Analysis of Composition; Topography of Volcanic Materials Erupted from Mount Sinabung, Karo Regency, Indonesia

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Abstract. Volcanic rocks and ashes erupted from mount Sinabung has been analyzed to understand the composition and topography of the materials contained within them. The crystalloid system of the samples were analyzed through X-Ray Diffraction (XRD), while the analysis of chemical elements and the microstructures were tested by performing the Scanning Electron Microscopy, Energy Dispersive X-Ray (SEM-EDX), and the metal analysis was performed by Atomic Absorption Spectroscopy (AAS). The samples collected were black volcanic rocks, red volcanic rocks and volcanic ashes. The analysis obtained from the analysis of the black volcanic rocks depicted four phases of materials which are Anorthite (87.11 wt.%), Quartz (2.26 wt.%), Cristobalite (7.72 wt.%), and Alunite (2.91 wt.%). Respectively, the crystalloid lattices of those phases were Triclinic, Hexagonal, Tetragonal and Hexagonal.

Three phases of materials which are Anorthite (89.20 wt.% with Orthorhombic lattice, Quartz (2.63 wt.%) with Hexagonal lattice, Cristobalite (5.56 wt.%) with Tetragonal lattice, and Alunite (2.52 wt%) with Hexagonal lattice were obtained from volcanic ashes. Meanwhile, the analysis of composition measured by AAS indicated that the heavy metals were not found within the erupted materials.

1. Introduction

Mount Sinabung, located in province of North Sumatera in Indonesia, had erupted after being stable for hundreds of years. The first volcanic activity was recorded for the first time in 27 August 2010 indicated by the eruptions, and the eruption events produced hot cloud, volcanic ashes, and volcanic rocks. These three volcanic materials also spurted another phases of materials, and those were including sand, stones, and ashes altogether. According to the digital document provided by the Centre of Volcanology and Geological Hazard Mitigation of Indonesia stated that status of Sinabung volcano is altered from type-B to type-A volcano because of its eruptions in 2010. And based on its type of eruption, the Sinabung is categorized with Strombolian type.

Given that to its location, which is located in the volcanic cluster of Eurasia from northern part of Sumatra along to Sunda arc with 5000 km of length, Sinabung is an active volcano, and the last eruption happened 400 years ago. The first eruption was recorded in August 2010, followed by six eruptions which was occurred during September 2010 [1]. Gunawan et.al. , has reported that the geodynamic aspect of Sinabung had produced explosion column, disperse tephra, crater-limited lava
domes, flank-depending lava flows, vent-derived pyroclastic density currents (PDCs), and lava flow margin collapse-generated PDCs (Construction for eruption forecasting). While the volcanic materials which were generally produced during the 2015 eruptions were dominated by silica oxide (SiO$_2$) for 74.3%, aluminium oxide (Al$_2$O$_3$) for 3.3%, and potassium oxide (CaO) for 1.79% in form of sand, rocks, and ashes [2]. And all of these chemical compounds has different crystalline systems with certain phases.

The materials which were erupted has certain characteristics. Unlike the findings reported by Karolina et. al., [2], the September eruptions contain three highest pristine elements which were aluminium (Al), potassium (Ca), and sulphur (S) [3]. Meanwhile, the chemical contents within the Sinabung’s volcanic ashes are (SiO$_2$), magnetite, anorthite, pyrite, and illite which have been deposited inside its pyroclastic currents for over a thousand of years [4]. Providing that the pyroclastic flows involve heat and pressure, then the chemical compounds have been deformed into certain phases and crystalline system and those are including the silica dioxide. Interestingly, it has been reported that there were slight differences of materials erupted between 2013 eruption and 2015 regarding the highest chemical compounds composition.

Nevertheless, the significant differences occur between active volcanoes in Indonesia and those in Mediterranean. Volcanic materials which are from active volcanoes in Indonesia, such as Sinabung and Merapi, were reported containing magnetite, anorthite, pyrite, and cristobalite [5]. While the most mineralogy contents found in Vesuvius and Etna mountains are plagioclase and silica oxide glass respectively [6]. The differences between these two areas in their mineralogy compounds indicate that certain mechanism have been occurring to each volcano within their pyroclastic flows. For Sinabung, the formation of minerals compound were formed during the phreatomagmatic phase which was happened during November 2013 [7].

