



Element Mobilization During Weathering Process of Ultramafic Complex in North Konawe Regency, Southeast Sulawesi Based on A Profile from Asera

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Abstract - The North Konawe Regency, located in the northern part of the southeast arm of Sulawesi Province, is occupied mainly by Ophiolite Complex. Recent studies on weathering of ultramafic complex have been focussed on the composition of laterite in relation to heavy metal explorations. In Asera area, North Konawe, a 3.1 m wide outcrop of ultramafic rocks is related to nickel laterite potential. In this study, an elemental change during the weathering process is discussed, including the mobilization of rare earth elements. XRF and ICP-MS from The Centre for Geological Survey of Indonesia are the two important geochemistry instruments used in this study. Si, Mg, and Ca are depleted during weathering, whilst the enriched elements are Fe, Al, Ti, and some heavy metals such as Cr, Mn, and Co. A different mobilization pattern is detected on Ni, because of its relation to Mg. Cs, Rb, and Ba are concentrated in a clayey horizon of upper laterite. The increase of REE concentrations is parallel to both Fe and Mn which rises to the top of laterite. Ce and Eu negative anomaly trends indicate oxidizing condition through the weathering process, although the studied profile, influenced by allochthon material, morphology condition, and geochemistry composition, indicates that the transported rock fragments were originated from ultramafic rock.

Keywords: North Konawe, ultramafic, weathering, element mobilization

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INTRODUCTION

Ultramafic rock in Southeast Sulawesi, Indonesia, is cross-cut by Lasolo Fault into two geological provinces: Tinondo and Hialu. Ultramafic rock in contact with sediments is detected at Hialu path on the southwest, whilst its contiguity to metamorphic rock is characterized at Tinondo path on the northeast (Tonggiroh *et al.*, 2017). Tinondo Geological Province is largely occupied by Ophiolite Complex in the northern part of southeast arm of Sulawesi. The province is located on the equator of an altitude below 1,000 m with the tropical climate.

The range of the average temperature is 30° - 36°C (maximum) and 20° - 23°C (minimum) with the annual rainfall exceeded 1,500 mm³ in 2012 (Badan Pusat Statistik, 2013). Most of the North Konawe Regency area, located in Southeast Sulawesi Province, comprises Early Cretaceous Ophiolite Complex. Nickel commodity in the North Konawe is classified as a national strategic resource and part of Sorowako National Strategic Area together with South Konawe Regency (Nurhasanah *et al.*, 2013).

Chemical weathering/lateritization of the rocks is the most important process that changes the chemical composition of the earth surface

causing the geochemical redistribution of elements. Primary minerals can be decomposed by chemical weathering and resulted in a different composition of weathering products to the parent rocks (Jianwu *et al.*, 2014). Topography, parental rock type, climate conditions, mineral stability, pH, plant, and biological activities are factors that control geochemical redistribution (Purwanto and Agustini, 2014; Calagari *et al.*, 2015). These factors influence the genesis of soils and chemical composition of sediments. Chemical compositions of the sediments and soils have been used effectively to evaluate weathering and soil formation conditions to trace the provenance of sediments and soils leading to the reconstruction of paleoclimate records (Jianwu *et al.*, 2014). Moreover, pathfinder elements of Bi, Sn, Mo, In, Sb, As, Cu, and Au in weathering layers can more specifically be used for locating base-metal deposits than the target of elements, Cu, Pb, and Zn at the Gossan Hill Deposit, Golden Grove, Western Australia (Cornelius *et al.*, 2001). During weathering, some elements become leached (*e.g.* Mg, Ca, and Si), and others either secondarily enriched (*e.g.* Ni, Mn, Co, Zn, and Y) or residually concentrated (*e.g.* Fe, Cr, Al, Ti, and Zr) within profiles (Sagapoa *et al.*, 2011).

Nickel laterites are regolith materials derived from ultramafic rocks containing economically exploitable reserves of nickel. The nickel laterite deposits are found over ultramafic rock outcrop that developed on olivine-bearing ultramafic rocks, mainly dunite, olivine-pyroxene peridotite, and their serpentinized equivalents. Approximately 40% of world annual Ni production was produced from this kind of deposit (Sagapoa *et al.*, 2011) which developed because of chemical weathering of the ultramafic rocks. A negative correlation of SiO₂ and MgO to Fe in Pakal Island, North Maluku Province, is a key factor on determining the degree of nickel laterite development (Purwanto and Agustini, 2014).

