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Composition and Distribution Patterns of Major and Trace Elements in Gradually Weathered Andesite Rock from FELDA Jengka 4, Pahang, Malaysia

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ABSTRACT The composition of selected trace elements and major elements in gradually weathered andesite rock collected from FELDA Jengka 4, Pahang were determined using XRF technique. Eleven samples consisting of concentric layers from the weathered rock (outermost layer) to the fresh rock (inner layer) were obtained. The exfoliated layer, soil and fresh rock samples were pulverized for the determination of trace and major elements. For major elements the SiO_2 was the most abundant followed by Fe_2O_3, Al_2O_3, MgO and CaO. Other elements such as TiO_2, MnO, Na_2O, K_2O and P_2O_5 were present in amounts less than 1% content by weight. The percentage of SiO_2, MgO and CaO decreased as the andesite layer gradually weathered, whereas the percentage of Fe_2O_3 and Al_2O_3 increased. In general, the concentration of trace elements in the most weathered layer was higher than their content in most fresh layer and soils. Correlation analysis showed that Co, Cr, Cu, and Pb negatively correlated at more than the 5% level of significance with MgO. Co, Cr, Cu, and Pb positively correlated at more than the 5% level of significance with Fe_2O_3 and Al_2O_3. Some of the trace elements were positively correlated with each other indicating a similar favorable condition for their enrichment. Fe and Al became enriched as weathering progressed leading to the formation of more Fe and Al oxides and hydroxides in the weathered layer.

ABSTRAK Komposisi unsur major dan surih terpilih dalam sampel batuan andesite terluluhawa daripada FELDA Jengka 4, Pahang telah ditentukan dengan teknik XRF. Sebanyak sebelas lapisan eksfoliasi daripada bahagian paling luar (paling terluluhawa) hingga kepada lapisan paling ke dalam (paling segar) telah diambil. Sampel lapisan tereksfoliasi, batuan dan tanih telah dihancurkan untuk penentuan kandungan unsur major dan surih. Bagi unsur major, kandungan SiO_2 merupakan kandungan paling melimpah diikuti oleh Fe_2O_3, Al_2O_3, MgO dan CaO. Unsur major lain seperti TiO_2, MnO, Na_2O, K_2O dan P_2O_5 mempunyai kandungan kurang daripada 1% mengikut berat. Peratusan kandungan SiO_2, MgO dan CaO menurun apabila keadaan lapisan batuan semakin terluluhawa, manakala peratusan kandungan Fe_2O_3 dan Al_2O_3 bertambah. Secara amnya, kandungan unsur surih di dalam lapisan paling terluluhawa adalah lebih tinggi berbanding kandungannya dalam lapisan paling segar dan tanih. Analisis korelasi menunjukkan Co, Cr, Cu, dan Pb mempunyai hubungan signifikan negatif pada aras melebihi 5% dengan MgO, serta mempunyai hubungan signifikan positif pada aras melebihi 5% dengan Fe_2O_3 dan Al_2O_3. Sebahagian daripada unsur surih berhubungan positif secara signifikan di antara satu sama lain menunjukkan keadaan yang sama sesuai untuk pengkayaannya. Pengkayaan Fe dan Al berlaku di dalam lapisan batuan yang semakin terluluhawa menyebabkan pembentukan lebih banyak hidroksida dan oksida Fe dan Al dalam lapisan terluluhawa.

(XRF technique, major and trace elements, exfoliated layer, andesite)

INTRODUCTION

Andesite is a dark grey, fine grained igneous rock associated with arc volcanism, found both as lava flow and in shallow dykes of intermediate composition, with aphanitic to porphyritic texture. Between the Kuantan/Temerloh area and Segamat, several occurrences of andesite (sometimes with plagioclase phenocrysts) occur. The mineral assembly was typically dominated by plagioclase plus pyroxene and/or hornblende. Biotite, quartz, magnetite and sphene were common accessory minerals, and alkaline feldspar was occasionally present in minor amounts. In Malaysia, the weathering of this rock tends to produce soil that is known as the Segamat Series. The colour of this soil is normally dark reddish brown to dark red. The soil is clay textured with subangular blocky structure and friable to very friable [1]. In the Temerloh-Maran area, this type of soil underlies oil palm plantations such as those in FELDA Jengka 4, and the rubber plantations in FELCRA Gugusan, Kg. Sentosa [2]. Ultrabasic and basic types of rock naturally contain high concentration of trace elements [3]. Thus, it may contain heavy metal concentrations that range from slightly less to much higher than the original content in the protolith. Enrichment of trace elements in the soil are characterized by the formation of mineral oxides [4], where high trace element content can be correlated significantly with the existence of concretions in soil which develop from basic and ultrabasic parent material [5]. This paper attempts to report the pattern of major elements and selected trace element enrichment in a more exclusive condition with reference to their changes in content during weathering.

