

Variation of Chemical Elements and their Associations in Laterite Soil Profile

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ABSTRACT

The objective of this study was to evaluate the variations of twelve chemical elements (Ni, Fe, Co, Mg, Mn, Al, Si, Zn, Ti, P, Ca and Cr) in laterite soil profiles from Wantulasi area in South East Sulawesi Province of Indonesia. Eighty four (84) samples of three profiles (*i.e.* each profile consists of eight samples) had been used to study their variations in soil using the X-Ray Fluorescence (XRF). Results analysis of the chemical elements content in three profile using XRF indicated that there were good correlations between the chemical elements in the soil profile with the significant correlations were found in Ni and Fe, Ni and Si, Ti and P, Fe and Al, and Co and Mn, respectively. On the other hand, the results of study showed that the variations of the chemical elements could be related to the enrichment and translocation of the elements in soil profile and also their possibilities to be related with a given chemical elements in soil profile. Therefore, we suggest that the observed patterns in chemical elements with a good correlation in laterite profile can be used as proxies to integrate the evaluation of the chemical and physical weathering process based on the elements characteristics in soil profiles.

Keywords: Chemical distribution in soil profile, weathering process, X-Ray Fluorescence

INTRODUCTION

Understanding the content of chemical elements and their variation in laterite soil is the most important case since they are related to the chemical weathering of parent rock that change the primary minerals in rock (Munroe *et al.* 2007; Jianwu *et al.* 2014; Calagari *et al.* 2015). The elements variation in soil sometime express the interaction between elements from chemical weathering process and their interactions with the elements derived from plant (Mukhomorov *et al.* 2011; Zhang *et al.* 2013), the trace of element entering the plant (Narwal *et al.* 2013) as well as its influences to the soil properties (Lebow *et al.* 2006) that are related to the reduction of certain elements (Munroe *et al.* 2007). In hillslope area, degradation of soil causes the changes of distribution of chemical elements (Petrovsky *et al.* 2006) which implicate to the reduction of the quality of soil *i.e.* decreasing of nutrient content (Mupenzi *et al.* 2011), plant growth (Mukhomorov and Anikina 2011), unbalance between soil denudation and soil production (Suresh

and Huh 2014), as well as geotechnical properties for engineering projects (Adebisi *et al.* 2013). On the other hand, understanding the association between chemical elements in soil can lead to the lower cost of chemical analysis. In many studies, it has been performed that the variation of the chemical elements in soil and their distributions related to pedogenic history (Jelenska *et al.* 2008; Safiuddin *et al.* 2011; Bijaksana *et al.* 2013; Maniyunda *et al.* 2015) that are controlled by the climate (Munroe *et al.* 2007), and their development is also often associated with the economical-valued chemical elements such as Ni, Co, and Mn (Yongue *et al.* 2006) at limonite and saprolite layers. One potentially important pattern of variation in laterite soil profile that is not yet well understood is how the correlation between the chemical-elements content in laterite soil profile and their possibilities of formulation between elements.

The objective of this study was to assess the variation of the chemical elements content in three soil profile, and their possibilities of associations, as well as their possible formulations between combination of elements in laterite soil profile. This information in soil profile is crucial part of understanding since they are related to the pedogenic

and lithogenic processes. Improving the understanding of variation both of them, therefore, will provide useful information for soil management and expand our ability to model the processes involved in the soil development.

MATERIALS AND METHODS

Study Site

The study site was located in the Wantulasi Labuantobelo, southeast arm of the Sulawesi island, Indonesia (Figure 1). The samples were taken at the hillslope area on the three different profile (with geographic position *i.e.* 04 24 57.29"S 122 58'32.45"E" for profile P, 04 24' 57.05"S 122 58'32.21"E for profile Q and 04 24' 56.99" S 122 58'32.05"E for profile Q). Geologically, this area located in an ophiolite complex consisted of harzburgite, dunite, serpentinite, and werlite (Surono

and Hartono 2013). Soil in the study area is red soil and rich in sesquioxides or called Oxisols according to the basic system of soil classification (Soil Survey Staff 2010).

