Gas geochemistry analysis in Candradimuka Crater, Mount Lawu, Central Java, Indonesia

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Abstract. Mount Lawu is a stratovolcano in Central Java that holds a large geothermal energy potential. Within Mount Lawu Geothermal Area, several thermal manifestations could be located one of them being Candradimuka Crater located at the proximity of Mount Lawu peak. This study aims to assess the gas geochemistry in Candradimuka Crater by obtaining gas sample within the crater area. Gas geochemistry analysis uses geothermometer, geoindicator, and N₂-He-Ar ternary diagram to analyse the subsurface condition. The analysis reveals that the fluid circulating in the crater originated from meteoric water and that Mount Lawu reservoir temperature ranged between 250°C - 289°C. Based on geological observation and gas geochemistry, Candradimuka Crater is located within the upflow zone of Mount Lawu.

1. Introduction
Indonesia holds a large amount of geothermal energy potential approximately around 28 GW energy or almost equal to 40% of the world’s total geothermal energy potential [1]. The large sum of geothermal energy can be contributed to Indonesia’s proximity to the convergence boundary of several major tectonic plates, such as Eurasia, Indo-Australia, Philippine, and Pacific plate or also known as the Ring of Fire [2]. The convergence plate boundary resulted in active volcanic activity in the region, especially in Java Island of Indonesia. Volcanic formation stretches along the archipelago of Indonesia resulting in around 252 geothermal fields where 71 of the fields are located in Java Island [3]. Mount Lawu is an established Geothermal Working Area located in the border of Central Java and East Java (Figure 1). Mount Lawu contains 137 MW hypothetical energy and has been set as a Geothermal Working Area by Indonesia Ministry of Energy and Mineral Resources in 2012 [1].

Geological and geochemical investigations are used to evaluate a geothermal system. Geological investigations focus on determining lithology variation, stratigraphy, and structural geology in the area. Geochemical investigations focus on the chemical characteristics of the thermal manifestations that can provide an overview of the subsurface condition. These data are combined to get a better understanding of the geothermal system in the area [4].

Assessing the geothermal system of Mount Lawu using gas geochemistry investigation is the objective of this research. The gas sample is obtained from Candradimuka Crater fumaroles. Gas sample analysis is considered the most suitable method for this type of thermal manifestation (fumaroles) because fumaroles release an intense geothermal gas to the surface.
2. Geological overview

Mount Lawu is an active volcano located in the border between Central Java and East Java. It still has an active geothermal system that is marked by some active thermal manifestations, such as fumaroles, hot pools, and hot springs. Some of the rock within the area has been altered [4]. The research area is primarily composed of 2 rock units, which are Candradimuka Lava and Lawu Volcanic Rocks. Candradimuka Lava consists of andesitic lava, while Lawu Volcanic composed of tuff and volcanic breccia intercalating with andesitic lava. Both of these rock units formed during the Holocene period [4,5].

Figure 2. Geological Map of Mount Lawu (modified from [5] and Hermawan & Permana, 2018).

Based on regional geological map by [5], there are several structural features that could be observed. The major fault found in the area has NW-SE orientation as its dominant orientation (Figure 2). Other minor structure consists of faults trending N-S, E-W, and NE-SW. The appearance of thermal
manifestation around Mount Lawu are presumably controlled by faults with most of the manifestations are located 200-700 meters not far from the faults [5,6]. Based on the water geochemistry analysis conducted by Sahdarani et al. (2020), thermal manifestations around Mount Lawu comprised of all different type of geothermal water such as acidic sulphate water and diluted chloride carbonate water. Some of the manifestation located on the western flank contains a high amount of Fe and As indicating an intense rock-water interactions. Mount Lawu has only one reservoir underlaying in the subsurface based on the Cl/B ratio comparison from different manifestations. The estimated reservoir temperature is around 160°C - 170°C based on the Na/K geothermometer calculation, therefore Mount Lawu is considered as an intermediate-high enthalpy system [4].

3. Research Methodology

The Candradimuka Crater fumarole gasses were sampled. The number of samples obtained from the crater is one sample with LWU as its sampling code. The sampling location is marked by the green plot on Figure 2. Before conducting gas sampling, the gas sample bottle needs to be prepared by vacuuming the bottle with 100 mL NaOH solution inside the flask. A stainless-steel funnel is needed to capture the gas from the crater. The funnel needs to be connected to the gas sample bottle by using heat proof silicone tube. The bottle must be placed inside a water filled bowl during the sampling process. The gas will start flowing to the bottle when the bottle’s valve is opened.

The chemical components of the gas samples were analysed in Central Volcanology and Geological Hazard Mitigation Laboratory. The chemical components obtained from the analysis are CO₂, H₂S, He, H₂, N₂, Ar, and CH₄. These components are useful to evaluate the geothermal system. Based on gas chemical analysis, several calculations on geothermometer and geoindicator were performed. The interpretations include N₂-He-Ar ternary diagram analysis. Geoindicator is used to indicate the flow zone of the manifestation to determine the upflow or outflow zone. Meanwhile, N₂-He-Ar ternary diagram is used to determine the fluid origin. Subsequently, we conducted geothermometer most appropriate to the chemical analyses result to calculate the reservoir temperature [7].