EXPERIMENTAL PROCEDURE

Weathered andesite samples were collected from an outcrop at FELDA Jengka 4, Pahang (Figure 1). Eleven samples of successive exfoliation layers from fresh rock (inner layer) to weathered rock (outermost layer) were obtained by peeling the exfoliated layers. The layers were generally 5 mm in thickness. Several samples of topsoil and fresh rock found in nearby localities were also collected for comparison purposes. The exfoliated layer as well as soil and fresh rock samples were pulverised for determination of major elements such as SiO_2, Fe_2O_3, Al_2O_3, MgO, CaO, TiO_2, MnO, Na_2O, K_2O and P_2O_5, and selected trace elements of Co, Cr, Cu, Ni, Pb, and Zn.

Major and trace element contents in the rock, soil and weathered samples were analyzed using X-ray fluorescence (XRF) [6] with a Phillips PW 1480 X-ray digital instrument controlled by a Digital Software X-44 Microcomputer. Powdered samples were fused with lithium borate flux to produce buttons for the major element analysis and pressed into pellets for trace elements determination. The method for graph calibration was obtained using the Alpha on Line Program [7, 8].

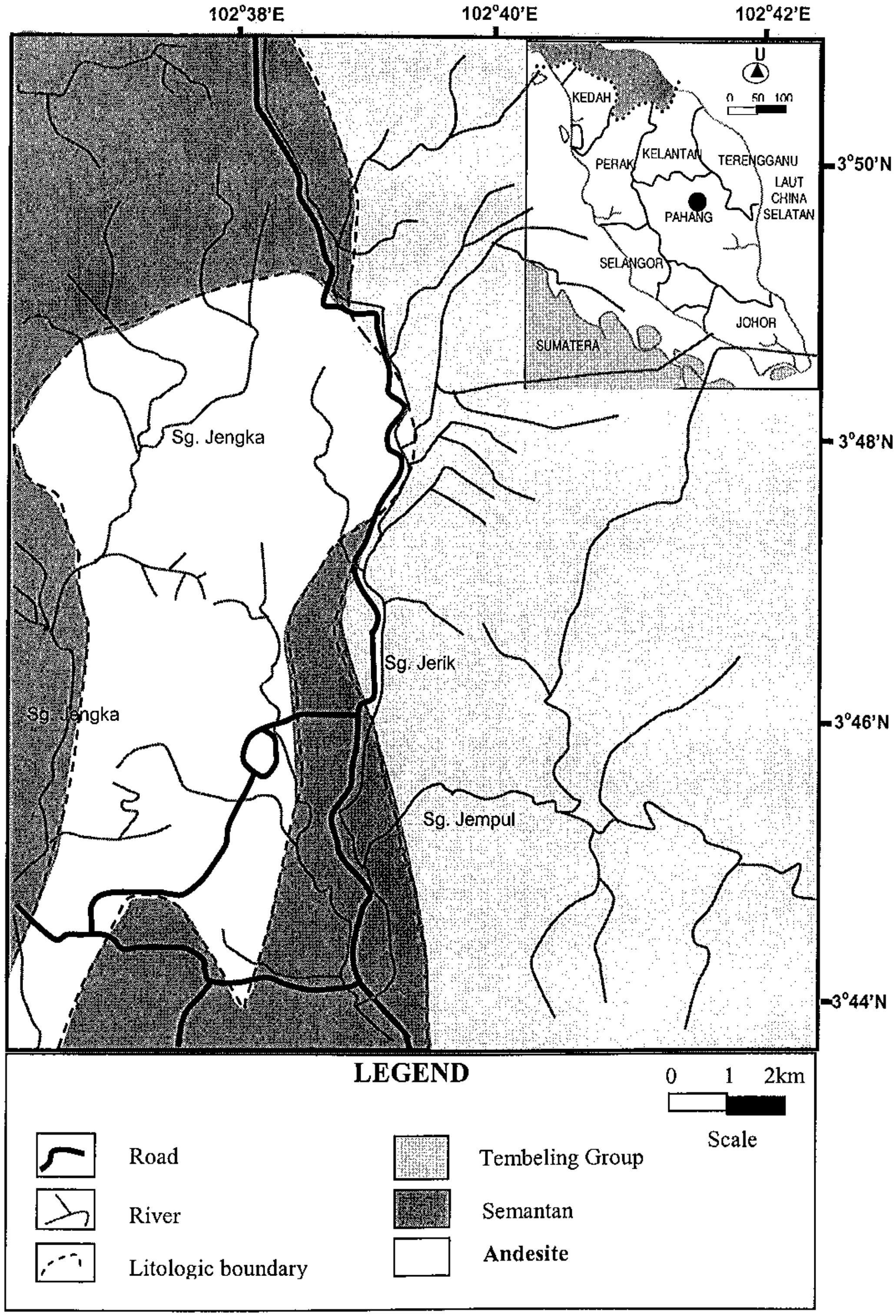