Sample Collection and Soil Chemical Analysis

Soil samples from three different soil profiles (*i.e.* profile P, Q and R) at the hillslope area were collected vertically at interval of 30 cm from surface (0 cm) to the bottom (*i.e.* 180 cm), and also their rock samples at the position of >180 cm (this is depending on the existing of the rock in each profile (Figure 2). Soil samples and rocks were taken from each profile placed in the plastic bag then labeled P for higher profile 1, Q for profile 2 and R for profile 3.

In this study, the content of chemical elements in the samples were analyzed using XRF Spectrometry. Chemical analysis was performed by Kendari Assay Laboratory (PT IOL Indonesia) on 21 soil samples and 3 rock sample (<2-mm) and on

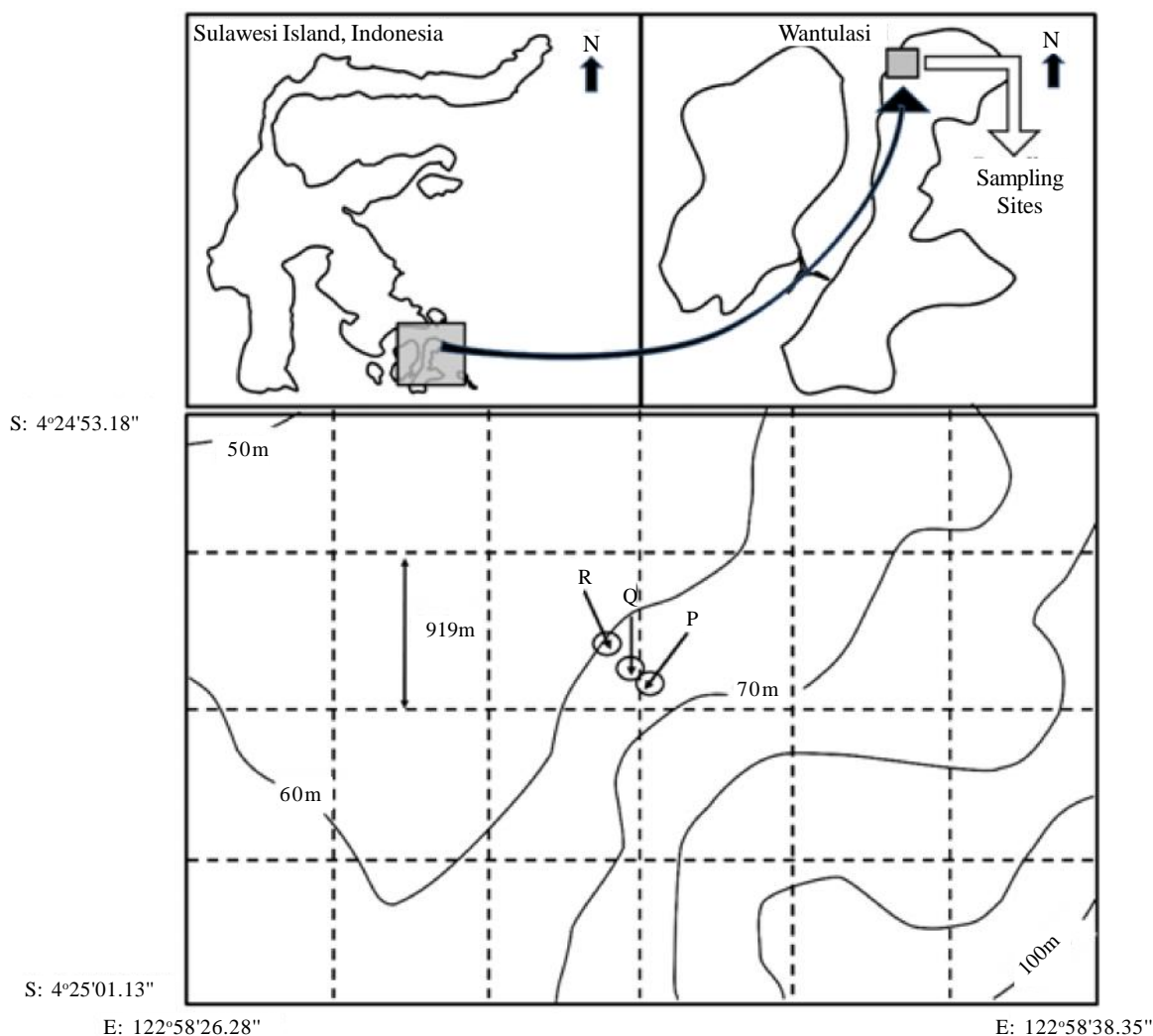


Figure 1. Schematic map of the sampling site in Wantulasi area, southeast arm of Sulawesi island, Indonesia. Sampling sites within the study area for each profile (P, Q and R, respectively) are marked with the circle and the distance between the profile is 16 m and 18 m, respectively.