The current work is related to chemical weathering of ultramafic rock from Asera region, North Konawe Regency. The geochemical composition in a profile of weathered layers of ultramafic rock is to be discussed, including the mobilization of

heavy metals such as Ni, Co, and Mg. Moreover, even rare earth elements are not normally based on ultramafic rocks. The compositional change in relation to weathering is worth to be discussed. The element distribution in the profile is drawn in graphics to simply understand about its mobilization. This study is part of ultramafic laterite project of The Centre for Geological Survey of Indonesia in 2014.

Regional Geology

Southeast Sulawesi region is cross-cut by a number of large faults striking NW±SE: *i.e.* Lasolo, Matano, Kolono, and Kolaka Faults (Charlton, 2000). The studied area is located in Lasusua-Kendari Quadrangle (Rusmana *et al.*, 1993), and can be distinguished into two geological provinces separated by Lasolo Fault, Tinondo, and Hialu. The Tinondo Geological Province is characterized by continental shelf deposits, whilst Hialu is occupied by oceanic crust deposits (Syafrizal *et al.*, 2011). Meluhu Formation and Tokala Formation are the two oldest metasedimentary rock units distributed in the southern part of Lasusua-Kendari Quadrangle. Both of the Triassic rock formations are included into Hialu Geological Province. This study focused on the Tinondo Geological Province occupied by Ophiolite Complex in North Konawe Regency (Figure 1). The studied Ophiolite Complex is considered to be emplaced in Early Cretaceous. Rusmana *et al.* (1993) stated that the ultramafic group ranged in composition from peridotite, harzburgite, dunite, gabbro, and serpentinite. Late Cretaceous Matano Formation unconformably overlies the ultramafic rocks, and it is composed of calcilutite with shale and chert intercalations. Oligocene Salodik Formation, which comprises calcilutite and oolitic limestone, is distributed in Tampakura Mountains, north-eastern of the quadrangle. Conglomerate, sandstone, and claystone built Pandua Formation as part of Sulawesi Molasse Deposits.

Some studies have been conducted in Lusuua-Kendari Quadrangle in relation to its nickel resource. Rوتا, Mandiodo, Laronaga, Amesi, and Tapunopaka are Ni laterite prospective locations with nickel content is over 1.5% (Moe'tamar,

