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Trace analysis of Indonesian volcanic ash using thermal and epithermal neutron activation analysis

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Abstract. There is continued great interest in determining the trace element and heavy metal content of volcanic ash for a variety of reasons. The motivation stems from the desire to understand the geochemistry of volcanic ash in imbedded geological formations, the impact on seawater, and the possible release of toxic elements into the environment that may impact livestock grazing and water systems. Ash from volcanic plumes can go as high 8–18 km thus affecting climate and air traffic. We have employed Compton suppression neutron activation analysis (NAA) with thermal and epithermal neutrons to determine trace elements in volcanic ash from Indonesian eruption of Mount Merapi in October 2010. We found a wide range of elements, including several rare earth elements.

Key words: neutron activation analysis (NAA) • trace elements • volcanic ash • rare earth elements • Mount Merapi

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Introduction

For the past century, Indonesia has been subjected to much volcanic activity, with over 60 volcanoes that have erupted in Indonesia since 1900 [15]. Volcanic eruptions can temporarily alter the chemistry of the soil, rivers, oceans, and air on a local and global scale. The 2010 Merapi eruption was a major one, and was observed to have a high range, reaching the coast of Africa seventeen days after the eruption [18] with a total amount of ash estimated to be around 160 million tonnes [17]. Because of the large quantity and the high mobility, the ash from this volcano could have had effects in far reaching areas. It is important to know in detail the elements in the ash, since many people are subjected to it. Although trace elements make up a small percentage of the ash material, the amount of ash entering the ecosystem during a volcanic eruption makes even trace elements relevant. While some elements create more fertile soil and aid in agriculture, other trace elements such as As, Cu, F, Mo, Ni, Pb, and Zn are potentially toxic [14]. When compounded with the fact that some elements are especially mobile, such as Ni, Zn, As, Mo, [14] this can have negative effects on the ecosystem over a large area. Other elements, such as Zn, Cu, Cd, F, Pb, and Ba, are more readily leached into bodies of water and could be toxic to fish and wildlife [16].

The goal of this research was to identify a number of trace elements in fresh volcanic ash from the 2010 Merapi eruption using instrumental neutron activation analysis (NAA), using thermal and epithermal methods in conjunction with Compton suppression. A perusal of

Table 1. Irradiation, decay and counting times used to find various elements

Element	Technique	Method	Power (kW)	Irradiation time	Decay time	Count time
Al, Mn, Na, V	Thermal	Normal	100	10 s	15 min	15 min
Ti	Thermal	Compton	100	10 s	15 min	15 min
Si	Epithermal	Normal	100	2 min	15 min	15 min
Ba, Dy, K, Sr, U	Epithermal	Compton	100	2 min	1 h	1 h
Co, Cr, Cs, Eu, Fe, Hf, La, Rb, Sc, Ta, Tb	Thermal	Normal	950	1 h	3 weeks	2 h
Ce, Nd, Zn, Th	Thermal	Compton	950	1 h	3 weeks	2 h
As, Sb	Epithermal	Normal	500	2 h	1 week	1 h
Sm	Epithermal	Compton	500	2 h	1 week	1 h
Ni	Epithermal	Compton	500	2 h	3 weeks	3 h

the literature indicates that these combined techniques are being used for the first time in volcanic ash. We then briefly compared our results to studies of how these elements could alter soil.

Experimental

Ten samples of 200 μm sieved ash were supplied by the National Nuclear Energy Agency of Indonesia (BATAN) in Yogyakarta, all from different locations around 16 km from the center of Mount Merapi. About 300 mg of ash from five of these locations were put into clean polyethylene containers. Two additional samples were made from one location in order to check the homogeneity of the ash. The samples were irradiated at the University of Texas at Austin in a 1 MW TRIGA reactor for a variety of periods of time and power levels, as seen in Table 1. The irradiated samples were counted with a Gamma-X germanium detector with an efficiency of 32.7% and FWHM (full width at half maximum) of 2.0 keV at 1.33 MeV from a Co-60 source. For some elements, it was beneficial to use a NaI detector to act as a Compton suppression system [2, 11].

Using different irradiation methods allowed us to find a wide variety of hard to detect elements and elements present in low concentration. Compton suppression greatly reduced the background, especially in the low Compton scattering energies, which allowed for higher precision measurements of gamma rays between 150–1500 keV. Compton suppression also suppressed elements that have more than one gamma rays that are coincident with each other, such as ^{24}Na, which releases the 2754 keV and 1368 keV gamma rays in coincidence with each other. If the Compton NaI detector and the normal detector each detect one of the coincident rays, the data will be considered as a Compton event and will be thrown out. This method can be used to purposely suppress overpowering peaks, such as those arising from ^{24}Na, ^{56}Mn, ^{60}Co, ^{46}Sc, and ^{59}Fe.