Figure 1. Geological map showing location of the study area

RESULTS AND DISCUSSIONS

Composition of Major Elements

The distribution pattern of major elements in the successive layers of andesite is shown in Figures 2a, 2b and Figures 3a, 3b. The content of major elements in the successive layers of andesite, and in samples of soil and rock around the area are presented in Tables 1 and 2.

In successive exfoliated layers of gradually degrading andesite rock, SiO_2 was found to be the most abundant, followed by Fe_2O_3, Al_2O_3, MgO and CaO. Other elements such as TiO_2, MnO, Na_2O, K_2O and P_2O_5 were present in less than 1% content by weight.

The composition of major elements in fresh andesite rocks within the study area as reported by previous researchers [9] was used for benchmarking their composition in fresh rock, whereas their composition in the iron pan samples collected from within the study area was used as the benchmark for weathered rock (Table 2).

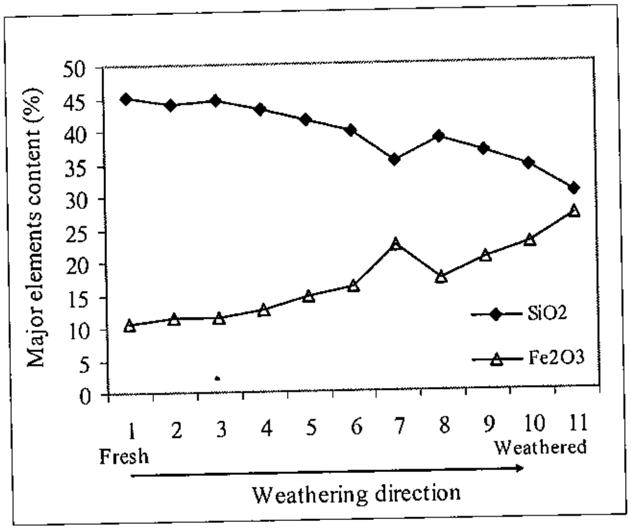

Figure 2a. Correlation between SiO_2 with Fe_2O_3

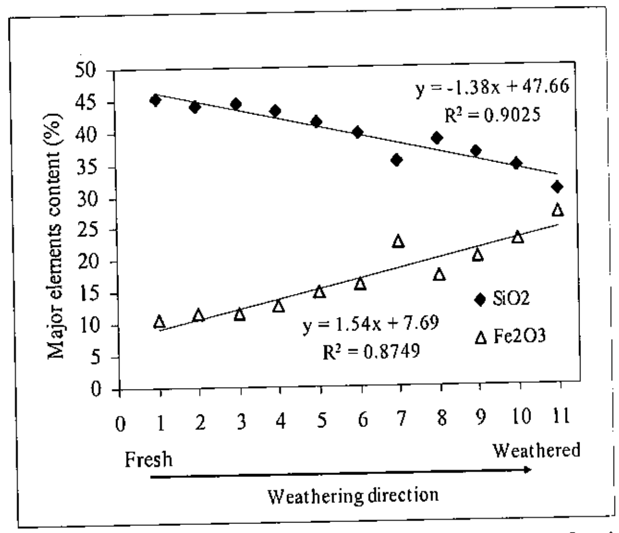

Figure 2b. Regression of SiO_2 and Fe_2O_3 in progressive weathered were rock layers

