

Original Research

Characterizing Volcanic Ash Elements from the 2015 Eruptions of Bromo and Raung Volcanoes, Indonesia

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Abstract

The volcanic eruptions of Mt. Bromo and Mt. Raung in East Java, Indonesia, in 2015 perturbed volcanic materials and affected surface-layer air quality at surrounding locations. During the episodes, the volcanic ash from the eruptions influenced visibility, traffic accidents, flight schedules, and human health. In this research, the volcanic ash particles were collected and characterized by relying on the detail of physical observation. We performed an assessment of the volcanic ash elements to characterize the volcanic ash using two different methods which are aqua regia extracts followed by MP-AES and XRF laboratory test of bulk samples. The analysis results showed that the volcanic ash was mixed of many materials, such as Al, Si, P, K, Ca, Ti, V, Cr, Mn, Fe, Ni, and others. Fe, Si, Ca, and Al were found as the major elements, while the others were the trace elements Ba, Cr, Cu, Mn, P, Mn, Ni, Zn, Sb, Sr, and V with the minor concentrations. XRF analyses showed that Fe dominated the elements of the volcanic ash. The XRF analysis showed that Fe was at 35.40% in Bromo and 43.00% in Raung of the detected elements in bulk material. The results of aqua regia extracts analyzed by MP-AES were 1.80% and 1.70% of Fe element for Bromo and Raung volcanoes, respectively.

Keywords: characterization, volcanic ash, Bromo Mountain, Raung Mountain

Introduction

Natural disasters such as volcanic eruptions become significant natural processes that emit volcanic materials such as gaseous species or aerosol particles

into the atmosphere. The implication of the eruption of a volcano was generated from heavy volcanic ash [1]. As an example, the eruption of Mt. Kelud (East Java, Indonesia) in 2014 generated volcanic ash without any warning. The volcanic ash even was carried as far as approximately 350 km to the west side [2]. A similar disaster occurred in Iceland in May 2011, when the Grimsvötn eruption affected the surface-layer air quality of the surrounding area [3]. The recent examples

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in polyethylene bags and stored in polyethylene tubes. Due to the high relative humidity, all samples were collected from single ashfall events as clean as possible. Samples collected from accumulation events will have high potency to be exposed by moisture that can influence their physical profiling. They were collected in succession at the same location for more than one eruption phase.

Microwave Plasma Atomic Emission Spectrometry (MP-AES)

The sample preparation was carried out by aqua regia extraction under high pressure according to the reference method described in (Norm DIN EN ISO 16174, 2012). About 1 g of the volcanic ash was weighed and transferred to the digestion vessel. Two drops of distilled water, 2 ml concentrated (65 %) nitric acid and 6 ml concentrated (37 %) hydrochloric acid were added to the volcanic ash. The closed digestion vessels were placed in the microwave digestion system, heated at a rate of 10°C/min to a temperature of 180°C and remained there for 10 min. After cooling down to room temperature the sample was filtered into a 50 ml volumetric flask. The solid remaining in the digestion vessel was transferred into the funnel using distilled water and washed with 5 ml diluted (about 2.3%) nitric acid, and the volumetric flask was filled with distilled water. Parallel to the digestion, a reagent blank test digestion was carried out. The sample solutions were stored in a refrigerator. Microwave Plasma Atomic Emission Spectrometry (Agilent Technologies, 4200 MP-AES) was used to analyze the volcanic ash sample extracts quantitatively. Each sample solution was filtered using a syringe filter (0.45 µm). The analysis used calibration solutions (Calibration mix 2 (Part. No. 6610030600) and

Calibration mix majors (Part. No. 6610030700), Agilent Technologies), "Matrix" solution (20 ml HNO₃ (65 %, suprapur MERCK) and 60 ml HCl (37 %) in 500 ml, filled up with distilled water), and stock solution. This method measured the elements of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Th, Tl, U, V, and Zn for the Calibration mix 2 and Ca, Fe, K, Mg, and Na for the Calibration mix majors. The speed of the pump was 15r/ min, with the stabilization time of 15 s (sample uptake time 15 s). The concentration of the analyzed element was calculated by:

$$\text{Concentration} = \frac{\bar{x}_{aw} \cdot d \cdot V_{\text{solution}}}{m_{\text{ash}}} \quad (1)$$