The main study in the analysis of the volcanic eruption material composition lies in the chemical content that affects the health of human and the environment. The main chemical contents other than alkali metals in volcanoes are radioactive elements and transition metals, for instance on the eruption happened in Merapi Volcano in Yogyakarta in 1984, was enriched in Selenium (Se), Rhenium (Re), Bismuth (Bi), and Cadmium (Cd), and four of them are heavy metals. Meanwhile, in Fogo mountains in the Fiji archipelago, it was reported that the soil composition at the top of the mountain contains Chromium (Cr) and Arsenic (As) which are classified as contaminants for the environment [8].

Volcanic materials from the eruptions cover the area around the mountain. Geographically, the deposition of volcanic material is influenced by the direction of eruption and wind. However, almost completely surface soil around the mountain slope consists of eruption material. Thus, as much as 1.2% of global land is contributed by eruption material [9]. Meanwhile, the gas emissions that occurred in the eruption between 2010- until present contains sulphide compounds (SO$_2$) [10]. And in this study, the erupted rocks used as samples to analyze the composition.

We examine three types of eruption material from Sinabung Mountain which were erupted in 2015. The three samples are red volcanic rocks, black volcanic rocks, and volcanic ashes. Characterizations are performed by analyzing the topology of eruption material using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) instrument. Meanwhile, the analysis of chemical composition of eruption materials were performed by using Atomic Absorption Spectroscopy (AAS) instrument to determine the content of toxic and hazardous elements.

2. Experimental Method
The samples are material eruptions which were black volcanic rocks, red volcanic rocks, and volcanic ashes, obtained from Simacem, sub-district Namanteran, Karo regency located 2 kilometers from the center of eruption. Each of the samples which accounted for 200grams were collected from three different places. All of the samples then were carried to Medan at the same day.

After arriving in Medan, the samples then were dried in oven to remove the water contents. Afterwards, the samples were divided into three cups to be prepared. The volcanic ashes from three places were mixed, whereas the rocks, which are either the red and black, were grinded. After being
grinded, the rocks samples were sieved with 100 mesh of sieve. Lastly, the rocks samples were heated in oven to remove the water contents left. All samples were prepared to be analyzed through XRD, SEM-EDX and AAS instrumentations for obtaining crystalline; phases systems, microstructures and chemical elements respectively.

3. Results and Discussion

3.1 Analysis of the black volcanic rocks structure

Firstly, the black volcanic rocks were sieved until 100 mesh, then it becomes powder. The powder then is placed into a mold to be pressed with 100 kPa for 10 minutes. After being pressed, 5gram of samples then are taken to be placed onto the samples holder. Finally, the samples are ready to be analyzed for its crystalline and phases systems.

According to the XRD’s analysis (Figure1) which we performed, it can be seen that the black volcanic rocks contains Anorthite (Al₂CaO₈Si₂), Quartz (SiO₂), Cristobalite (SiO₂), and Alunite (Al₃H₁₂K₀.₈₇O₁₄.₁₂₅S₂). The XRD patterns illustrate each stones with different peaks. The highest peak is Anorthite, and it is followed by Cristobalite. Whereas, the lowest peak is contributed by Quartz.

More importantly, the peaks indicate the quantity of the stones’ contents.

![Figure 1. The XRD patterns of black volcanic rocks](image)

Table 1. The weight percentage of chemical composition and crystalline system

| No. | Phases           | Crystalline System | a (Å)  | b (Å)  | c (Å)  | Density (g/cm³) | Wt %  |
|-----|------------------|--------------------|--------|--------|--------|----------------|-------|
| 1   | Anorthite (Al₂CaO₈Si₂) | Triclinic          | 8.1742 | 12.844 | 14.204 | 2.768          | 87.11 |
| 2   | Quartz (SiO₂)     | Hexagonal          | 4.799  | 4.799  | 5.397  | 4.262          | 2.26  |
| 3   | Cristobalite (SiO₂) | Tetragonal         | 4.970  | 4.970  | 6.998  | 2.308          | 7.72  |
| 4   | Alunite (Al₃H₁₂K₀.₈₇O₁₄.₁₂₅S₂) | Hexagonal        | 6.990  | 6.990  | 17.282 | 2.843          | 2.91  |