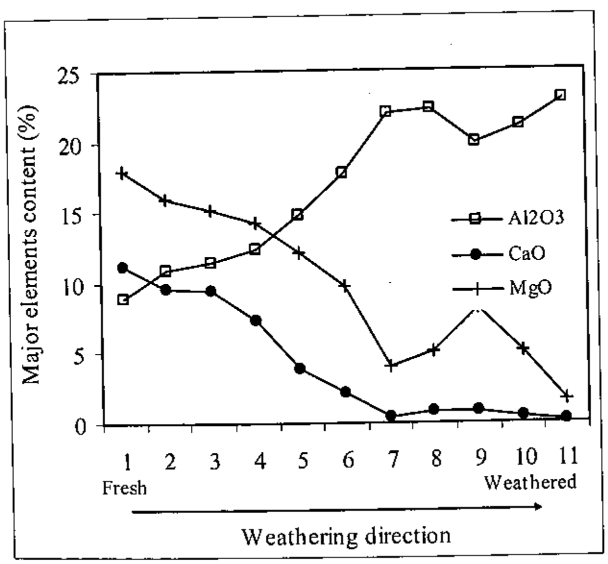

Figure 3a. Correlation of CaO and MgO with Al_2O_3

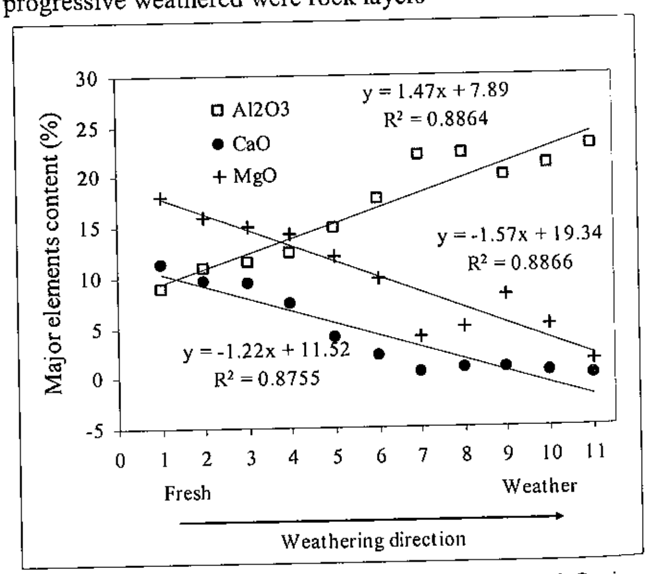

Figure 3b. Regression of CaO, MgO and Al_2O_3 in progressive weathering rock layers

Table 1. Composition of major elements in gradually degrading andesite rock

WEATHERED	←										**FRESH**
SAMPLE (LAYER)	**11**	**10**	**9**	**8**	**7**	**6**	**5**	**4**	**3**	**2**	**1**
Oxides	%	%	%	%	%	%	%	%	%	%	%
SiO_2	30.4	34.4	36.5	38.6	35.1	39.6	41.3	43.2	44.5	44.1	45.2
TiO_2	0.8	0.8	0.8	0.7	0.7	0.6	0.6	0.5	0.5	0.5	0.4
Fe_2O_3	27	22.7	20.2	17.1	22.4	16.1	14.7	12.7	11.4	11.4	10.7
Al_2O_3	22.9	21	19.8	22.2	22	17.7	14.8	12.4	11.5	10.9	8.9
MnO	0.3	0.5	0.5	0.7	0.6	0.6	0.4	0.2	0.2	0.2	0.2
CaO	0.1	0.4	0.8	0.8	0.4	2.1	3.9	7.3	9.4	9.6	11.2
MgO	1.6	5.1	8.1	5	4	9.7	12.1	14.2	15.1	16	18
Na_2O	0.9	0.9	0	0	0	0	0	0.1	0.1	0.3	0.3
K_2O	0.6	0.5	0.3	0.7	0.5	0.4	0.3	0.3	0.3	0.3	0.3
P_2O_5	0	0.1	0.1	0	0	0	0	0	0	0.1	0.1
LOI	14.4	13	12.3	13.3	13.1	12.4	10.4	8.6	6.9	6.2	4.7
Total	**98.8**	**99.2**	**99.3**	**99.1**	**98.9**	**99.3**	**98.6**	**99.5**	**99.9**	**99.4**	**100**

