Geochemical characterization of volcanic soils from Tawau, Sabah

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Abstract— This paper discusses the geochemical characteristics of volcanic soils from Tawau, Sabah. The concentration of major elements and trace elements were determined using XRF analysis whereas mineralogical studies were carried out using XRD and SEM techniques. The results of the analyses show that SiO_2 and Al_2O_3 are abundant in volcanic soils with concentrations from 43.06% - 67.96% and 12.55% - 29.92%, respectively. The concentration of Fe_2O_3 is next in abundance with the concentration of between 6.82% and 11.29%. The concentrations of CaO, K_2O, MgO, Na_2O, P_2O_5, and TiO_2 are less than 5%. The high concentrations of SiO_2 and Al_2O_3 are due to the high abundances of vermiculite and quartz as detected from XRD, while the high concentration of Fe_2O_3 is due to the presence of geothite. The average concentrations for Ba, V, Zr and Zn in volcanic soils are 341 ppm, 315 ppm, 239 ppm, and 124 ppm, respectively. The strong correlations between Zn and Al_2O_3, Fe_2O_3 and SiO_2, indicate that Zn is being adsorbed by secondary minerals especially vermiculite and goethite.

Keywords: volcanic soil, geochemistry, trace elements, Tawau

Abstrak— Kertas kerja ini membincangkan ciri-ciri geokimia tanah vokanik dari Tawau, Sabah. Kajian kelimpahan unsur-unsur major dan unsur-unsur surih adalah menggunakan analisis XRF, manakala kajian mineralogi menggunakan teknik XRD dan SEM. Hasil analisis menunjukkan kepekatan SiO_2 dan Al_2O_3 adalah yang paling tinggi dalam tanah volkanik dengan kepekatan masing – masing di antara 43.06%-67.96% dan 12.55% -29.92% Kepekatan tertinggi yang seterusnya ialah Fe_2O_3 dengan nilai di antara 6.82% and 11.29%. Kepekatan CaO, K_2O, MgO, Na_2O, P_2O_5, dan TiO_2 adalah kurang daripada 5%. Nilai kepekatan yang tinggi pada SiO_2 dan Al_2O_3 adalah disebabkan oleh kelimpahan vermikulit dan kuarza seperti yang telah dikesan menggunakan XRD manakala nilai kepekatan yang tinggi oleh Fe_2O_3 adalah disebabkan oleh kehadiran goetit. Purata kepekatan bagi Ba, V, Zr, dan Zn masing-masing dalam tanah volkanik adalah 341 bpj, 315 bpj, 239 bpj dan 124 bpj. Korelasi yang kuat antara Zn dengan Al_2O_3, Fe_2O_3 dan SiO_2 menunjukkan bahawa Zn telah dijerap oleh mineral sekunder khususnya vermikulit dan geotit.

INTRODUCTION

Volcanic activities in Tawau involved lava flows and pyroclastics. The rocks produced by lava flows consist of basalt, andesite and dacite, while pyroclastics deposits are consisting of scoria, lapili, ashes, breccia, and tuff. The age of the volcanic rocks is from Miocene to Quaternary (Kirk, 1968; Tjia *et al*., 1992). The Pliocene volcanics occur in Mt. Magdalena, Mt. Wullersdorf, Mt. Pock, and Mt Lucia. Middle Miocene to Pliocene volcanic rocks of dacitic composition is located in Andrassy, Upper Tawau, and Tinagat (Kirk, 1968; Ueno *et al*., 1994; Takashima, 2005). Quaternary volcanics are found in Mt. Maria, Bombalai Hill, Tiger Hill and Mostyn Hill. According to Takashima *et al., (*2005) the age of volcanics and intrusive rocks in Tawau are from Middle Pleistocene to Late Pleistocene. Ueno *et al.* (1994) have described the petrology and geochemistry of major elements in volcanic rocks from this area, whereas Takashima *et al.* (2003) has made a preliminary petrological study of the Tawau volcanics. The physico–chemical properties of volcanic soils were reported by Baba Musta *et al.* (2006). No detailed study on major and trace elements of volcanic soils from this area were reported. Therefore, the objective of this study is to examine the concentration of major and trace elements in volcanics soils. The mineralogy of the volcanic soils was determined using X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques.