The mass of ash sample is shown by m_{ash} . d is the dilution factor (see Table 1). V_{solution} was 50 ml. Calibration function was calculated by:

$$w_i = \frac{s_i^{-2}}{\sum s_i^{-2} / m} \quad (2)$$

Weighted calibration is referred to w_i (weighting factor), while s_i and m represent the standard deviation of i (calibration solution) and the number of calibration solutions including blank, respectively. To calculate the statistical parameters for each solution (calibration and digested sample), we measured them three times. The complete analysis procedure sample preparation, calibration and MP-AES measurement were carried out two times for both Bromo and Raung ash samples on different days in order to check the reproducibility. Not all the elements present in the calibration solutions could be determined quantitatively in the volcano ash samples because of spectral interference caused by major elements.

Table 1. Groups of the different elements for the measurement by MP-AES and calibration.

No.	Elements	Dilution of the Sample Solution	Calibration Solutions (mg/L)	Calibration Function Concentration (mg/L)
1	Ba	-	0.4; 0.6; 1; 2; 3	Intensity = 503·10 ³ ·Concentration+0.081
2	Cr	-	0.4; 0.6; 1; 2; 3	Intensity = 35,6·10 ³ ·Concentration-0.12
3	Cu	-	0.4; 0.6; 1; 2; 3	Intensity = 110·10 ³ ·Concentration-0.367
4	V	-	3; 5; 8; 12; 16	Intensity = 8.86·10 ³ ·Concentration-0.15
5	Mn	-	3; 5; 8; 12; 16	Intensity = 42.2·10 ³ ·Concentration-0.018
6	Al	1:200	3; 5; 8; 12; 16	Intensity = 31.5·10 ³ ·Concentration-16.3
7	Fe	1:200	1; 4; 8; 12; 16	Intensity = 8.12·10 ³ ·Concentration-2.29
8	Mg	1:200	0.1; 0.2; 0.5; 1; 2	Intensity = 204·10 ³ ·Concentration+9.11
9	Ca	1:2000	0.5; 1; 1.5; 2; 3	Intensity = 892·10 ³ ·Concentration-341
10	K	1:20	0.5; 1; 1.5; 2; 3	Intensity = 44.9·10 ³ ·Concentration+20.6
11	Na	1:200	0.5; 1; 2; 3; 4	Intensity = 325·10 ³ ·Concentration+615

