 | 7,291.06 | 7,025.61 |
| SO ₄ | 453.39 | | |
| HCO ₃ | 20.44 | | |
| CO ₃ | 0.00 | | |
| δ ¹⁸ O | -4.15 | | |
| δD | -23.43 | | |

(*) water samples from Idral *et al.* (2003)

neutral chloride water (Figure 3). The high chloride concentrations are around 6068.66 - 7291.06 ppm due to contamination by seawater (Figure 4). It is supported by salty water, high electrical conductivity, pH neutral, and the hot water which are located on the side of chloride in the triangular diagram Cl-Li-B. The estimation of subsurface

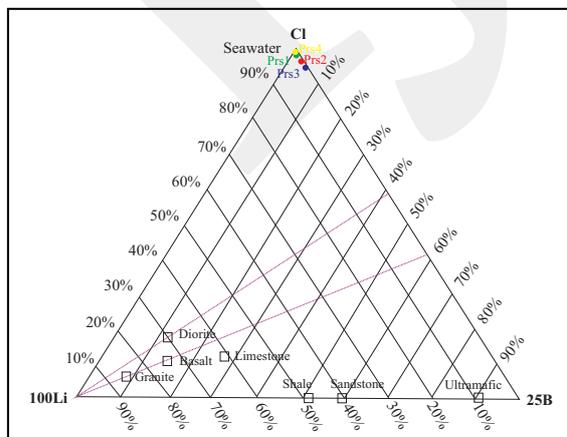


Figure 3. Hot water composition determination using Cl-Li-B triangular diagram (Giggenbach, 1986). Hot water comes from sea water.

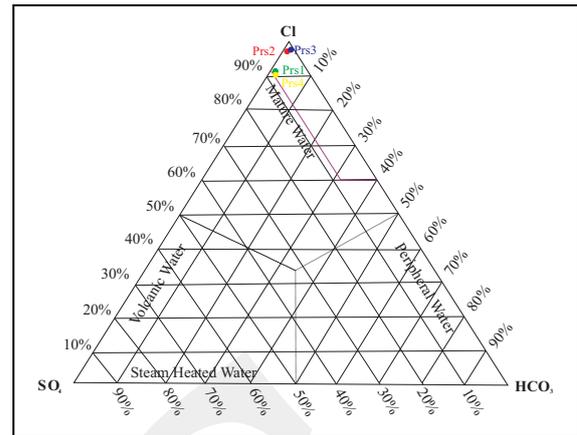


Figure 4. Hot water type determination using SO₄-Cl-HCO₃ Giggenbach's diagram (Giggenbach, 1991). The water type is chloride water.

temperature using Na-K-Mg diagram shows the subsurface temperature of around 120 - 140°C, and the hot water was in partial equilibrium conditions (Figure 5). Then calculation of subsurface temperature of Parangtritis hot springs using Quartz adiabatic geothermometer of Anorsson (1975), Fournier (1981), Giggenbach (1988), and Nicholson (1993) was around 90.63 - 115°C (Table 2).

Some of the basic concepts used by geochemists are stable isotopes such as isotopes of hydrogen, carbon, nitrogen, oxygen, and sulfur, to interpret the geological and environmental processes (Taylor, 1967; Hoefs, 1980). In this case, the stable isotope chemistry can trace the history of the system by measuring the abundance isotope ratios in the current phase simultaneously pres-

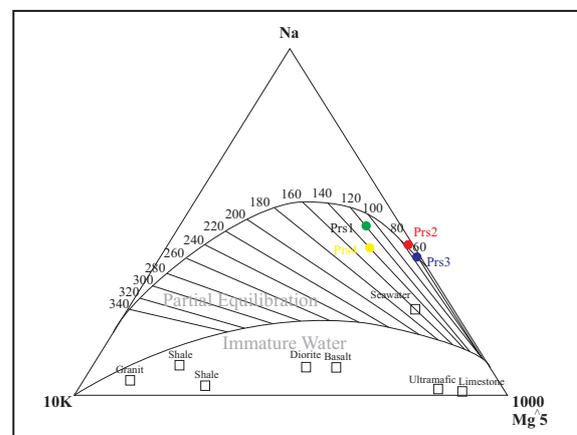


Figure 5. Giggenbach's Na-K-Mg triangular diagram (Giggenbach, 1986) for the Parangtritis hot waters.