Similarly, epithermal neutrons were used to suppress overpowering peaks that have large thermal neutron cross sections. During epithermal irradiations, we used a cadmium sleeve around the sample, which absorbed thermal neutrons and only allowed epithermal neutrons to reach the sample, as opposed to thermal irradiations when the vast majority of the neutrons reaching the sample were thermal neutrons. Some elements that have a high ratio of epithermal resonance integral to thermal cross section are ^{75}As, ^{123}Sb, ^{87}Sr, and ^{238}U [12], which can be seen in Table 2.

Two examples of using different irradiation and detection techniques are shown in Figs. 1 and 2. Figure 1 is the classic interference of the 1120 keV from ^{46}Sc with the 1115 keV photopeak belonging to ^{65}Zn. The Compton suppression system suppressed ^{46}Sc because of its strongly coincident gamma rays (889 and 1120 keV), giving the best results for the ^{65}Zn peak both in the thermal and epithermal spectra, as can be seen in Fig. 1.

Figure 2 shows how epithermal spectra give much more precise measurements of ^{87}Sr than thermal spectra. As can be seen in Table 2, the ratio of the resonance

Table 2. Ratio of resonance integral (I) to thermal cross section (σ) for all the elements we found. High ratios indicate that it may be advantageous to measure the element in epithermal spectra [12]

Element	I/σ
Al	$7.35 \times 10^{-4} \pm 0.44 \times 10^{-4}$
As	15.2 ± 0.6
Ba	0.79 ± 0.13
Ce	0.93 ± 0.09
Co	1.99 ± 0.05
Cr	0.76 ± 0.02
Cs	14 ± 1
Dy	0.13 ± 0.01
Eu	0.26 ± 0.06
Fe	1.12 ± 0.06
Hf	2.53 ± 0.08
K	0.97 ± 0.05
La	1.34 ± 0.07
Mn	1.00 ± 0.04
Na	0.60 ± 0.02
Nd	1.72 ± 0.012
Ni	0.65 ± 0.09
Rb	15.6 ± 0.6
Sb	32 ± 5
Sc	0.44 ± 0.02
Si	5.88 ± 0.30
Sm	14.4 ± 0.6
Sr	6.23 ± 0.58
Ta	32 ± 1
Tb	17.9 ± 0.9
Th	11.3 ± 0.2
Ti	0.66 ± 0.06
U	103 ± 1
V	0.60 ± 0.02
Zn	1.73 ± 0.09

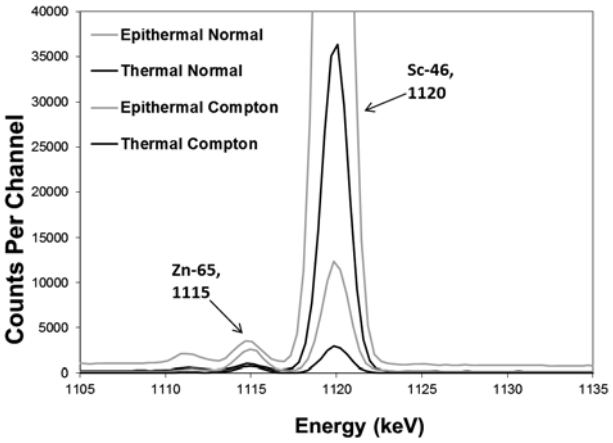

Fig. 1. Comparison of measuring the concentration of ^{65}Zn using different irradiation and detection methods. Since ^{46}Sc has two gamma rays in coincidence with each other, it is suppressed in the Compton spectra. The thermal Compton spectra give the highest precision measurements of the ^{65}Zn peak.

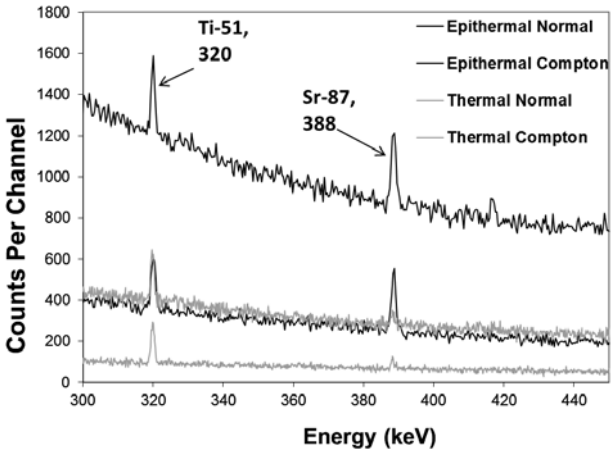

Fig. 2. Comparison of the ^{87}Sr peak in the epithermal spectra and the thermal spectra. Since ^{87}Sr has a higher resonance integral than thermal neutron cross section, it is advantageous to measure this peak in epithermal spectra. Since it is a low energy peak, the Compton suppression system suppresses the background and scattering gamma rays, and the epithermal Compton spectra give the highest precision measurements.

integral to thermal cross section is high for ^{87}Sr, so the epithermal spectra give a much higher peak than the thermal spectra, whereas the same ratio for ^{51}Ti is close to 1, so the peak for ^{51}Ti in the epithermal spectra is comparable to the thermal spectra.