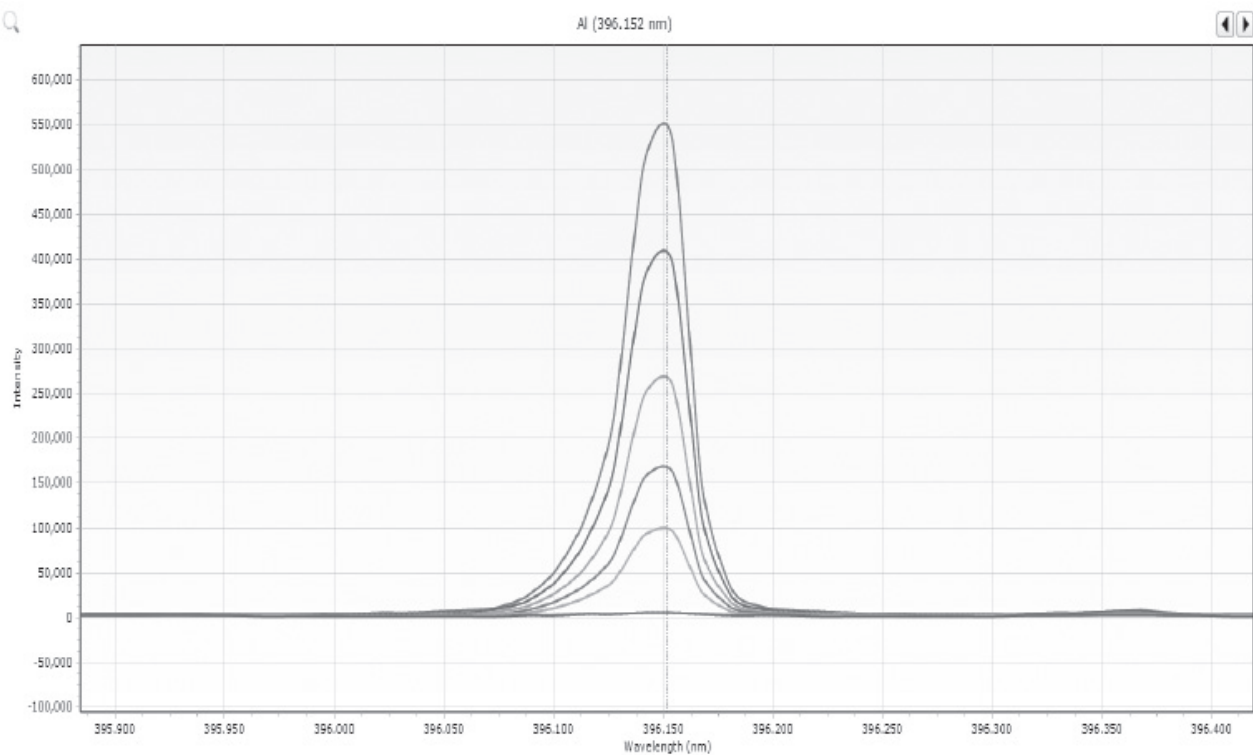


Fig. 2. Spectra of Al in different concentrations used for calibration.

XRF Spectroscopy

An XRF (x-ray fluorescence spectroscopy, PANalytical, Model MiniPal 4) test was used to determine the elemental composition of the volcanic ash qualitatively. The information of the components was interpreted as a spectrum graph. The results were expressed as the element concentration in weight percentage (*wt* %) by the reference 100% representing the sum of the detected elements.

Results and Discussion

Microwave Plasma Atomic Emission Spectrometry (MP-AES)

In order to measure the different elements in the sample solutions, it was necessary to group up the elements. The dilution of the sample solution and the calibration solution used are interpreted in Table 1 and Fig. 2 (the representative spectra of Al in different concentrations of the calibration solutions). Results

Table 2. Mass-Concentrations of the elements in aqua regia extracts ($p = 0.95$).

No.	Elements	Bromo	Raung	State
1	Ba	49.9 (± 1) ppm	29.0 (± 0.7) ppm	Traces elements
2	Cr	11.0 (± 1) ppm	5.9 (± 0.6) ppm	
3	Cu	64.5 (± 5) ppm	40.3 (± 3) ppm	
4	Mn	275.0 (± 19) ppm	351 (± 49) ppm	
5	V	66.7 (± 7) ppm	46.5 (± 8) ppm	
6	Al	1.5 (± 0.24) %	2.9 (± 1) %	Major elements
7	Ca	1.2 (± 0.3) %	2.5 (± 0.2) %	
8	Fe	1.8 (± 0.1) %	1.7 (± 0.1) %	
9	K	1.5 (± 0.2) ‰	0.95 (± 0.2) ‰	
10	Mg	3.6 (± 0.5) ‰	8.2 (± 1.4) ‰	
11	Na	4.2 (± 0.5) ‰	6.0 (± 1.4) ‰	

from the analysis of MP-AES in the volcanic ash samples of the volcanoes Bromo and Raung are of a similar magnitude with a little difference. Table 2 below interprets the analysis results of the aqua regia extractable fraction from Bromo and Raung ash.