MATERIAL AND METHODOLOGY

Four volcanic soils samples were collected from Tawau district, at the eastern part of Sabah (Figure 1). The handspecimen of the soils are light brown to yellow reddish in colour. The study area experience tropical climate, which contributes to intense weathering resulting in very thick soil profiles. The physico-chemical properties of the soil samples are shown in Table 1 (Baba Musta *et al*., 2006). Based on the data obtained, the soil samples can be classified as clayey soils with percentage of clay in the range of 68.77% to 72.53%. The plastic limit of the soil samples is between 30.55% and 39.87%, liquid limit is from 70.47% to 99.64% and the range of plasticity index is from 39.92% to 60.16%. This indicates that plasticity index of the samples is high. The specific gravity is from 2.53 to 2.58.

The samples were air dried in open air, crushed and ground to powder form before being analysed by a X-ray fluorescence (XRF) machine. Major elements were determined using fused discs while pressure pellets were used for the trace elements determination (Norrish &

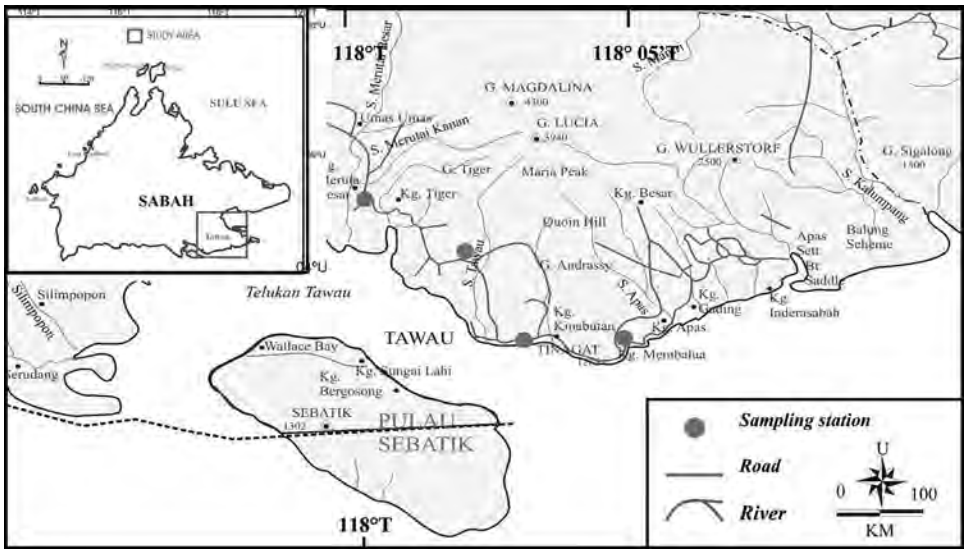

Figure 1: Map of the study area showing the location of sampling stations in Tawau district, Sabah.

Hutton, 1969). For mineralogical studies, X-ray diffraction (XRD) technique and scanning electron microscope (SEM) were employed. For XRD analyses, samples were scanned at a goniometer speed of 1° 2θ per minute. The scanning electron microscope (SEM) studies were carried out using Philips XL40 model with a pressure of 60 psi and a voltage of 15-20 kV.

RESULTS AND DISCUSSION

Mineralogy

X-ray diffraction study on the volcanic soils shows the presence of vermiculite, quartz, and goethite, with vermiculite as the most dominant mineral (Table 2). In addition to vermiculite, quartz, and goethite, illite also appears in sample VS3 with low peaks. The minerals detected by XRD appear in the SEM study (Figure 2). SEM photomicrographs indicate the presence of sub-angular quartz, layered vermiculite and goethite. The presence of pore spaces was indicated by the dark background area in the photomicrographs.

Major Elements

The concentrations of major elements in volcanic soil from four stations in Tawau district are given in Table 3. The most abundant major elements is SiO_2, which ranges from 43.05% to 67.96%. It is followed by Al_2O_3 with concentration ranges from 12.55% to 29.92% and Fe_2O_3 with concentration between 6.82% and 11.29%. Other major elements such as CaO, K_2O, MgO, Na_2O, P_2O_5 and TiO_2 show low concentrations that range from below detection limit to 1.60%.

High concentrations of SiO_2 and Al_2O_3 are contributed by clay minerals such as vermiculite and illite. The clay minerals originated from the hydrolysis of plagioclase in the volcanic rocks. Beside clay minerals, SiO_2 is also contributed by quartz. The rocks in study area are basaltic–andesitic–dacitic associated rocks, consisting mainly of of olivine, plagioclase and quarts. The concentration of Fe_2O_3 in soils indicates the presence of iron oxides particularly goethite as shown by the brown to reddish colour of the samples. The formation of iron oxide from oxidation processes is also confirmed by XRD analysis. The others elements such as CaO, K_2O, MgO, Na_2O, P_2O_5 and TiO_2 are lower than 2.00% due to leaching during the weathering process and also due to the low concentration of the elements in parents minerals. The high concentration if K_2O in VS3 samples compared to the other samples is contributed by illite minerals.