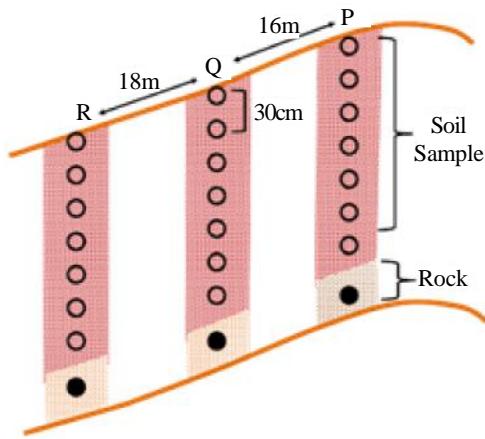


Figure 2. Schematic representation of the sampling site in soil profile. The hollow circles are the sampling site of the soil and solid circles are sampling site of the rock in the profile.

sand, silt and clay size (200 mesh) fractionated samples using XRF Spectrometry, Advant “Xp” type reported as percent weight. Percent weight of major elements as oxides was determined based on comparison with a certified standard reference material (SY-4, Canadian Certified Reference Material Project) and organic-C was estimated based on weight loss on ignition at 1,010 °C. Samples were analyzed for the

following 12 elements: Al, Co, Mn, Ti, P, Mg, Cr, Zn, Ca, Ni, Fe, and Si

Evaluation of Trend and Statistical Analysis

The content of the twelve chemical elements (*i.e.* Al, Co, Mn, Ti, P, Mg, Cr, Zn, Ca, Ni, Fe and Si) in each profile was plotted as function of depth and used to assess the trend of data. The similar trends were selected to regression analysis using the linear trendline analysis in Microsoft Excel to perform R-square value and its equation on chart, and also its correlation coefficient between the pair of element for all above elements and it were displayed in the table. Thus, the combination and ratio between the elements with similar trend were also plotted to evaluating the shifting of the trend due to the combination and also its relation with the mobility of elements that may also being related to assess the degree of weathering of soil.

RESULTS AND DISCUSSION

Figure 3 shows the variation of the chemical elements content (Al, Co, Mn, Ti, P, Mg, Cr, Zn and Ca) in the three soil profiles. As shown in the figure, elements content of Al, Co, Mn, Ti and P have a tendency of similar trend in all profiles, while the