According to Table 1, it clearly can be seen that Anorthite has the most quantity among the others. The percentage of Anorthite is 87.11wt%, while the lowest quantity is Quartz contributed for 2.26 wt%. The percentage also shows that the lowest two percentages have the same crystalline system.
They are Quartz and Alunite with the same hexagonal crystal. These findings have the similarity which were found by Igan et. al.,[4]and Damby et. al.,[5] which both of them had analyzed the composition of materials erupted from Sinabung and Merapi volcanoes respectively. Microstructure analysis of black volcanic rocks is performed with SEM-EDX instrumentation, and the photograph is shown below in Figure 2.

![Microstructure of black volcanic rocks](image)

**Figure 2.** The microstructure of black volcanic rocks

Based on the photograph, it can be seen that the topography of the rocks contains four characteristics. They are irregular, angular, aggregate and rounded. While, the chemical elements are shown by the Table 2 below.

| Element | Mass (%) | Error (%) | Atom (%) |
|---------|----------|-----------|----------|
| C       | 23.22    | 0.14      | 33.10    |
| O       | 45.64    | 0.22      | 48.84    |
| Na      | 1.26     | 0.13      | 0.94     |
| Mg      | 0.30     | 0.10      | 0.21     |
| Al      | 8.44     | 0.09      | 5.36     |
| Si      | 14.32    | 0.10      | 8.73     |
| S       | 0.85     | 0.08      | 0.45     |
| K       | 0.78     | 0.12      | 0.34     |
| Ca      | 3.71     | 0.13      | 1.59     |
| Fe      | 1.48     | 0.30      | 0.45     |

The Table 2 shows the percentage of chemical compositions analyzed by the SEM-EDX instrumentation. Based on the Table 2, the highest element is Oxygen (O) with 45.64% of mass, while the lowest amount of element is Magnesium (Mg) which is accounted for 0.30% of mass. The top three highest elements are Oxygen (O), Carbon (C) and Silica (Si).

### 3.2 Analysis of the red volcanic rocks structure

The preparation of red volcanic rocks was conducted exactly the same to the black volcanic rocks. The first step is by sieving the rocks into sieve after being crushed into the ball mill instruments. And then the samples were sieved with 100 mesh of sieve. After being sieved, the samples were pressed with 100 kPa before placing onto the samples holder. 5gram of samples then were taken to be analyzed to the XRD instrument.
According to the XRD’s analysis (Figure 3) which we performed, it can be seen that the red volcanic rocks contain only two phases of rocks which are Cristobalite (SiO$_2$), and Alunite (Al$_3$H$_{12}$K$_{0.875}$O$_{14.125}$S$_2$). The XRD patterns illustrate each stones with different peaks. The highest peak is Anorthite, and it is followed by Cristobalite. Whereas, the lowest peak is contributed by Quartz. More importantly, the peaks indicate the quantity of the stones’ contents. Figure 3 depicts each peaks of phase systems. The highest peak is illustrated by Alunite with red colour coding, while the lowest peak is Cristobalite showed with green colour.

Table 3. The weight percentage of chemical composition and crystalline system

| No | Phases                          | Crystalline System | a (Å) | b (Å) | c (Å) | Density (g/cm$^3$) | Wt%  |
|----|---------------------------------|--------------------|-------|-------|-------|-------------------|------|
| 1  | Cristobalite (SiO$_2$)          | Tetragonal         | 4.986 | 4.986 | 6.943 | 2.308             | 21.71|
| 2  | Alunite (Al$_3$H$_{12}$K$_{0.875}$O$_{14.125}$S$_2$) | Hexagonal         | 6.9885| 6.9885|17.223 | 2.843             | 78.29|

According Table 3, it clearly can be seen that red volcanic rocks only contain two phases of rocks. Alunite has higher percentage than the Cristobalite. Their percentages are 78.29% with tetragonal crystalline system and 21.71% with Hexagonal crystalline system respectively. These findings have the similarity which were found by Igan et. al.,[4]and Damby et. al.,[5] which both of them had analyzed the composition of materials erupted from Sinabung and Merapi volcanoes respectively. Microstructure analysis of black volcanic rocks is performed with SEM-EDX instrumentation, and the photograph is shown below in Figure 4.