Table 2. Estimation of Subsurface Temperatures Based on Calculation of Quartz Adiabatic Geothermometer

| Sample | Amorphous Silica | Alpha Cristobalite | Beta Cristobalite | Chalcedony Conductive | Quartz Conductive | Quartz Adiabatic |
|--------|------------------|--------------------|-------------------|-----------------------|-------------------|------------------|
| PS | -25.67 | 38.01 | -7.85 | 57.22 | 88.59 | 90.63 |
| Prs 1* | -4.98 | 61.76 | 14.42 | 83.22 | 112.61 | 111.60 |
| Prs 2* | -1.36 | 65.89 | 18.32 | 87.75 | 116.74 | 115.16 |

ent (Steiner, 1953; Faure, 1977; Richardson and McSween, 1989). The isotope abundances were measured using isotope ratio mass spectrometer (IRMS) or isotope ratio mass spectrometer.

The composition of meteoric water in nature, according to Richardson and McSween (1989), and Field and Fifarek (1985), is composed of two stable isotopes of hydrogen (¹H and ²D) and three stable isotopes of oxygen (¹⁶O, ¹⁷O, and ¹⁸O). δ¹⁸O and δD analyses are to identify isotopes of meteoric water in certain areas, and to study the evolution of surface and subsurface water. The analyses were usually displayed on a plot of two isotopes. Plotted meteoric water located along a straight line (Craig, 1961; Craig, 1966) is given by the equation:

$$D = 8 \delta^{18}O + 10 \dots\dots\dots(1)$$

The results of geochemical analyses of hot water in the researched area show that the value of δ¹⁸O and δD is -4.15 ‰ and -23.43 ‰ (Table 1). Then, the isotope values were plotted on a diagram variation δ¹⁸O and δD which lies in the meteoric line. Thus, the origin of hydrothermal fluids were derived from meteoric water (Figure 6).

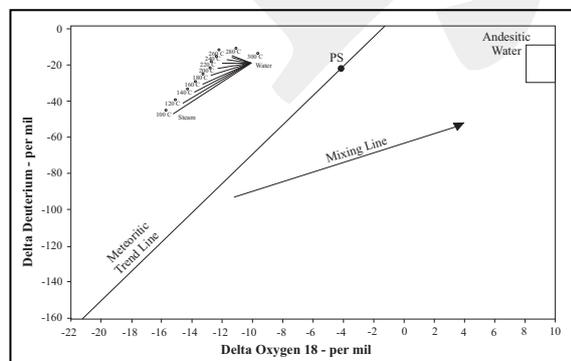


Figure 6. Origin of hydrothermal fluids in the researched area was meteoric water type that was plotted into meteoric water diagram (Craig, 1966).

Mineral Alteration

The study of altered minerals used eight rock samples covering five samples of pyroxene andesite and three samples of hornblende andesite. The eight samples consisted of rocks obtained around Parangtritis. The samples were analyzed by petrographic and scanning electron microscopic (SEM) modes. The results of petrographic analysis conducted on these samples, show that the types of rocks were pyroxene andesite and hornblende andesite that have undergone alteration.

The rocks are composed of primary minerals, such as plagioclase, pyroxene, hornblende, opaque mineral, and volcanic glass. In general, primary mineral that has hydrothermally been altered becomes mineral alteration. The result of mineral identification (primary and secondary minerals) using petrographic analysis is presented in Figure 7 and Table 3. The presence of alteration minerals can be explained as follows:

Quartz replaces phenocrysts and groundmass, and as a filler mineral in veins and cavities. As vein filler, it can be present with calcite. Meanwhile, as the filler cavity (vuggy), it may be present together with quartz, chalcedony, amorphous silica, and hematite. **Chalcedony** mineral fills the cavity (vuggy) together with quartz, amorphous silica, and hematite.