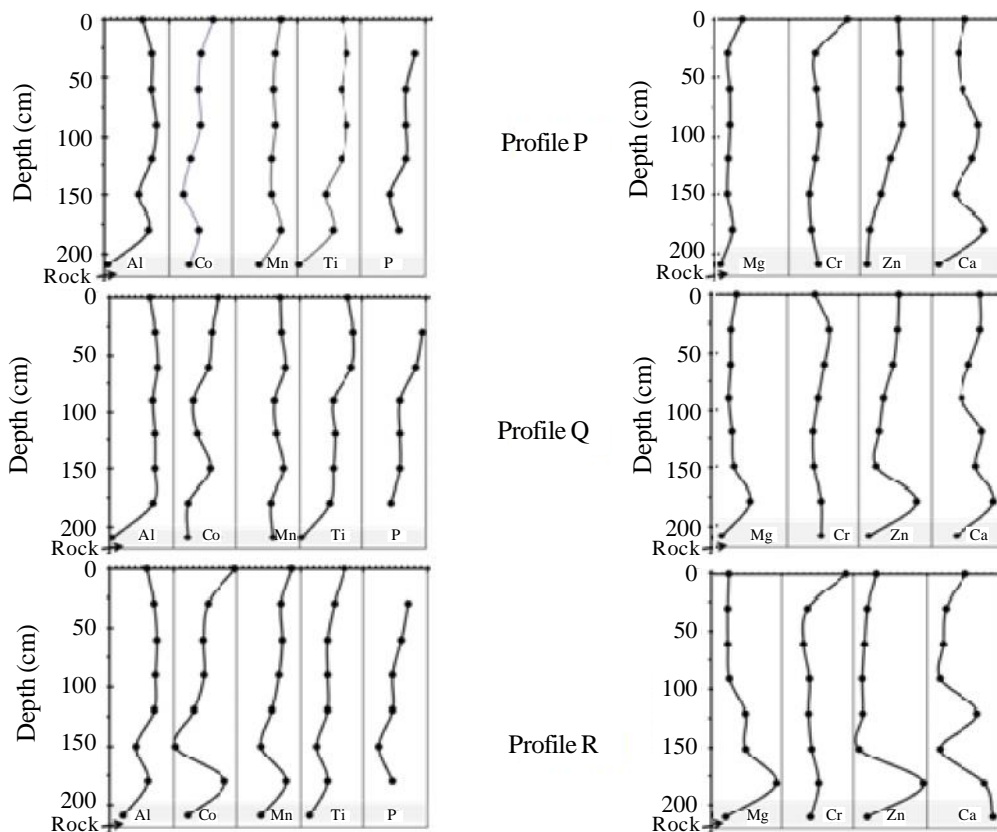


Figure 3. The trend of variations of the chemical elements (Al, Co, Mn, Ti, P, Mg, Cr, Zn, and Ca) in relation to the depth for Profile-P, Profile-Q and Profile-R.

other elements content such as Al, Mg, Cr, Zn, and Ca have unsimilar trend in all profiles. The similar trend of these variations may represent their tendencies to associate in soil like shown between Co and Mn and also between Ti and P. These tendencies of similar trend may express the similar mobility of these elements to respond the external factors.

Figure 4 shows the variation of the chemical-elements content (Ni, Fe, and Si) in all profiles. As shown in the figure, all profiles show the same variation of Ni, Fe, and Si with the depth. The maximum percentage of elements of Ni and Fe are located to depth of 90 cm for profile P and to depth

of 180 cm for profile Q and R. While the minimum percentage are located on the depth of 210 cm (rock) for all profile expressing the significant consistency of these elements in their variations in laterite soil. These similar trends in variations may be caused by the similar type, direction and degree of pedogenesis (Maniyunda et al. 2015) of these soil profiles. On the other hand, the contrasting variation is shown by the element of Si compared to the elements of Ni and Fe. It means that the increasing of Si expresses the decreasing of Ni and Fe. These results indicate that the increasing of Fe and decreasing of Si may be caused by the leaching of Si that change the distribution of elements in the

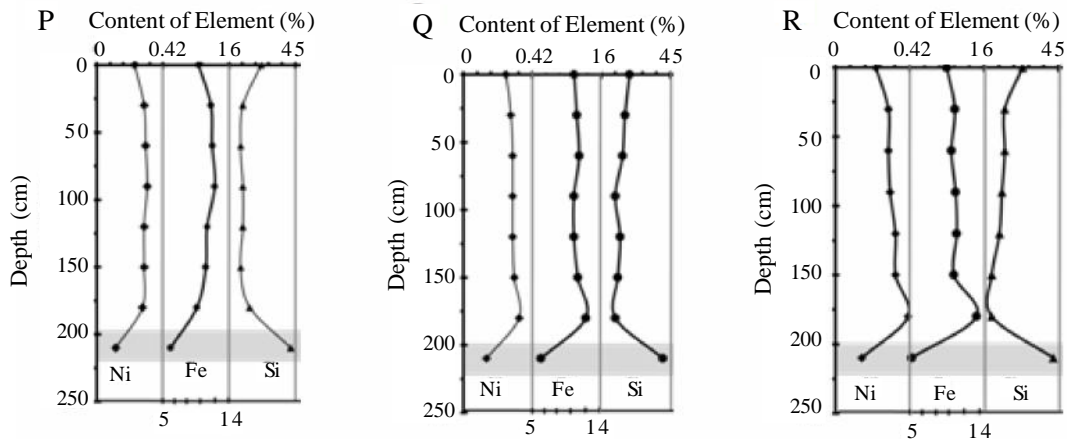


Figure 4. The trend of variations of the chemical elements (Ni, Fe, and Si) with respect to depth for the Profile-P (left), Profile-Q (center), and Profile R (right).