Table 1: The physico-chemical properties of volcanic soils from Tawau, Sabah (after Baba Musta *et al*., 2006).

Physico-chemical properties	VS1	VS2	VS3	VS4
Moisture Content (%)	38.61	38.09	31.99	23.23
Organic Matter (%)	4.16	2.19	2.39	6.80
pH	4.76	5.16	5.34	4.29
Liquid Limit, LL (%)	99.64	99.14	70.47	91.35
Plastic Limit, PL (%)	39.87	38.98	30.55	38.45
Plasticity Index, PI (%)	59.77	60.16	39.92	52.90
Specific Gravity, SG	2.53	2.54	2.57	2.58
Grain Size				
Clay (%)	72.53	69.62	68.77	69.04
Silt (%)	12.35	18.16	12.55	18.23
Sand (%)	15.12	12.22	18.68	12.31
Permeability, k (m/s)	$3.33x10^{-10}$	$3.16x10^{-10}$	$2.54x10^{-10}$	$2.66x10^{-10}$

Trace Elements

Table 4 shows the concentration of trace elements in soil samples. Barium (Ba) has the highest concentration, which ranges from 293 ppm to 404 ppm, followed by vanadium (V), with concentration from 246 ppm to 366 ppm. Zircon (Zr) is from 171 ppm to 299 ppm, and zinc (Zn) from 114 ppm to 132 ppm. The average concentrations

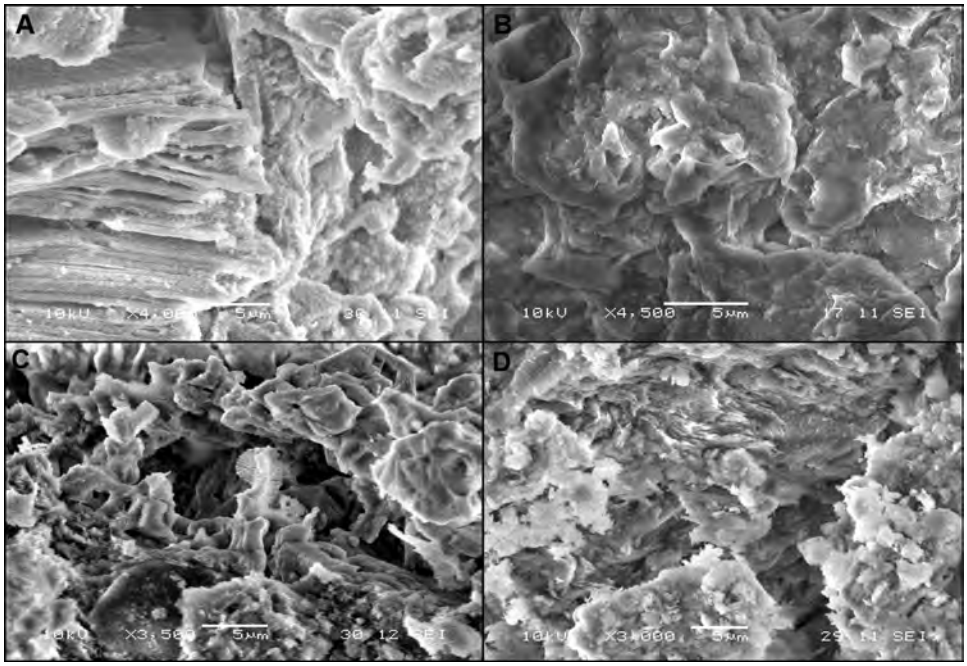

Figure 2: Scanning electron photomicrographs of volcanic soils showing (A) the layered of vermiculite minerals (B) sub-angular shapes of quartz minerals, (C) goethite in VS1 and (D) small dark spots showing the micropores within the layered structure of clay minerals.

Table 2: Minerals content in the soil sample from Tawau, Sabah using XRD.