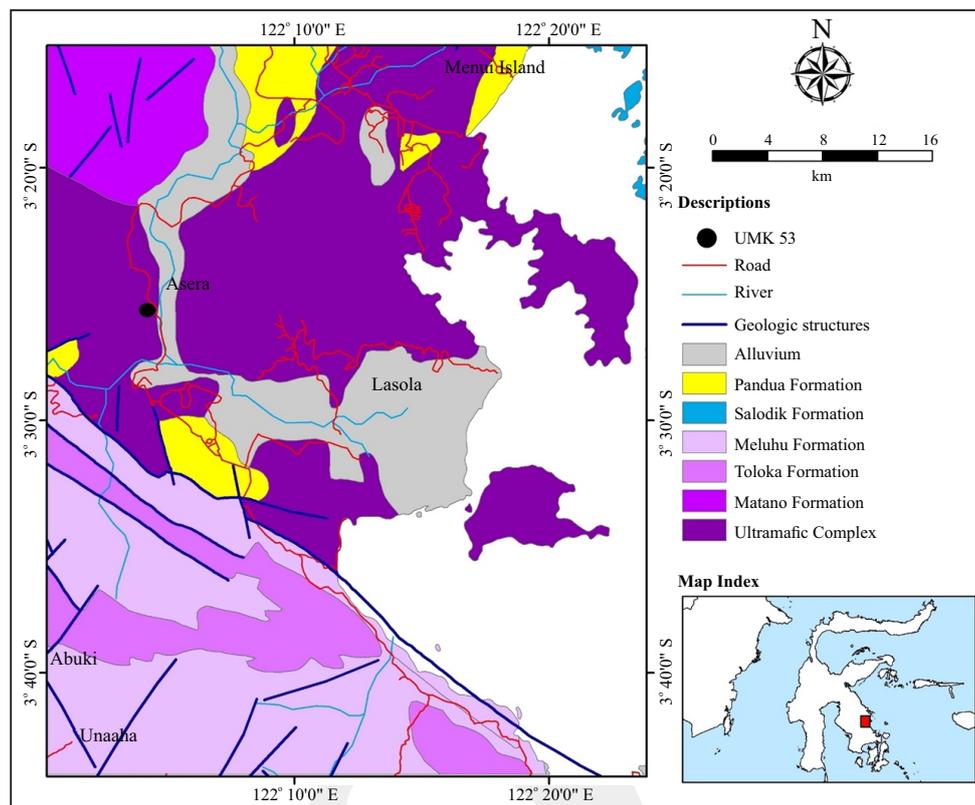


Figure 1. Geological map of the researched area in North Konawe Regency (modified from Rusmana *et al.*, 1993).

2007). Fe and Cr mobilities are higher than Ni and Co ones because of the formation of ferrochrome compound in settling ponds post laterite nickel mining study in Motui (Chaerul *et al.*, 2015), and it strongly influences environmental disturbances in the area. Soil and fertilizer management based on soil characterization in Langgikima are needed because soil derived from fresh ultramafic has poor nutrient content (N, P, and K), low exchangeable base cations, very low to low cation exchange capacity, and low to medium base saturation. Moreover, soils from harzburgite and serpentinite rocks were silty, whilst those from olivine websterite rocks were clayey (Tufaila *et al.*, 2011). Ultramafic Complex in Southeast Sulawesi Province mainly comprises peridotites and serpentinites with olivine, antigorite, enstatite, hornblende, plagioclase, feldspar, and anthophyllite as constituent minerals (Alam *et al.*, 2012).

Profile Description

UMK 53 section is located in Asera Village, not more than 50 m to the main road connecting

Central Sulawesi and Southeast Sulawesi. The outcrop is totally 3.1 m in height and mainly divided into three units: soil, laterite/limonite, and saprolite. Moreover, the three units were further classified into seven subunits in various thicknesses based on their genetic horizon. Brief description of layer distribution is shown in Table 1. The first layer is dark reddish undisturbed top soil subunit with 30 cm thick. Plant roots were detected in the top layer (layer 1). Some rock fragments were found in the second layer of colluvium with the thickness of 60 cm. Normal weathered rock profile does not consist of colluvium, therefore the disturbance confirms that the location was affected by debris. The two limonite layers are totally 80 cm thick with both the dark red limonite (layer 3) and the reddish one (layer 4) attaining the same thickness of 40 cm. Decomposed base rock built the saprolite layers partially. Ultramafic rock as the basement of the weathering profile can still be recognized in saprolites (Figure 2). The upper reddish saprolite (layer 5) is the boundary to lower laterite

Table 1. Layer Description of Ultramafic Weathered Layer in Asera Village

Layer Number	Sample	Depth	Brief description	Colours as used in Figures 3 and 4
1	UMK 53 -1	0 - 0.3 m	Top soil	
2	UMK 53 -2	0.3 - 0.9 m	Colloivium which consist of rock fragments on soil	
3	UMK 53 -3	0.9 - 1.3 m	Dark red limonite	
4	UMK 53 -4	1.3 - 1.7 m	Reddish limonite	
5	UMK 53 -5	1.7 - 2 m	Reddish saprolite	
6	UMK 53 -6	2–2.5 m	Yellowish saprolite	
7	UMK 53 -7	2.5–3.1 m	Bright saprolite	