Results

A comparison of our concentrations and the NIST concentrations for coal 1632c are given in Table 3. Most of our measurements were less than 15% different than the NIST concentration values, and those that were more than 15% different (Eu and Hf) were at very low concentrations that were near the detection limit. The concentrations of the elements found in our ash are given in Table 4. The trace elements found in the volcanic ash are congruent with other findings [3, 5, 6, 19]. The results of comparing three samples from the same location showed that the standard deviation was 13% for most elements, where most of the larger standard deviations were from elements of low concentration that were close to the detection limit.

The elemental concentrations in the volcanic ash were compared to that of average soil in order to understand the effects of ash on plant life [1, 7, 13]. Many of the elements found in volcanic ash have comparable values to those found in soil. The main differences are in Cr, Ni, Ti, and V. The traces of chromium and nickel are lower than the average values usually found in soil. However, both are found at various concentrations in soil, and it is not very unusual for soil to have less than 5 μg/g of Cr or Ni [1], and although they are essential micronutrients, having lower levels of either in ash is unlikely to affect the plants. Although titanium and vanadium are higher than the average amount in soil, they are within the reasonable range of values. Titanium is hardly toxic, except in extreme levels. Vanadium is slightly toxic, but is not at extreme enough levels to where it is likely to affect the plants negatively [7].

We found several rare earth elements (Ce, Dy, Eu, La, Sm, Tb), which is not unusual since igneous rocks are known to have high concentrations of rare earth elements [9]. Table 5 shows a comparison of the values of rare earth elements' concentrations in the ash compared to the estimated concentration in the earth's crust. Since the earth's crust is estimated to be 64.7%

Table 3. Comparison of our measurements of the NIST coal sample 1632c and the NIST fly ash sample 1633a to the values given by NIST

1632c	Measured (μg/g)	NIST values (μg/g)
Al	9 838 ± 716	9 150 ± 137
As	6.17 ± 0.17	6.18 ± 0.27
Ba	43 ± 11	41 ± 2
Ce	11.7 ± 0.6	11.9 ± 0.2
Co	3.31 ± 0.30	3.48 ± 0.20
Cr	13.6 ± 0.5	11.9 ± 0.2
Eu	0.21 ± 0.02	0.124 ± 0.003
Fe	7 253 ± 227	7 350 ± 11
Hf	0.48 ±0.04	0.59 ± 0.01
K	967 ± 122	1 100 ± 33
Mn	14 ± 1	13.0 ± 0.5
Na	277 ± 18	299 ± 5
Ni	9.43 ± 0.07	9.32 ± 0.51
Rb	7.56 ± 0.69	7.52 ± 0.33
Sb	0.51 ± 0.03	0.46 ± 0.03
Sc	2.76 ± 0.14	2.91 ± 0.04
Si	17 664 ± 1413	16 540 ± 340
Sm	1.10 ± 0.06	1.08 ± 0.03
Sr	59 ± 5	64 ± 1
Th	1.40 ± 0.08	1.40 ± 0.03
Ti	458 ± 55	517 ± 32
U	0.56 ± 0.04	0.51 ± 0.01
V	23 ± 1	23.7 ± 0.5
Zn	12.3 ± 0.7	12 ± 1
1633a	**Measured (μg/g)**	**NIST values (μg/g)**
Dy	12.1 ± 0.7	16 ± 1
La	100 ± 11	84 ± 8
Nd	88 ± 5	74 ± 10
Ta	1.89 ± 0.14	2.0 ± 0.2
Tb	2.46 ± 0.17	2.5 ± 0.3

Table 4. Elemental concentrations in volcanic ash. Uncertainty given in average is propagated error from each measurement and added in quadriture