Sample	Minerals
VS1	Vermiculite, Quartz, Goethite
VS2	Vermiculite, Quartz, Goethite
VS3	Vermiculite, Quartz, Goethite, Illite
VS4	Vermiculite, Quartz, Goethite

Table 3: Concentrations of major elements in volcanic soils from Tawau, Sabah.

Major Elements (%)	VS1	VS2	VS3	VS4
SiO_2	43.05	56.38	67.96	55.69
TiO_2	1.18	1.60	0.76	1.32
Al_2O_3	29.92	21.73	12.55	22.75
Fe_2O_3(T)	11.29	8.09	6.82	8.57
MnO	0.02	0.01	0.01	0.02
MgO	0.11	0.38	1.14	0.46
CaO	0.08	0.07	0.08	0.12
K_2O	0.05	0.29	0.44	0.12
Na_2O	0.89	1.53	0.24	1.44
P_2O_5	0.07	0.05	0.03	bdl
L.O.I.	13.34	9.87	9.97	9.49
Total	100.00	100.00	100.00	99.98

Note: bdl: below detection limit, L.O.I.: Loss On Ignition

Table 4: The concentrations of trace elements in volcanic soils from Tawau, Sabah.

Trace Elements (ppm)	VS1	VS2	VS3	VS4	Average
As	5	7	5	10	7
Ba	293	404	293	375	341
Co	66	36	34	56	48
Cr	118	134	139	93	121
Cu	88	69	55	59	68
Ni	23	17	69	10	30
Pb	24	3	3	2	8
Rb	20	43	25	28	29
Sr	21	79	33	47	45
V	337	366	309	246	315
Zn	114	128	132	122	124
Zr	202	283	171	299	239

Table 5: The coefficient of correlations between Ba, V, Zr and Zn with Al_2O_3, Fe_2O_3 and SiO_2.

	Ba	V	Zr	Zn
Al_2O_3	0.0002	0.0230	0.0827	0.8831
Fe_2O_3	0.0375	0.0254	0.0001	0.9505
SiO_2	0.0015	0.0409	0.0316	0.9037

for Ba, V, Zr and Zn in volcanic soils are 341 ppm, 315 ppm, 239 ppm, and 124 ppm, respectively. The range of chromium concentrations is from 93 ppm to 139 ppm and cobalt (Co) from 34 ppm to 66 ppm. Other trace elements such as arsenic (As), nickel (Ni), lead (Pb), rubidium (Rb), strontium (Sr) are less than 46 ppm.

The concentrations of these elements are controlled by their mobility and the leaching process during chemical weathering. The high concentration of trace elements is also due to the high concentration in the parent rocks and their adsorption into the secondary minerals. According to Baba *et al.*, (2000) the trace elements such as Cu, Zr, Ni and Zn in concretions from volcanic soil were adsorbed in the secondary minerals such as clay minerals, goethite and gibbsite. Table 5 shows the correlation between the most abundant trace elements (Ba, V, Zr and Zn) with Al_2O_3, Fe_2O_3 and SiO_2. The results indicate significant positive correlations between Zn and Al, Fe and Si, with values of correlation coefficient of 0.88, 0.96 and 0.90, respectively. This suggests that Zn is being held by the secondary minerals. Ba, V

and Zr show poor correlations with correlation coefficient values less than 0.5.

The low concentration of As, Ni, Pb, Rb, and Sr could be explained by their higher mobility in the leaching processes (Mordberg, 1993) and also due to the low concentration of these elements in parents minerals.

CONCLUSION

The geochemical study of major elements of volcanic soils shows high abundance of SiO_2, Al_2O_3 and Fe_2O_3 with concentrations ranging from 43.06%-67.96%, 12.55%-29.92% and 6.82%-11.29%, respectively. The average concentrations for Ba, V, Zr and Zn are 341 ppm, 315 ppm, 239 ppm and 124 ppm, respectively. The concentrations of the elements are controlled by the presence of secondary minerals, their mobility and the leaching processes. Scanning electron microscope and X-ray diffraction analyses show that the volcanic soils samples are mainly consisting of vermiculite, quartz and goethite.

ACKNOWLEDGEMENTS

This study was funded by the UMS research grant No. B-0202-01-PR/U028. The author would like to express special gratitude to Mr. Abdul Hamid Othman for helping in the XRF and XRD analyses. Thanks are also due to Mr. Nordin Wahid for the preparation of SEM analysis and Danny Tan Chern Han and Liew Lian Fui for soil sampling and analysis the physical properties of soils.

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Manuscript received 11 May 2007
Revised manuscript received 17 May 2008