Figure 3. The XRD patterns of red volcanic rocks

Figure 4. The microstructure of red volcanic rocks
Based on the photograph, it can be seen that the topography of the rocks contains four characteristics. They are irregular, angular, aggregate and rounded. While, the chemical elements are shown by the Table 4 below.

**Table 4. The analysis composition of black volcanic rocks**

| Element | Mass (%) | Error (%) | Atom (%) |
|---------|----------|-----------|----------|
| C       | 21.90    | 0.08      | 31.13    |
| O       | 50.29    | 0.13      | 53.65    |
| Al      | 11.39    | 0.07      | 7.21     |
| Si      | 8.85     | 0.07      | 5.38     |
| K       | 2.68     | 0.08      | 1.17     |
| Fe      | 4.00     | 0.21      | 1.22     |
| Cu      | 0.88     | 0.34      | 0.24     |

The Table 4 shows the percentage of chemical compositions analysed by the SEM-EDX instrumentation. Based on the Table 4, the highest element is Oxygen (O) with 50.29% of mass, while the lowest amount of element is Copper (Cu) which is accounted for 0.88% of mass. The top three highest elements are Oxygen (O), Carbon (C) and Aluminium (Al).

3.3 Analysis of the volcanic ashes structure

The ashes sample was sieved with 100mesh of sieving. Before being placed onto the molding, the ashes was pressed with 100kPa for ten minutes. Afterward, the volcanic ashes were placed onto the samples holder to be analysed the crystalline and phases systems.

According to the XRD’s analysis (Figure 5) which we performed, it can be seen that the volcanic ashes contains Anorthite (Al2CaO3Si2), Quartz (SiO2), Cristobalite (SiO2), and Alunite (Al3H12K0.875O14.125Si2). The XRD patterns illustrate each stones with different peaks. The highest peak is Anorthite, and it is followed by Cristobalite. Whereas, the lowest peak is contributed by Alunite. More importantly, the peaks indicate the quantity of the stones’ contents.

Figure 5 depicts each peaks of phases systems. The highest peak is illustrated by Anorthite with red color coding, while the lowest peak is Quartz.
Table 5. The weight percentage of chemical composition and crystalline system

| No | Phases                        | Crystalline System | a (Å) | b (Å) | c (Å) | Density (gcm⁻³) | Wt %  |
|----|-------------------------------|--------------------|-------|-------|-------|-----------------|-------|
| 1  | Anorthite (Al₂CaO₈Si₂)        | Orthorombic        | 8.174 | 12.844| 14.204| 2.768           | 89.20 |
| 2  | Quartz (SiO₂)                | Hexagonal          | 5.135 | 5.135 | 5.443 | 4.262           | 2.63  |
| 3  | Cristobalite (SiO₂)          | Tetragonal         | 4.957 | 4.957 | 6.779 | 2.308           | 5.65  |
| 4  | Alunit (Al₃H₁₂K₀.₈₇₅O₁₄.₁₂₅S₂) | Hexagonal          | 6.967 | 6.967 | 17.150| 2.843           | 2.52  |

According to Table 3.5, almost 90% of the composition is Anorthite with orthorombic crystalline system, while the lowest is Alunite with hexagonal crystalline system (2.52%). These findings also have the similarity which were found by Igan et al.,[4] and Damby et al.,[5] which both of them had analyzed the composition of materials erupted from Sinabung and Merapi volcanoes respectively. Microstructure analysis of black volcanic rocks is performed with SEM-EDX instrumentation, and the photograph is shown below in Figure 6.