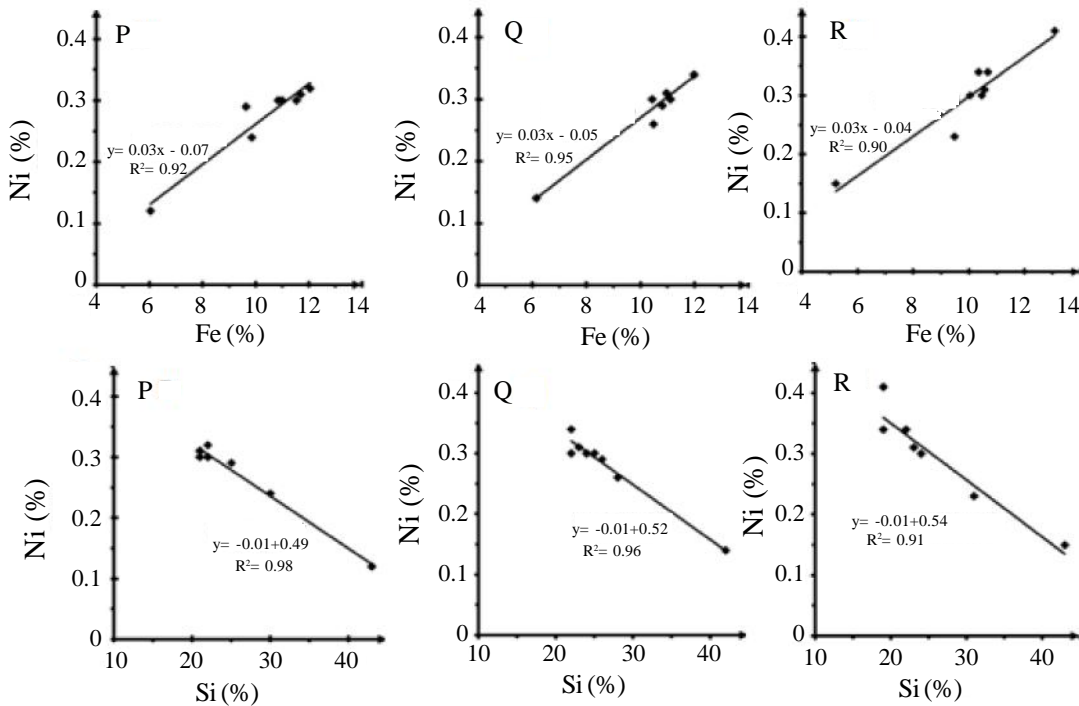


Figure 5. The relationship between the percentage of Ni vs Si (top), and Ni vs Si (down) for three soil profiles, i.e. P (left), Q (center), and R (right), respectively.

soil profile. On the other hand, variations of Ni or Fe compared to Al (Figure 3) also show similar variation indicating that the increasing the contents of Ni or Fe is followed by the increasing the content of Al in laterite soils.

Figure 5 shows the relationship between percentage of Ni and Fe, as well as between Ni and Si in the profile of P (left), Q (center) and R (right). As shown in the figure, the linear trend of Ni vs Fe and Ni vs Si were performed by their determination coefficients (R^2), at which both Ni vs Fe and Ni vs Si have the coefficient of determination (R^2) of > 0.9 . This means that these elements have a strong association in laterite soil profile. On the other hand, the strong correlation were also performed between the elements of Co and Mn and/or Fe and Al with the coefficient of correlation of $r = 0.85$ (Table 1). This means that the presence of Co, Mn and Al were also associated with the Ni, Fe, Si. These results indicated that the presence of

Ni, Fe, Co, Mn and Al in laterite soil profile are controlled by Si. A strong correlation between the elements in soil profile would indicate the strong association due to the similar transport, accumulation, and source (Acosta *et al.* 2011; Navas *et al.* 2014). In other words, the decreasing of Si expresses the increasing of Ni and Fe.