Eleven elements were quantified in both Bromo and Raung ash samples. The concentrations are given in Table 2, and Fig. 3(a-b) are the mean values of two complete analyses of each sample. They differed by less than 10% only in the case of Cr 20%. This indicates a good reproducibility of the analysis for all elements and a high homogeneity of the ash samples. In parentheses we give the confidence interval, which refers to the calibration function and the standard deviation of the sample measurement. In Fig. 3(a-b) the dominant of the detected elements are Fe, Al, and Ca. Interpreting the data in Table 3 it must be considered that the elements Si and O are not determined here, but it is well known

that they contribute to volcanic ash in a high amount. Mass concentration of more than 60% SiO_2 [10] and up to 70% were measured (Wahyuni, 2016) for Merapi. Even 77% SiO_2 have been found in the volcanic glass of Tyatya Volcano [11].

As mentioned in the methodology section, a solid residue after aqua regia extraction remained. The masses of unsoluble dried residue after aqua regia extraction of Raung sample was 58%, and in the case of Bromo even 82%. This is not surprising because in volcanic ash a high amount of SiO_2 and in aqua regia unsoluble silicates or oxides are expected. The higher amount of SiO_2 in Bromo sample could explain the lower concentration of major elements Al and Ca because we calculated the concentrations in relation to the complete sample mass. The color of both samples is dark grey, the Bromo sample is a little lighter, which supports the interpretation of a higher amount of SiO_2 and/or colorless silicates and oxides. In literature, often the exact acid digestion parameters for volcanic ash analysis are not given (e.g., [10, 12], and in some cases they are similar to ours [13]. Thus we conclude that the concentrations reported do not include the insoluble fraction, or it is calculated as different SiO_2 up to 100% (Wahyuni, 2016). Lump et al. [14] compared different digestion techniques for element analysis of silicates containing airborne dust and dust deposition. They report that only with digestion by acid mixtures containing HF can complete decomposition be achieved, but also for the most metals using aqua regia very high recoveries were observed, with the exception of Cr (62%), Al, and Na (50-80%). Thus we conclude that in the residue of the aqua regia extracts of Bromo and Raung samples, major elements like Al and Na are partially present in poorly soluble silicates or oxides. It should be mentioned that we found in both samples a very high amount of black magnetic particles, which indicates a high concentration of Fe_3O_4 . This fact agrees well with the very dark color of the complete samples. The low concentrations of Fe in the aqua regia extracts correspond to the poor acid solubility of Fe_3O_4 .

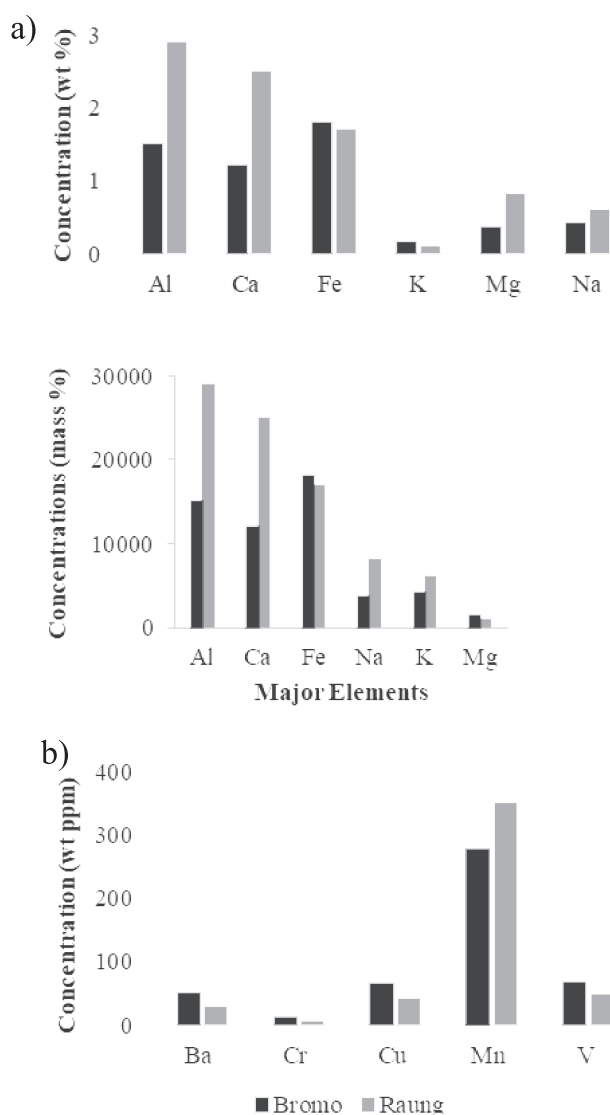


Fig. 3. The average concentration of elements measured in the aqua regia extracts of volcanic ash of Bromo and Raung volcanoes by MP-AES analysis: a) major and b) trace.