Based on the photograph, it can be seen that the topography of the rocks contains four characteristics. They are irregular, angular, aggregate and rounded. While, the chemical elements are shown by the Table 6 below

Table 6. The analysis composition of black volcanic rocks

| Element | (keV) | Mass (%) | Error (%) | Atom (%) |
|---------|-------|----------|-----------|----------|
| C       | 0.277 | 10.78    | 0.28      | 16.59    |
| O       | 0.525 | 49.72    | 0.24      | 57.47    |
| Na      | 1.041 | 0.54     | 0.17      | 0.43     |
| Al      | 1.486 | 9.40     | 0.12      | 6.44     |
| Si      | 1.739 | 27.41    | 0.14      | 18.05    |
| K       | 3.312 | 2.15     | 0.17      | 1.02     |

The Table 6 shows the percentage of chemical compositions analyzed by the SEM-EDX instrumentation. Based on the Table 6, the highest element is Oxygen (O) with 49.72% of mass, while the lowest amount of element is Sodium (Na) which is accounted for 0.54% of mass. The top three highest elements are Oxygen (O), Silica(Si), Carbon (C).
3.4 Analysis of Atomic Adsorption Spectroscopy (AAS)

5 gram of volcanic ashes that had been prepared from the pressing step were taken. The analysis of metals was performed by the AAS instruments, and it was performed in Pusat Penelitian Kelapa Sawit, Medan, Sumatera Utara, Indonesia.

Table 7. The composition of metals contained in volcanic ashes

| No. | Metals         | Units | Value    | Method |
|-----|----------------|-------|----------|--------|
| 1.  | Copper (Cu)    | ppm   | 46.35    | AAS    |
| 2.  | Lead (Pb)      | ppm   | <LoD     | AAS    |
| 3.  | Cadmium (Cd)   | ppm   | <LoD     | AAS    |
| 4.  | Arsenic (As)   | ppm   | <LoD     | AAS    |
| 5.  | Iron (Fe)      | %     | 4.37     | AAS    |
| 6.  | Zinc (Zn)      | %     | 0.02     | AAS    |
| 7.  | Mercury (Hg)   | ppm   | <0.001   | ICP    |
| 8.  | 100% of fineness | %  | 85.20 | SNI 02.2803.2005 |

According to the spectroscopy analysis, it is shown that four heavy metals are discovered within the volcanic ashes. The highest ppm unit for the metals is copper for 46.35 part per million (ppm), while the highest percentage of metals is iron with 4.37%. Interestingly, three metals which are lead, cadmium, and arsenic are in the level of under Limit of Detection (LoD), while the mercury is in under 0.001 ppm.

4 Conclusion

Volcanic activities reflect the geochemical events happened inside the pyroclastic chamber. Consequently, the physical and chemical system influence the materials which are the chemical elements or compounds. However, more importantly, the erupted material is deposited on the soil nearby the volcanoes for a very long duration even though the eruptions happen in short time. Therefore, chemical contents of the materials which are located nearby the active volcano are significantly influenced by the geochemical process [11].

Several studies have reported that erupted material from active volcano contains silica compounds. However, the difference lies on the crystalline phase, for instance plagioclase [6], andesine, quartz and cristobalite [5], [12]. The crystalline system which has physical form causes the human’s respiratory system as it is formed in certain shapes.

Based on the topological analysis that has been performed throughout the XRD and SEM-EDX instrumentations, each samples contain mainly Alumunium, Silica and Oxygen. The highest contents for black volcanic rocks; red volcanic rocks, and volcanic ashes are respectively Anothite (87.11 wt%) with triclinic crystalline system; Alunite (78.29 wt%) with tetragonal crystalline system, and Anorthite (89.20 wt%) with orthorhombic crystalline system. All the samples have similar microstructure characteristics which are irregular, angular, aggregate, and round.

Meanwhile, the highest content which was found in each samples are slight different. The highest chemical elements in black volcanic rocks is Oxygen (O) which contributes for 48.84 %, and it is followed Carbon (C) and Silica (S) as second and third for 33.10% and 8.73% respectively. While the red volcanic rocks contain Oxygen, Carbon and Alumunium as the three highest elements content, and they account for 53.65%, 31.13% and 7.21% respectively. Moreover, volcanic ashes analysis showed that the three highest elements are Oxygen (57.74%), Carbon (16.59%), and Silica (18.05%).
Interestingly, the Atomic Adsorption Spectroscopy (AAS) analysis showed that the heavy-metal elements are not presented in each samples, nonetheless the highest amount of metal element in volcanic ashes is Copper (Co) accounted for 46.35 ppm.

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