Element	Min (%)	Max (%)	Average (%)	SD[a] (%)
Al	8	35	13 ± 3	9.24
Fe	4.98	6.08	5.42 ± 0.43	0.38
K	1.67	1.75	1.70 ± 0.21	0.03
Na	0.76	2.75	2.11 ± 0.41	0.86
Si	24	27	26 ± 3	1.15
Ti	0.36	0.66	0.44 ± 0.10	0.09
Element	**Min (μg/g)**	**Max (μg/g)**	**Average (μg/g)**	**SD (μg/g)**
As	0.30	5.69	3.44 ± 0.58	2.15
Ba	381	539	479 ± 123	47
Ce	31	42	37 ± 5	3
Co	14	17	16 ± 2	1.26
Cr	3.52	8.43	5.90 ± 2.00	1.35
Cs	3.61	4.41	3.96 ± 0.63	0.28
Dy	2.04	3.88	3.20 ± 0.96	0.59
Eu	1.30	1.47	1.38 ± 0.22	0.05
Hf	2.78	3.34	2.94 ± 0.47	0.20
La	56	67	60 ± 18	4.42
Mn	255	1 494	1 048 ± 158	505
Nd	15	21	19 ± 3	1.68
Ni	0	4.79	2.62 ± 2.33	2.05
Rb	50	59	53 ± 10	2.89
Sb	0.36	2.46	0.77 ± 0.26	0.76
Sc	9	13	11 ± 1	1.30
Sm	4.09	4.62	4.29 ± 0.53	1.63
Sr	502	615	554 ± 53	36
Ta	0.31	0.34	0.33 ± 0.11	0.01
Tb	0.55	0.76	0.66 ± 0.15	0.06
Th	6.46	7.89	7.27 ± 0.99	0.51
U	1.38	2.29	1.62 ± 0.28	0.28
V	124	385	201 ± 18	81
Zn	95	113	106 ± 13	40

[a] SD – standard deviation.

Table 5. Concentrations of some rare earth elements found in ash compared to values estimated to be in the earth's crust (all values in μg/g [9])

Element	Our values	Wedepohl [20]	Lide [8]	McGill [10]
Ce	37.1	60.0	66.5	20 to 46
Dy	3.2	3.8	5.2	4.5 to 7.5
Eu	1.4	1.3	2.0	0.14 to 1.1
La	60.1	30.0	39.0	5 to 18
Sm	4.3	5.3	7.1	4.5 to 7
Tb	0.66	0.65	1.2	0.7 to 1

igneous rock [4], it is not surprising that the concentrations of rare earth elements are overall very similar to that of crustal rock.

Although the levels of the trace elements appear to be the same when compared to soil and crustal rock, the amount of these elements entering the ecosystem is much more impressive when considering the large quantity of total volcanic ash. Table 6 shows the estimated tonnes of elements that were present in the ash from the 2010 Merapi eruption.

Conclusions

We have utilized epithermal and thermal neutrons as well as a Compton suppression system in order to find a range of elements with high precision. These elements have varied from major elements, such as Fe, to rare earth elements, such as La and Hf, and trace heavy metals, such as As and Zn. It appears that this research is the first to employ all of these methods to find trace and major elements in volcanic ash. Our quality control indicates that our results are very good.

According to our results, volcanic ash should have little to no affect on plants due to the elements we observed. The trace elements that we observed in ash are in similar concentrations in soil, and should not have toxic or undernourishing affects on plants due to these elements mixing with the soil. We also found that the concentrations of rare earth elements were similar in concentration to that found in crustal rock, which also indicates that there should be little environmental

Table 6. The total tonnes of each element present in the ash during the Merapi 2010 eruption (160 million tonnes total of ash [17])

Element	Tonnes of element in ash
As	550 ± 90
Al	$21 \times 10^6 \pm 5 \times 10^6$
Ba	82 000 ± 23 000
Ce	5 900 ± 800
Co	2 500 ± 300
Cr	940 ± 320
Cs	630 ± 100
Dy	510 ± 150
Eu	220 ± 40
Fe	$8.7 \times 10^6 \pm 0.7 \times 10^6$
Hf	470 ± 80
K	$2.7 \times 10^6 \pm 0.3 \times 10^6$
La	9 600 ± 2 900
Mn	170 000 ± 30 000
Na	$3.4 \times 10^6 \pm 0.7 \times 10^6$
Nd	3 000 ± 500
Ni	420 ± 370
Rb	8 600 ± 1 700
Sb	120 ± 40
Sc	1 700 ± 200
Si	$41 \times 10^6 \pm 5 \times 10^6$
Sm	690 ± 90
Sr	90 000 ± 8 000
Ta	53 ± 18
Tb	110 ± 20
Th	1 200 ± 200
Ti	$7.0 \times 10^5 \pm 1.6 \times 10^5$
U	370 ± 150
V	32 000 ± 3 000
Zn	17 000 ± 2 000

effect due to the massive amount of ash. Although these elements are at harmless concentrations, the sheer magnitude of each element entering the ecosystem in large volcanic eruptions of the type we have investigated is very impressive.

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