Montmorillonite as one of clay minerals is generally present in the rock alteration which alters phenocrysts and groundmass.

Calcite mineral is present replacing plagioclase, pyroxene, and groundmass, and can occur as vein and cavity filling minerals. Some calcite may be present with quartz and montmorillonite.

Hematite/opaque replaces mostly plagioclase, pyroxene, and groundmass, and can be present as vein and cavity filling minerals, that sometimes as mineral inclusions in phenocrysts. As a filling mineral, veining can be present with quartz and amorphous silica.

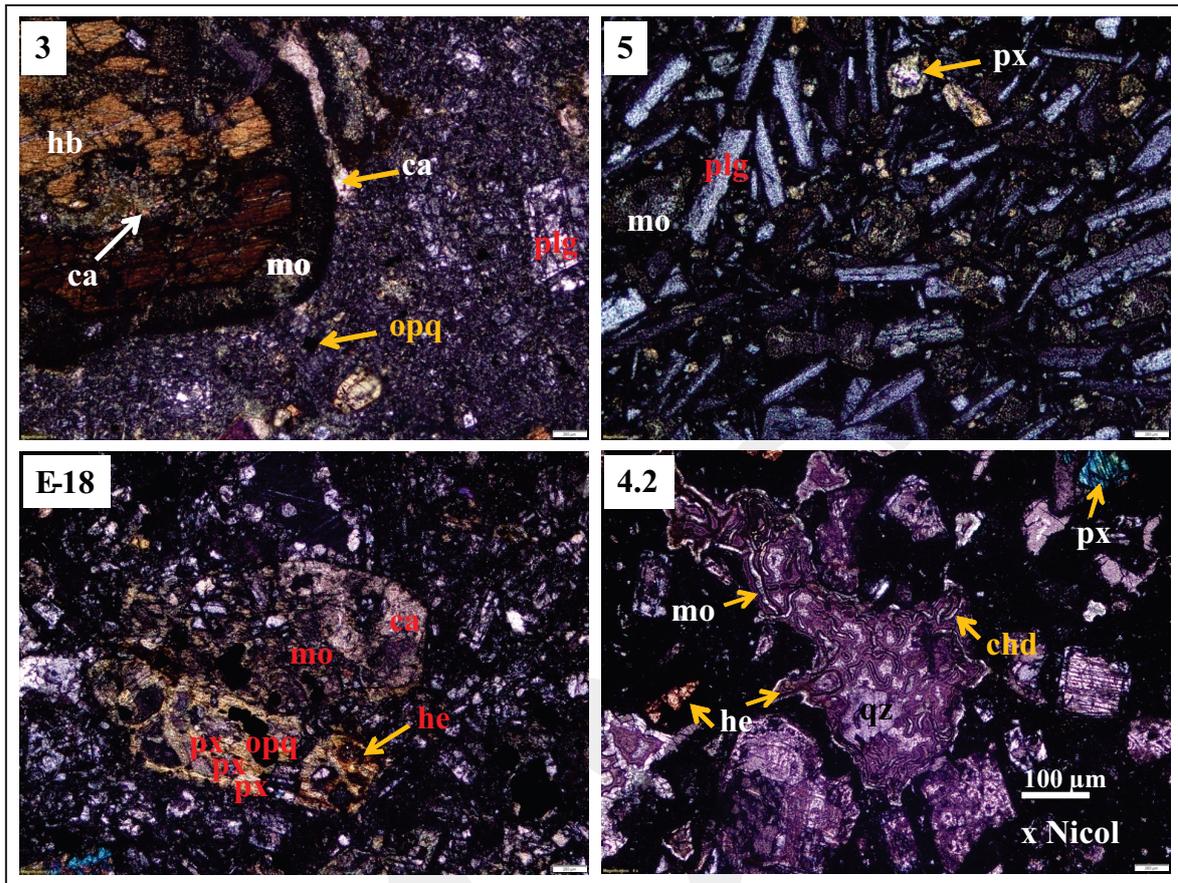


Figure 7. Photomicrographs of some mineral alterations in sample No. 5. Annotation: px: pyroxene, hb: hornblende, plg: plagioclase, qz: quartz, chd: chalcedony, mo: montmorillonite, ca: calcite, opq: opaque mineral.