To assess whether the high linear correlation between Ni and Fe or Ni and Si at each profile were also found for the three combination of profile, we conducted it as shown in Figure 6. As shown in the figure, the strong linear trend or high correlations are expressed by the determination coefficients (e.g. $R^2 = 0.86$ for Ni vs Fe and $R^2 = 0.92$ for Ni vs Si) indicating the similar response of the two elements in soil, eventhough the three profiles were located in the hillslope area with different positions. On the other hand, the high correlation for all samples of the profile were also performed between Ti and P ($R^2 = 0.87$) indicating the interactions of the elements

Table 1. The correlation coefficient between the pairs of elements in the samples of twenty four samples taken from three laterite soil profiles.

	Ni	Co	Mg	Mn	Fe	Cr	Al	Si	Zn	Ca	Ti	P
Ni	1	0,14	0,61	0,34	0,93	-0,19	0,78	-0,96	0,44	0,20	0,58	0,19
Co		1	0,22	0,85	0,31	0,58	0,38	-0,08	0,42	0,21	0,02	-0,18
Mg			1	0,12	0,45	0,18	0,17	-0,41	0,45	0,37	-0,07	-0,34
Mn				1	0,50	0,40	0,60	-0,33	0,36	0,16	0,31	0,06
Fe					1	-0,05	0,85	-0,93	0,62	0,18	0,64	0,31
Cr						1	-0,07	0,23	0,28	0,12	-0,24	-0,32
Al							1	-0,82	0,38	0,23	0,72	0,65
Si								1	-0,35	-0,05	-0,62	-0,30
Zn									1	0,49	0,36	0,12
Ca										1	0,13	-0,03
Ti											1	0,93
P												1

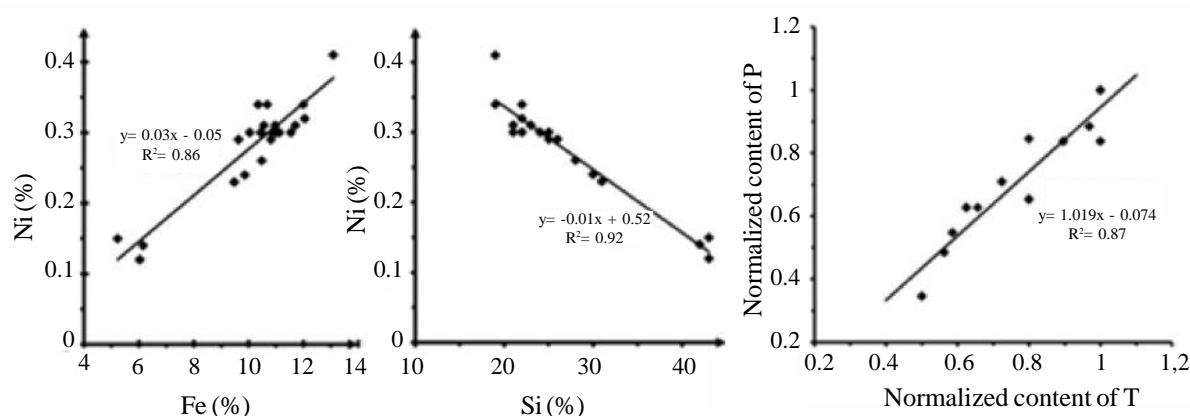


Figure 6. The relationship between elements content of Ni vs Fe (left), Ni vs Si (center) and P vs Ti (right) for the whole samples in three soil profiles.

of Ti (inherited from the rock weathering) and P (originated from plant) in the laterite soil profile. Eventhough the very strong variation of elements in space is generally founded in the hill slope soils (Mudd *et al.* 2006), the similar variations in soil profile expressed the strong association of these elements in soil. These results suggested that the increasing of Fe can be used as a marker on the increasing of Ni and the decreasing of Si. Moreover, the high association between Ti and P as well as Fe and Ni, but it is not followed by the high association between Ni and P, it might be linked to the role of Ni in decreasing the degree of the soil fertility on laterite soil.

Figure 7 shows the variations of Ni, (Fe/Si) and (Fe+Al)/ Si for each profile (*i.e.* P, Q, and R). As

shown in the figure, all profiles show the same variation of Ni with the depth and the distribution of the percentage of Fe/Si is very similar to that of Ni (Figure 7). The same variations are also performed by (Fe+Al)/ Si and its variation become more similar to the Ni compared to the Fe/Si indicating that the presence of Ni is also controlled by the Al.