Table 2. Composition of major elements in gradually degrading andesite rock

	QUARRY FRESH ROCK SAMPLE (BLACK)	**QUARRY FRESH ROCK SAMPLE (GREEN)**	***ANDESITE ROCK FROM THE SAME VICINITY**	**SOFT ROCK**	**IRON PAN**	***SOIL**
	%	%	%	%	%	%
SiO_2	48.8	48.9	46.3	24.9	22.9	37.7
TiO_2	1.2	1.2	1.1	0.6	0.5	3.2
Fe_2O_3	12.3	12.3	11.9	40.9	44.0	21.7
Al_2O_3	16.1	16.1	15.7	20.2	18.8	24.1
MnO	0.1	0.1	0.2	0.1	0.2	0.2
CaO	5.9	5.9	8.3	0	0	3.8
MgO	5.6	5.6	6.4	0.6	0.5	2.2
Na_2O	4.8	4.9	3.0	0	0	3.0
K_2O	1.8	1.8	1.4	0.6	0.4	0.4
P_2O_5	0.5	0.5	0.3	0	0	0.3
LOI	3.6	2.9	5.4	12.5	12.5	3.4
Total	**100.8**	**100.2**	**100**	**100.3**	**99.8**	**100**

*Based on previously published work [9], average of five samples

Composition of SiO_2, MgO and CaO were found to decrease as the exfoliated layer becomes weathered. SiO_2 content decreased from its fresh condition at 45.2% to 30.4% at its weathered condition. This records a reduction of more than 30% of its SiO_2 fresh content as the exfoliated layer undergoes weathering. Much higher loss in terms of percentage has occurred for MgO and CaO. The loss for MgO is more than 90%, whereas the loss for CaO is 99%. Fresh layer content of SiO_2 is comparable with the SiO_2 content in the andesite rock around the study area (46.3%) reported by Gasim *et al.* [9] as shown in Table 2.

Unlike the content of SiO_2, MgO and CaO, the content of Fe_2O_3 and Al_2O_3 were found to increase as the rock layer becomes weathered. Fe_2O_3 and Al_2O_3 content increases almost threefold in the most weathered layer, which means that there is almost 300% increment in weathered layer content compared to their content in the fresh layer. This is normal because the formation of oxides and oxyhydroxide of Fe and Al are favourable during weathering.

The compositions of TiO_2, MnO, Na_2O, K_2O and P_2O_5 in the sample were less than 1 % (Figure 4). These values are low and do not have a clear distribution pattern as the andesite layer gradually degraded.

The loss on ignition (LOI) value of the samples ranged from 4.7% to 14.4%. The LOI percentage showed an increasing pattern as the successive layer of rock degraded. The LOI content in the innermost rock layer (4.7%) was slightly lower than the content of andesite rocks (5.4%) obtained from the same vicinity [9]. LOI content in the outermost layer (14.4%) was slightly higher than that in the iron pan (12.5%).

Distribution pattern and correlation among major elements

At least two forms of identifiable distribution patterns which increased and decreased were shown by major elements as successive layers of exfoliated rock degraded. The increasing pattern was shown by TiO_2, K_2O, Al_2O_3 and Fe_2O_3, whereas the decreasing pattern was shown by SiO_2, CaO, and MgO.