Table 3. Tabulation of Mineralogical Analysis, plg: plagioclase, px: pyroxene, hb: hornblende, vg: volcanic glass, qz: quartz, chd: chalcedony, mo: montmorillonite: ca: calcite, he: hematite

| No. | Name Rocks | No. Sample | plg | px | hb | vg | qz | chd | mo | ca | he |
|-----|-----------------------|------------|-----|----|----|----|----|-----|----|----|----|
| 1 | Px andesite Intrusion | 5 | 0 | 0 | 0 | - | 0 | | 0 | 0 | 0 |
| 2 | Hb Andesite Lava | 3 | 0 | 0 | 0 | - | 0 | | 0 | 0 | 0 |
| 3 | Px andesite Lava | 9 | 0 | 0 | | - | 0 | | 0 | 0 | 0 |
| 4 | Px andesite Lava | 42.2 | 0 | 0 | 0 | - | 0 | 0 | 0 | 0 | 0 |
| 5 | Px andesite Lava | 44 | 0 | 0 | | - | 0 | | 0 | 0 | 0 |
| 6 | Hb andesite Lava | 44B | 0 | 0 | 0 | - | 0 | | 0 | 0 | 0 |
| 7 | Px andesite Lava | 49 | 0 | 0 | 0 | - | 0 | | 0 | 0 | 0 |
| 8 | Px andesite Lava | E-18 | 0 | 0 | 0 | - | 0 | 0 | 0 | 0 | 0 |

Annotation: 0: phenocrysts, 0 groundmass, o: attendance

Fluid-rock Interaction

Hydrothermal fluid interaction with rocks produces mineral alteration (Steiner, 1953). Alteration minerals replace the primary mineral in phenocrysts and groundmass. Igneous rock types in the studied area are pyroxene andesite and hornblende

andesite. In this study, the discussion is about the hydrothermal fluid-rock interaction using mobilization element analysis of pyroxene mineral that becomes montmorillonite. Pyroxene is a mineral that is always present in the rocks in the researched area. Thus, the replacement occurring in pyroxene

as the result of hydrothermal process can represent the geological conditions of the researched area.

To study mobilization element caused by fluid-rock interactions in this research is to study the change of primary minerals into secondary minerals are represented by the sample No. 5. The results of petrographic observations on sample No.5 show montmorillonite replacing the edges of pyroxene (Figure 7). Then, the measurement of the chemical composition was carried out from pyroxene to montmorillonite. Point measurements were taken at the edges of pyroxene to know the composition of montmorillonite, and at the central part of the pyroxene to determine the composition of pyroxene that has not been altered by hydrothermal fluids. By doing this, it is expected to obtain the pattern of change in the

chemical elements of primary minerals into secondary minerals as the result of the hydrothermal process. The mapping result of scanning electron microscope analysis shows the distribution of the elements in pyroxene that becomes montmorillonite (Figure 8). The interpretation of pyroxene chemical composition and montmorillonite used the interpretation from Deer *et al.* (1985, 1992). In the picture, the changes of pyroxene elements began from the middle to the edge. To study the mobilization of elements from the process of pyroxene replacement to become montmorillonite, the measurements of mineral chemical composition were carried out at three locations in pyroxene and three sites in the montmorillonite. The pyroxene crystal shows the composition of SiO₂ (50.34 - 51.12%), TiO₂ (0.54 - 0.88%),