XRF Spectroscopy

An XRF (x-ray fluorescence spectroscopy, PANalytical, Model MiniPal 4) test was used to determine the elemental composition of the volcanic ash qualitatively. The information of the components was interpreted as a spectrum graph (Fig. 4). Ash characterization based on the XRF analyses showed that Fe, Si, Ca, and Al are the major constituents of both Bromo and Raung ash. These elements became the highest concentrations of the main elements. Significant differences of Cr, Yb, and Zn were found as the trace elements. The concentrations of Cr, Yb, and Zn were lower. The trend of Bromo ash is quite similar to Raung ash. A little difference is found in the ash elements of Mt. Raung. We did not find the elements P, Rb, and Ba in the volcanic ash of Raung.

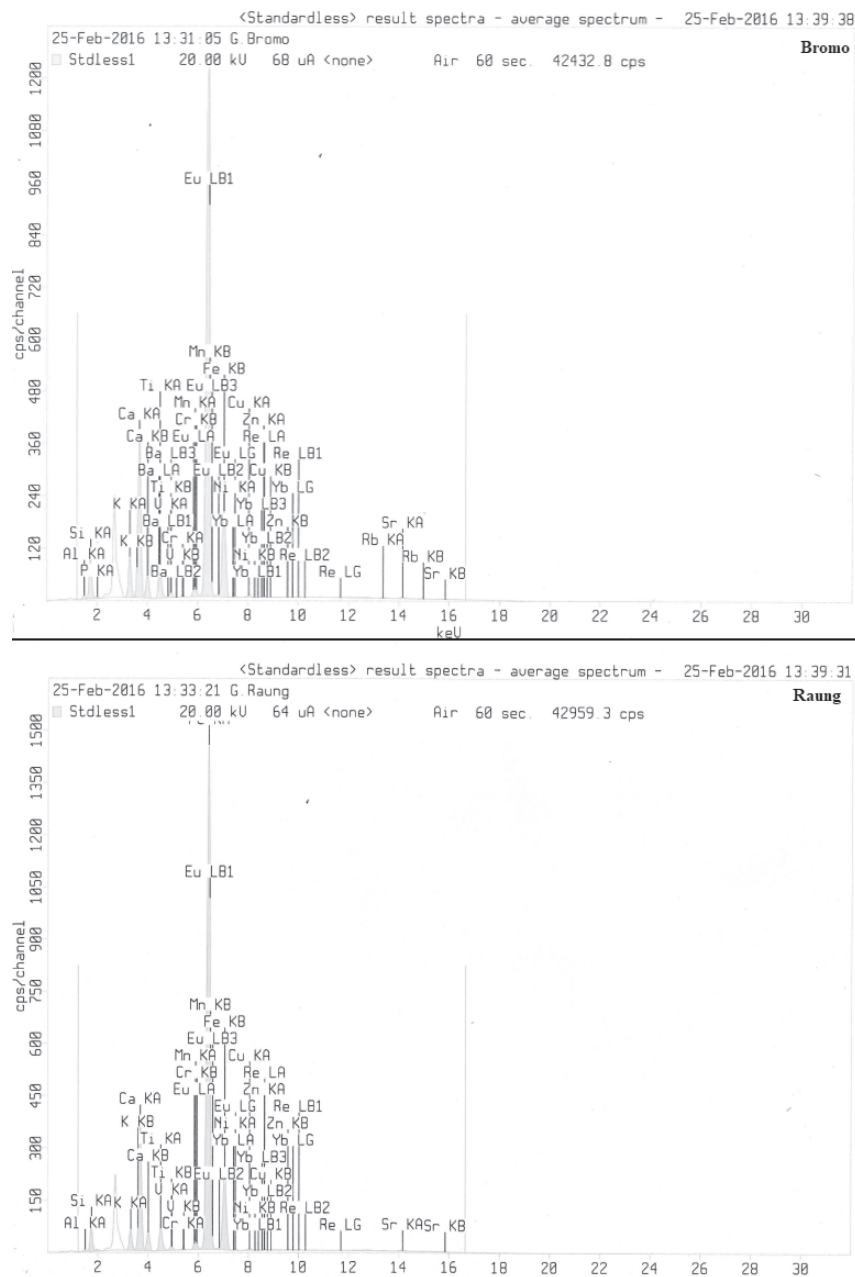


Fig. 4. Volcanic ash characteristics resulted by the XRF analyses.

The results of volcanic ash characterization and their chemical compounds derived by XRF are shown in Table 3. They are shown qualitatively and expressed as the concentration (percentage) calculated up to 100%, referring to the sum of the detected elements. Based on Table 3, the comparison of 16 elements detected in the volcanic ash of Bromo reveals that the element of Fe (35.4%) is much higher compared to other elements. The concentration of Si is 9.1% lower than Fe. An identical result can be seen in Raung, which has similar volcanic ash elements, where Fe dominates the element concentration (43.0%). The element of Si only is 22.1%, in which this concentration is 20.9% lower than Fe. It is remarkable that the concentrations of Fe and Ca are significantly higher compared to other volcanic ash

reported in the literature [12, 15, 16]. The high amount of Fe agrees very well with the magnetic property and the dark color of the ash samples, which indicate Fe_3O_4 as a dominant compound. According to all results above, both Bromo and Raung have similar ash characteristics. Because XRF is not able to detect elements with an atomic number lower than 9 (fluorine), the oxygen concentration is not included in Table 3. In order to estimate the influence of oxygen present in the ash on the mass concentration of the elements in relation to the mass of the complete sample, we calculated the amount of oxygen by the assumption that the major elements are bound as oxides. In that case, the concentrations listed in Table 3 must be multiplied by the factor 0.61 (Bromo) or 0.62 (Raung).