A significant negative correlation occurred between SiO_2 with Al_2O_3 and Fe_2O_3. The degree of correlation between the three major elements was very significant, and this indicates that primary minerals in fresh rock samples underwent weathering to produce other minerals. The high degree of significance between SiO_2 and Fe_2O_3 is indicated by the values of $r = -0.96$, $n = 11$. This is also supported by the almost symmetrical distribution pattern of SiO_2 vs Fe_2O_3 as shown in Figures 2a and 2b. Correlation analysis in Table 3 also showed that CaO and MgO were positively correlated with SiO_2 at the 1% level, indicating their mutual decrease in content as the andesite layer becames degraded. Ca and Mg which are components in pyroxene minerals were probably released during weathering together with Ca from plagioclase feldspar. In contrast, the Al_2O_3 and Fe_2O_3 were negatively correlated with SiO_2 at more than the 5% level. This means that the Al_2O_3 and Fe_2O_3 content increased as the SiO_2 content decreased.

This is a normal occurrence in weathering of rocks where most of the primary silicates found in rock are transformed into Fe or Al oxides. Musta [4] determined the mineral composition of soils and concretion developed from basic rock from Kuantan and found out that their mineral composition constituted mainly maghemite (Fe_2O_3), gibbsite ($Al(OH)_3$), magnetite (MnO), goethite ($FeO(OH)$), nacrite/kaolinite ($Al_2Si_2O_5(OH)_4$), hematite (Fe_2O_3) and anatas (TiO_2).

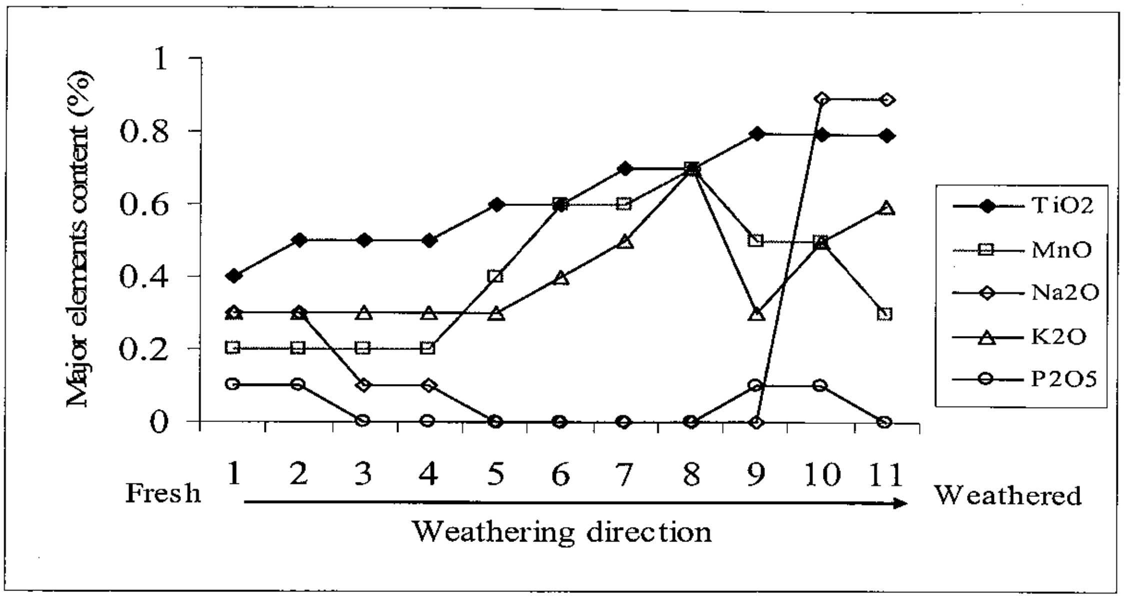

Figure 4. Contents of major elements in successive degrading layers of andesite rock