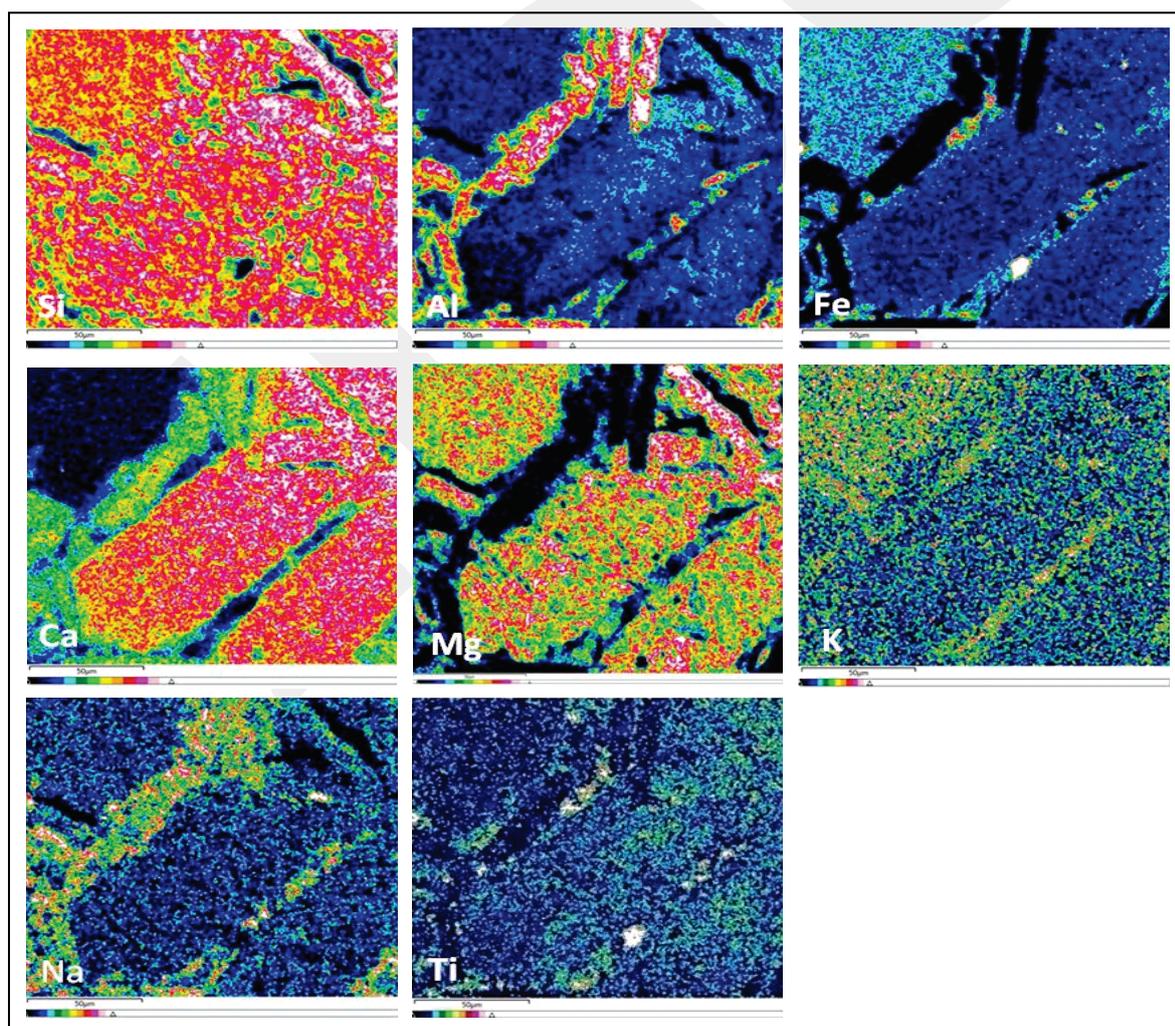


Figure 8. SEM-EDS backscattered images of elemental mapping for pyroxene replaced by montmorillonite on sample No.5.