Table 3. Concentration (wt %) of the elements in the volcanic ash from XRF analysis.

No.	Elements	Bromo	Elements	Raung
1	Al	8.50	Al	7.50
2	Si	26.30	Si	22.10
3	P	0.54	K	3.59
4	K	5.51	Ca	18.20
5	Ca	18.10	Ti	2.47
6	Ti	2.41	V	0.16
7	V	0.10	Cr	0.08
8	Cr	0.07	Mn	0.69
9	Mn	0.59	Fe	43.00
10	Fe	35.40	Ni	0.16
11	Ni	0.16	Cu	0.25
12	Cu	0.23	Zn	0.02
13	Zn	0.03	Sr	1.00
14	Rb	0.32	Eu	0.40
15	Sr	0.86	Yb	0.00
16	Eu	0.40		
17	Yb	0.01		

Data of Bromo and Raung are rare in the literature. The measured concentrations of Fe and Al are in the same magnitude but lower than that found in the ash of Merapi as measured by thermal and epithermal neutron activation analysis: Fe 5%, Al 13%, Ca not detected [16]. The concentration of K (1.7%) is about 10 times higher as in Bromo and Mn (1 %) is about 3-4 times higher. Element concentrations in Merapi volcanic ash have been determined also using AAS and ICP-OES (Wahyuni 2016). These data are comparable to our results, since the analysis methods are similar. Wahyuni

(2016) was found at different locations on Merapi Mountain: Al 8-10%, Ca 2-6%, Fe 5-6%, K 1.7-1.9%, Mg 1.7%, Mn 0.17%, and Na 2.7%. These concentrations are in plausible agreement with ours concerning the fact that we compared different volcanoes of Java, which may contain different amounts of SiO_2 and other constituents. Kusmartini et al. [12,15] analyzed volcanic ash of Mt. Sinabung and compared the elemental concentrations with volcanoes of other regions. They found 11.8 ppm Cr for Mt. Sinabung, which is in excellent agreement with our results for Bromo (Table 2). In volcanic ash from the South Andes, Cu concentrations between 8.45 ppm and 108.7 ppm were measured, which again is very similar to the data we found for Bromo and Raung [15]. The concentrations of the other trace elements in Table 3 also are in good agreement with data from the ash of other volcanoes [12, 15].