Table 3. Correlation among major elements

	SiO_2	TiO_2	Fe_2O_3	Al_2O_3	CaO	Na_2O	K_2O
SiO_2	-	-	-	-	-	-	-
TiO_2	-	-	-	-	-	-	-
Fe_2O_3	-0.96***	-	-	-	-	-	-
Al_2O_3	-0.61*	-	-	-	-	-	-
CaO	0.78**	-	-0.72**	-0.94***	1	-	-
MgO	0.72**	-	-0.78**	-0.86***	0.87***	-	-
Na_2O	-	0.88***	-	-	-	1	-
K_2O	-	0.89***	-	-	-	0.96***	1
P_2O_5	0.57*	0.84***	-	-	-	0.97***	0.91***

n = 11; r ≥0.567*, r ≥0.708**, r ≥0.823***

Trace element content

Selected trace element contents in gradually degrading andesite rock are shown in Table 4. Some soil, fresh rock, soft rock, and hardened layer of rock composition were also included (Table 5). The pattern of trace element composition in progressive weathering rock is shown diagrammatically in Figures 5a and 5b, whilst correlation among trace element and trace element with major oxides are shown in Table 6

Table 4 shows that Cr content ranged from 480 to 2157 ppm, whereas Co contents ranged from 75 to 981 ppm. Cr displayed a clear increasing pattern with the lowest content occurring in fresh rock and the highest in the outermost layer of rock. The Cr content increased gradually from the innermost layer to the outermost layer.

The concentration of Cr in the outermost layer was four times more than that in the innermost layer. The pattern of increase in Co content in successive degraded layers differed with that of Cr. The Co content showed an increase only up to the 8^{th} layer at 981 ppm then decreased to 520 ppm in the 11^{th} layer. The Co content at the outermost layer still registered a seven fold increase compared to its content in the innermost layer.

The Cu content ranged from 31 to 159 ppm. The general pattern of Cu content increased as the layers degraded. The highest concentration occurred in the outermost exfoliated layer which was five fold higher than the innermost layer. The Cu content in the inner layer was lower than the content in fresh black and green rock samples, the iron pan and in soil. The content of

Ni and Zn generally increased in the middle portion then decreased as it reached the outermost portion of the exfoliated layer. The content in the outermost layer was about twofold higher that of the innermost layer.

Table 4. Selected trace element content in gradually weathered andesite layers from Jengka 4, Pahang

WEATHERING LAYER	**11**	**10**	**9**	**8**	**7**	**6**	**5**	**4**	**3**	**2**	**1**
	Weathered	← Increased in degree of weathering									Fresh
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Co	520	694	781	981	914	864	524	210	97	104	75
Cr	2157	2154	1495	1688	1019	789	824	728	558	480	549
Cu	159	133	170	132	134	135	131	102	82	70	31
Ni	481	672	787	519	524	613	614	617	558	486	279
Pb	5	9	7	18	17	3	6	6	bdl	Bdl	bdl
Zn	106	147	223	125	168	284	302	258	198	152	53

Table 5. Selected trace element content in fresh rock, soil and iron pan

SAMPLES	**FRESH ROCK SAMPLE (BLACK)**	**FRESH ROCK SAMPLE (GREEN)**	**SOFT**	**IRON PAN > 2cm**	**IRON PAN < 2cm**	**SOIL**
Trace elements	ppm	ppm	ppm	ppm	ppm	ppm
Co	51	45	99	14	78	32
Cr	45	142	3527	4954	4993	1152
Cu	78	44	108	97	105	86
Ni	22	62	176	116	130	162
Pb	bdl	9	12	3	63	18
Zn	101	70	27	11	23	21