Al₂O₃ (4.00 - 4.20%), Fe₂O₃ (7.39 - 12.41%), MgO (16.00 - 18.15%), and CaO (16.83 - 18.81 %). The measurement results of montmorillonite, which is on the edge of pyroxene crystals, are SiO₂ (46.92 - 49.55%), Al₂O₃ (0.26 - 0.46%), Fe₂O₃ (1.02 - 1.54%), MgO (0.26 - 0.46%), CaO (13.30 - 15.66%), and Na₂O (2.62 - 3.88%) (Table 4). In the hydrothermal process, mobilization elements occur due to fluids-rock interactions. The process produces alteration mineral (Browne, 1978, Browne and Brown, 1996). The mobilization of elements that occur in pyroxene to become montmorillonite can be studied on a triangular diagram of element variations of SiO₂, Al₂O₃,

Fe₂O₃*+MgO, and CaO (Figure 9). The diagram showing the process of mobilization elements from pyroxene to become montmorillonite are: SiO₂, Al₂O₃, Fe₂O₃*+ MgO, and CaO decreases followed by an increase in element content of Al₂O₃. The mobilization of these elements also occurs in an advanced argillic zone in Kamojang geothermal field (Yudiantoro, 1997; Yudiantoro *et al.*, 2012). The hydrothermal alteration process occurs at the temperature of 100°C (Reyes, 1990, Reyes *et al.*, 1993), with the composition of hydrothermal fluids is acid included in argillic zone (Inoue, 1995; Corbett and Leach, 1998; and Hedenquist and Richards, 1998).

Table 4. Composition of Pyroxene and Montmorillonite Minerals

| Spectrum | 1 | 2 | 3 | 4 | 5 | 6 |
|--------------------------------|----------|----------|----------|-----------------|-----------------|-----------------|
| Mineral | Pyroxene | Pyroxene | Pyroxene | Montmorillonite | Montmorillonite | Montmorillonite |
| Oxide % | | | | | | |
| SiO ₂ | 51.12 | 50.38 | 50.34 | 49.55 | 46.92 | 48.89 |
| TiO ₂ | 0.54 | 0.88 | 0.78 | | | |
| Al ₂ O ₃ | 4.00 | 4.19 | 4.20 | 31.28 | 33.52 | 32.07 |
| Fe ₂ O ₃ | 7.39 | 12.41 | 9.90 | 1.54 | 1.02 | 1.41 |
| MgO | 18.15 | 15.31 | 16.00 | 0.46 | 0.26 | 0.40 |
| CaO | 18.81 | 16.83 | 18.78 | 13.30 | 15.66 | 13.71 |
| Na ₂ O | | | | | | |
| K ₂ O | | | | | | |
| V ₂ O ₅ | | | | | | |
| Total | 100 | 100 | 100 | 100 | 100 | 100 |
| Element (Wt%) | | | | | | |
| Si | 23.9 | 23.55 | 23.53 | 23.16 | 21.93 | 22.98 |
| Ti | 0.32 | 0.53 | 0.47 | | | |
| Al | 2.11 | 2.22 | 2.22 | 16.55 | 17.74 | 16.98 |
| Fe | 5.17 | 5.17 | 6.93 | 1.08 | 0.71 | 0.99 |
| Mg | 10.95 | 10.95 | 9.65 | 0.27 | 0.16 | 0.24 |
| Ca | 13.44 | 13.44 | 13.42 | 9.50 | 11.19 | 9.80 |
| Na | | | | 2.88 | 1.94 | 2.60 |
| K | | | | | | |
| O | 44.11 | 44.11 | 43.78 | 46.55 | 46.32 | 46.54 |
| V | | | | | | |
| Total | 100 | 100 | 100 | 100 | 100 | 100 |
| Element (Atomic %) | | | | | | |
| Si | 18.61 | 18.62 | 18.53 | 17.39 | 16.56 | 17.18 |
| Ti | 0.15 | 0.24 | 0.22 | | | |
| Al | 1.71 | 1.82 | 1.82 | 12.94 | 13.94 | 13.28 |
| Fe | 2.02 | 3.45 | 2.74 | 0.41 | 0.27 | 0.37 |
| Mg | 9.85 | 8.44 | 8.78 | 0.24 | 0.14 | 0.21 |
| Ca | 7.34 | 6.67 | 7.40 | 5.00 | 5.92 | 5.16 |
| Na | | | | 2.64 | 1.79 | 2.39 |
| K | | | | | | |
| O | 60.32 | 60.75 | 60.51 | 61.37 | 61.41 | 61.41 |
| V | | | | | | |
| Total | 100 | 100 | 100 | 100 | 100 | 100 |