Figure 8 shows the relationship between variables of Ni vs Fe/Si , Ni vs (Fe+Al)/Si . As shown in the figure, the relations between that variables are highly correlated, with the higher correlations are performed by relation of Ni vs (Fe+Al)/Si. These linear correlations may also express the relation of these variables in soils which related to the degree of weathering of soil. Although several soil samples

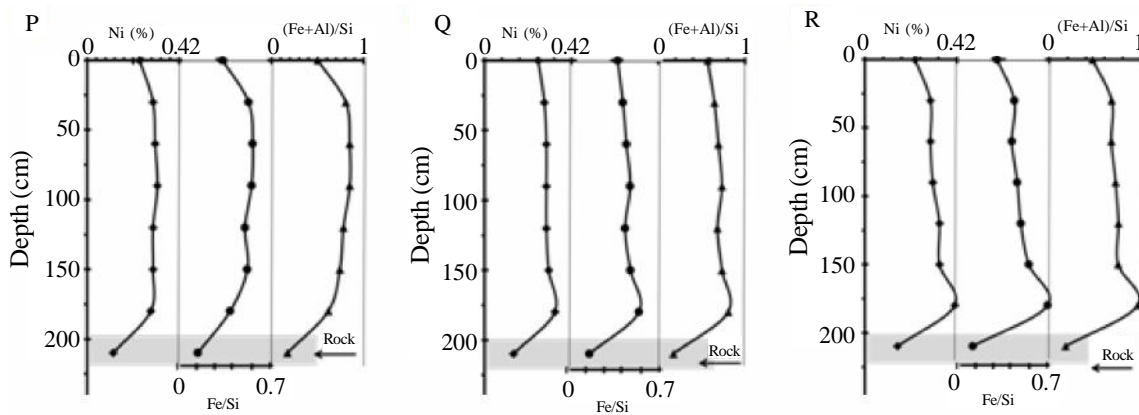


Figure 7. The trend of variation of Ni, Fe/Si and (Fe+Al)/Si in the profile of P (left), Q (Center) and R (right)