The most appropriate geothermometer analysis are H₂S, H₂, FT-CO₂, and CAR-HAR. CO₂ and CH₄/CO₂ cannot be used because the predicted reservoir temperature from the analysis is beyond the possible temperature range (Table 1). Moreover, CO₂/H₂ and H₂S/H₂ is considered unsuitable because these geothermometers are only producing valid number when the reservoir temperature is between 200°C - 300°C with chloride concentration above 500 ppm [8]. Chloride concentration in Candradimuka Crater is relatively low based on the Cl/B ratio [4], therefore CO₂/H₂ and H₂S/H₂ value are not valid.

4. Results and Discussion

Candradimuka Crater main fumaroles covering an area of approximately 10 m x 8 m. The fumarole temperature is around 90°C. The acidity level of the gas is around 3. Based on field observation, there were abundant of sulphur deposits that surrounded the gas outlet.

![Figure 3. Candradimuka Crater fumaroles.](image-url)
Fluid origin interpreted by using N$_2$-He-Ar diagram (Figure 4, red plot), revealing that Candradimuka Crater fluid originated from meteoric water. The geothermal fluid has N$_2$/Ar value of 54.67 where this value is ranged between the Air ratio composition (N$_2$/Ar = 84) and ASW ratio composition (N$_2$/Ar = 38).

Based on FT-CO$_2$, CAR-HAR, H$_2$S, and H$_2$ geothermometer analysis, Mount Lawu geothermal field reservoir temperature is around 250°C (Figure 5, red plot), 260°C (Figure 6, red plot), 289°C, and 264°C, respectively. It is considered as a high enthalpy system [9]. Besides reservoir temperature, the state of the fluid inside the reservoir can also be determined. Based on CAR-HAR geothermometer (Figure 6, red plot), the plotting result lies just below the equilibrated liquid line. It indicates that the reservoir is a liquid-dominated reservoir.

**Table 1.** Gas geothermometer analysis result.

| Gas Geothermometer (in °C) | CO$_2$ | H$_2$S | H$_2$ | CO$_2$/H$_2$ | H$_2$S/H$_2$ | CH$_4$/CO$_2$ | FT-CO$_2$ | CAR-HAR |
|---------------------------|--------|--------|-------|--------------|--------------|--------------|-----------|---------|
|                            | 340    | 289    | 264   | 270          | 241          | 530          | 250       | 260     |
Candradimuka Crater is located in the upflow zone based on the manifestation type, temperature, and gas geochemical analysis (CO₂/H₂S ratio). The fumaroles emit distinguishable sulphuric gas at 90°C which signified an upflow zone [4,7]. The findings of CO₂/H₂S ratio in Candradimuka Crater is calculated at 8.32, which is considered as a relatively low value. The lower CO₂/H₂S ratio indicates the less interaction between the geothermal gas and the host rock. This minimum interaction shows that the migration of the gas is not far away from the magmatic source [7], so it concluded that Candradimuka Crater is in the upflow zone.

As it is in the upflow zone, Candradimuka Crater produces numerous amounts of gas. The gas is formed when there is a reduction of the confining pressure in the geothermal fluid which makes the fluid boiled. The boiling fluid then separated into two phases, i.e., liquid and vapour phase. Then, the vapour tends to migrate vertically along the upflow zone, while the liquid phase tends to migrate horizontally along the outflow zone [7]. This characteristic makes Candradimuka Crater able to produce a massive amount of gas with the help of fractures as its pathway.

In the case of Candradimuka Crater, gas analysis is more reliable than water analysis. The lightweight properties of gas drives gas migration along the upflow path and will be less likely to be mixed with other substances, such as groundwater. Therefore, gas chemical characteristic has more retention and can reflect the reservoir characteristics. However, the reservoir type also has a role in determining which analysis should be used. In liquid dominated reservoirs, water analysis is more reliable compared to gas analysis, because the thermal manifestation found in geothermal area tends to be a hot spring or hot pool.
type. Furthermore, based on statistic reasoning, the small number of manifestations appearance makes the data less reliable [10]. The existence of water-type manifestation has a greater number than the gas-type manifestation in Mount Lawu. In conclusion, gas analysis is less reliable than water analysis in Mount Lawu because of the liquid-dominated reservoir and the appearance of only one fumarolic manifestation area which located in Candradimuka Crater.

5. Conclusion
Mount Lawu fluid originated from meteoric water. Based on the geothermometer analysis, the reservoir temperature of Mount Lawu is approximately at 250°C - 289°C and can be classified as a high enthalpy system. The reservoir of the system is a liquid-dominated reservoir. Candradimuka Crater is within the upflow zone of the Mount Lawu geothermal system. Candradimuka Crater presence within the upflow zone makes it emits gas in a large amount. However, to have a better understanding of Mount Lawu geothermal system, water geochemistry analysis is more reliable than gas geochemistry analysis due to the phase of the reservoir and type of manifestation.

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