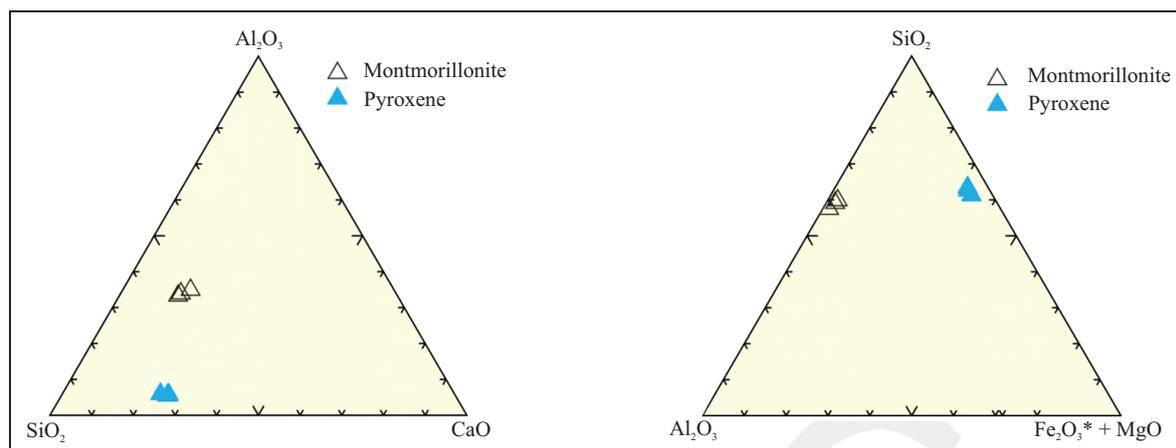


Figure 9. Mobilization elements of pyroxene replaced by montmorillonite.

CONCLUSION

The volcanic rocks of the studied area are composed of volcanic breccias, pyroxene andesite intrusion, basalt, pyroxene andesite, and hornblende andesite lavas. The magmatism activities took place at the Paleocene (58.58 ± 3.24 Ma) to Oligo–Miocene (33.15 ± 1.00 Ma - 24.25 ± 0.15 Ma). These activities have generated hydrothermal fluids until now and interact with meteoric water, wall rocks up on the surface to produce hydrothermal alteration rocks and manifestation of hot water.

The process of hydrothermal alteration replaces primary minerals such as plagioclase, pyroxene, hornblende, and volcanic glass to become quartz, chalcedony, calcite, montmorillonite, and hematite. The process of hydrothermal fluid-rock interaction can be observed in pyroxene crystals *i.e.* pyroxene is replaced by montmorillonite. In the replacement process, there occurred mobilization elements of decreasing SiO_2 , Al_2O_3 , $\text{Fe}_2\text{O}_3^* + \text{MgO}$, and CaO , followed by increasing Al_2O_3 . This alteration process took place at the temperatures of 100°C with acidic fluid composition. However, the current hydrothermal process from the analysis of hot water manifestations appearing on the surface is neutral chloride water, salty water, and estimated subsurface temperature about $90.63 - 115^\circ\text{C}$, and under the partial equilibrium condition.

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