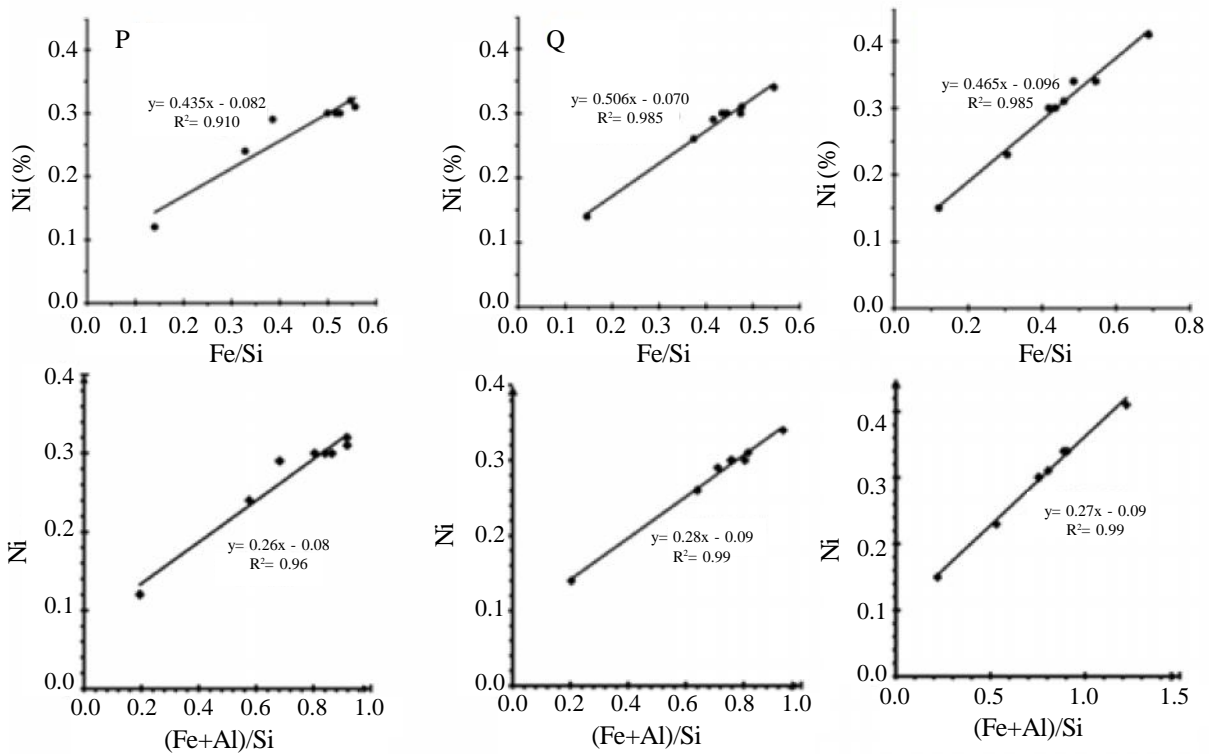


Figure 8. Comparison of the relationship between Ni vs Fe/Si and Ni vs (Fe+Al)/Si for profile P, Q, and R, respectively.

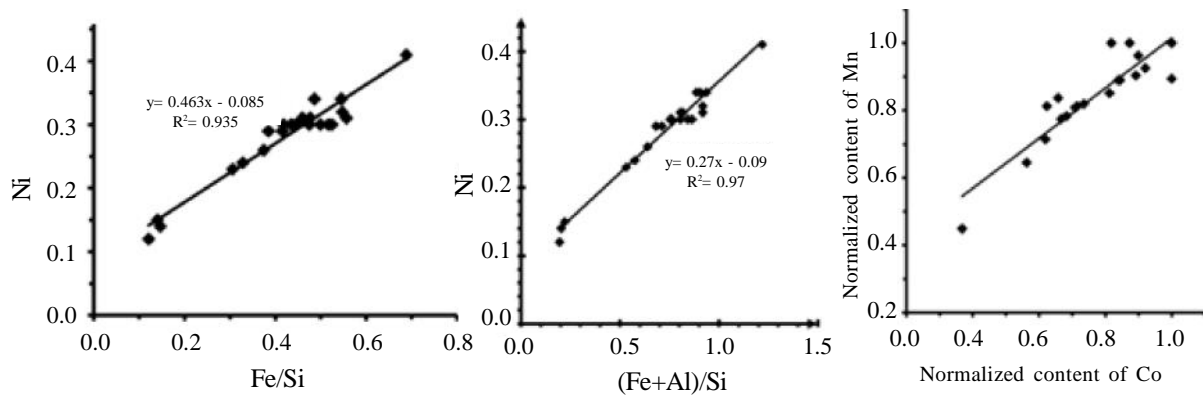


Figure 9. Comparison of the relationship between Ni vs Fe/Si and Ni vs. (Fe+Al)/Si for 24 samples taken from all the soil profiles.

performed the correlation between the chemical elements, the obtained results are still needed to be tested in the other samples. These result also showed the increasing determination coefficients from relation Ni vs Fe/Si to Ni vs. (Fe+Al)/Si in each profile and also in combination of all profiles (Figure 9) indicating that these formulation may also can be related to the history of the transport or accumulation that taken place in laterite soil, since both Fe and Al as well as Ni are mobile elements during extreme chemical weathering in the tropical region (Jianwu *et al.* 2014).

The similar trend and strong correlations between element of Ni with respect to Fe/Si or with (Fe+Al)/Si, may also express the characteristic of these elements (Ni, Fe, Si, and Al) in hillslope area that always associated strongly in laterite soil. Eventhough the positions of profile are different in the hillslope area that indicate the possibility the different amount of water infiltrating that influence of the precipitation of Fe or other elements during weathering process (Mudd *et al.* 2006), the observed pattern is within profile may also express the leaching process and chemical denudation in laterite soil. Further work is needed to explain the observed patterns in control soil and to identify specific mechanisms by which altered weathering conditions.

CONCLUSIONS

This study provides information that there were good correlations between elements in laterite soil profile at which the good positive correlations were found for relationship between Ni vs Fe, Ni vs Al, Fe vs Al, Mn vs Co and Ti vs P and good negative correlations were found for Ni vs Si. On the other hand, our findings from identification of the variation between Ni and Fe/S as well as

between Ni vs. (Fe+Al)/Si, performed a high linear correlation indicating that presence of these elements (Ni, Fe, Al, and Si) express a similar response in weathering processes but the parameters may also can be used as a marker to differentiate all the studied profile.

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