Volcanic ash particles indeed consisted of the main components Fe, Si, Al, O, Na, and other chemical compounds in varying concentrations [17, 18]. These results were similar to the composition of Icelandic volcanic ash as reported in the literature [19] with Fe, Si, Ca, and Al as the parts of the major elements and Ti, Mn, and P as the trace elements. Differences between the two different volcanic ashes for this eruption were not mainly manifest in the ash componentry. These results showed slightly different leaching characteristics. The main difference can be seen in the existence of Fe, Si, Ca, and Al in the XRF results (as the main elements) and only Fe, Ca, and Al in aqua regia extracts measured by MP-AES (as the main elements) (Fig. 5). In another side, the concentrations of Fe, Ca, and Al have mostly been found. This likely indicates greater contents of these three elements as the main ash componentry of Bromo and Raung. Moreover, re-mobilization of the ash deposits by the wind after an eruption can disturb and influence the data [8]. This re-mobilization, as expected, can influence the results of the XRF and MP-AES profiling. The concentration of the detected elements also depends on the distance of

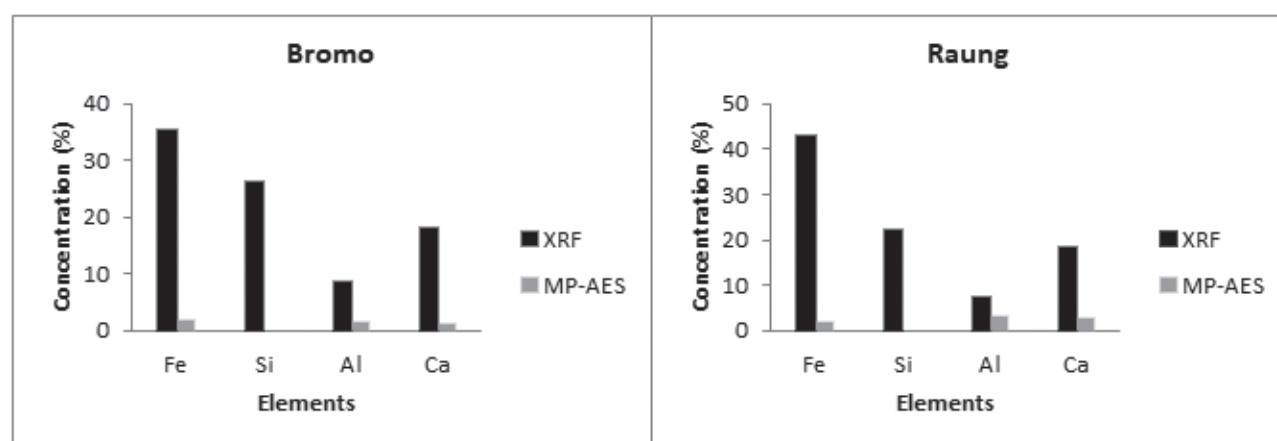


Fig. 5. The results of XRF and MP-AES (aqua regia extracts) analysis (major elements).

the vent area and the sampling area. These differences can influence the ash accumulation rate due to the different ash deposition abilities and the size of the major and trace elements of the volcanic ash [13, 20].

Conclusions

The presence of the major and trace elements in the volcanic ash of Bromo and Raung volcanoes (eruptions: July 2015) has been analyzed in this study. Very similar element concentrations were found in Bromo and Raung samples. Remarkable high concentrations of Fe and Ca have been measured compared to other volcanic ash described in the literature. The dominating element is Fe bound in magnetite Fe_3O_4 . The concentrations of trace elements in the volcanic ash soluble in aqua regia agree well with those reported for other volcanoes.

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Conflict of Interest

The authors declare no conflict of interest.

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