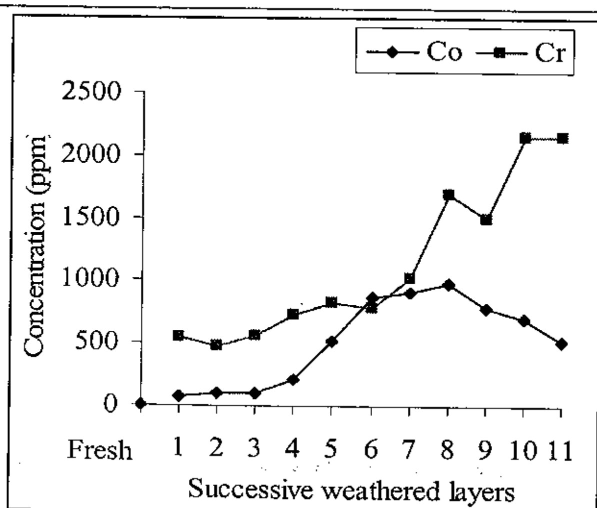

Figure 5a. Correlation between Co and Cr in degrading rock layers

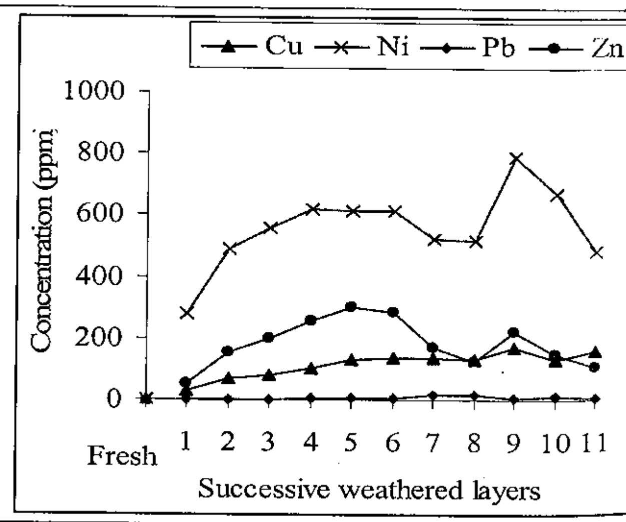

Figure 5b. Correlation between Ni and Zn, and Cu and Pb in degrading rock layers

Table 6. Correlation among trace element and trace element with major oxides

	Co	Cr	Cu	Ni	Pb	Zn
Co	1					
Cr	0.568*	1				
Cu	0.791**	0.697*	1			
Ni	-	-	0.713**	1		
Pb	0.792**	0.516	0.543		1	
Zn	-	-	-	0.687*		1
MgO	-0.804**	-0.858***	-0.834***	-	-0.729**	0.117
Fe_2O_3	0.653*	0.865***	0.797**	-	-	-
Al_2O_3	0.875***	0.839***	0.867***	-	0.764**	-0.058

n = 11; r ≥0.567*, r ≥0.708**, r ≥0.823***

There was positive significant correlation at the 5% level of significance between Cu and Pb with Co, Cu with Cr, Cu with Ni, and Ni with Zn. Negative significant correlation at the 1% level of significance occurred between Co, Cr, Cu and Pb with MgO. Positive significant correlation at 5% level of significant occurs between Co, Cr, Cu and Pb with Fe_2O_3 and Al_2O_3. This could indicate that in the case of Co, Cr, Cu and Pb, enrichment in successively exfoliated layers were strongly related to .Fe_2O_3 and Al_2O_3 formation, whilst MgO content would decrease in successive exfoliated layers.

The work by Musta [4] on soil profile developed from basic rock around Kuantan showed a similar decreasing and increasing pattern. However most of the profile showed a decreasing pattern towards the top. XRD analysis on concretions formed in this soil showed that their content were mostly gibbsite ($Al(OH)_3$), geothite ($FeO(OH)$) and hematite (Fe_2O_3) with some kaolinite [4]. Hardened rock samples (concretion) that were analysed (Table 5) showed a more concentrated Cr content as compared to other trace elements. The content of trace elements in fresh rock also seemed to be of lower concentration than that in the weathered exfoliated layer [10]. This means that the enrichment of trace elements in the soil may occur and the types of trace element concentration is influenced very much by factors inherent in the environment. Factors such as pH, organic matter and clay content, redox potential, and cation exchange capacity may contribute to trace element enrichment and mobility of the soil.

CONCLUSION

Trace element content in soil developed from andesite may be enriched if the environmental factors favour the formation of oxides and oxyhydroxides. Enrichment of trace elements is more localised depending on environmental factors.

There was a clear pattern in the distribution of major elements in the gradually degrading layers of andesite.

The contents of major elements such as SiO_2, MgO and CaO decreased as the rock degraded whereas the Al_2O_3 and Fe_2O_3 contents increased.

Very significant negative correlation seen between Al_2O_3 and Fe_2O_3 with SiO_2 indicated that weathering of SiO_2 resulted in the formation of more Al_2O_3 and Fe_2O_3. This occurrence was very clearly shown in the Figures 2 and 3.

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