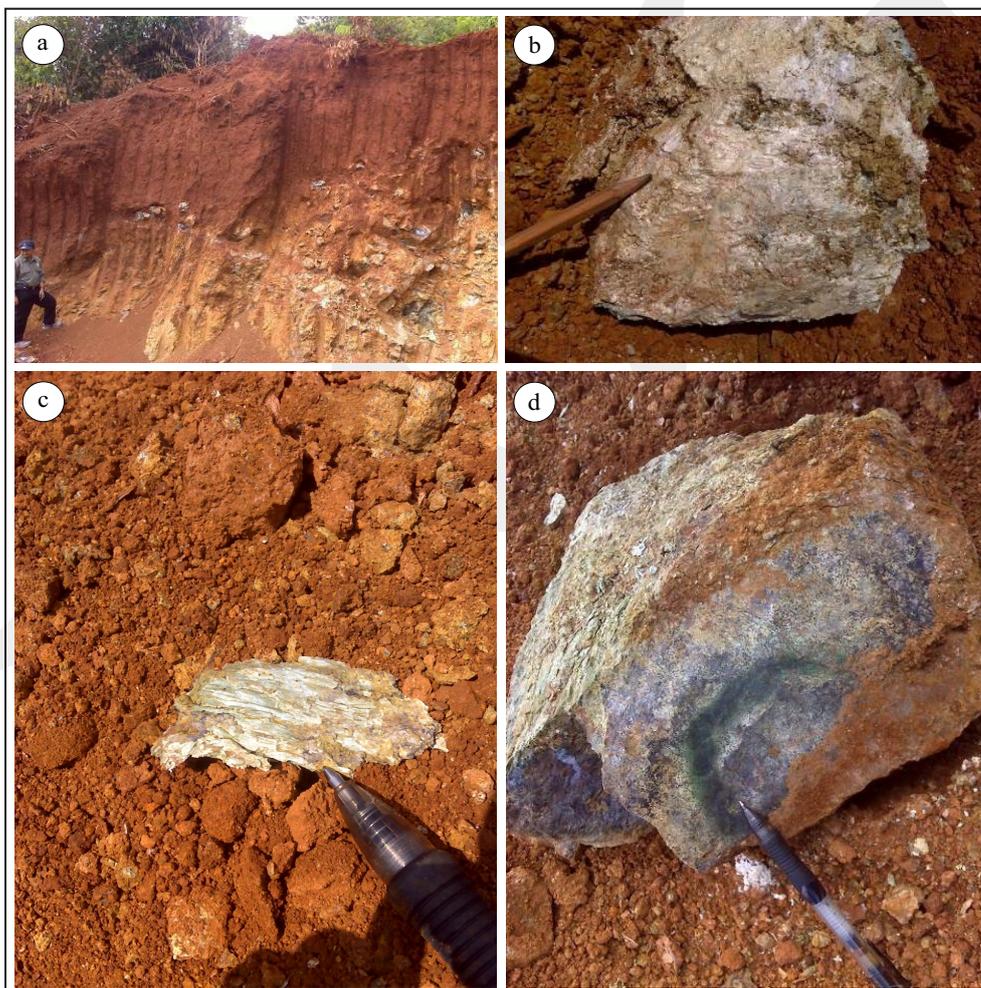


Figure 2. Photographs showing studied profile condition in Asera Village: a) the studied UMK 53; b) the bright saprolite in layer 7 of UMK 53; c) serpentinization in the profile; and d) garnierite (the greenish part) within weathered and serpentinized ultramafic rock.

(30 cm). The relatively yellow saprolite (layer 6) has the thickness of 50 cm. The lowest layer of this profile is the bright saprolite (layer 7) as

the least weathered ultramafic layer outcropping in the profile. Nevertheless, the fresh ultramafic rock is not outcropped in this location.

ANALYTICAL METHOD

The weathered ultramafic samples were analyzed at Geology Laboratory of The Centre for Geological Survey, Bandung, using two methods: X-ray fluorescence (XRF) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Major oxide content of the selected samples was measured using (XRF), whilst trace and rare earth elements were analyzed by using ICP-MS. In the laboratory, the collected soil and laterite samples were spread thinly on a plastic sheet or tray for air-drying as the most accepted procedure of sample preservation, and may reduce the rate of possible reactions in soil sample (Bashour and Sayegh, 2007). Both soil and laterite aggregates should carefully be broken to accelerate the drying process to minimize chemical and biochemical reactions in air-dry soils, although these reactions are still possible sources of error. Nevertheless, saprolites were simply dried under the sun light for at least one day without special pre-treatments. Whole samples were then crushed with jaw crusher and were grounded using a ball mill to gain particle size of 200 mesh. Pressed pellets were analyzed with the Advant XP X-ray fluorescence method (XRF) for thirteen oxides (SiO_2 , Al_2O_3 , K_2O , Na_2O , Fe_2O_3 , CaO , MgO , NiO , Cr_2O_3 , TiO_2 , SO_3 , P_2O_5 , and MnO).

Loss on Ignition (LOI) analysis was started by heating the weighted porcelain crucibles to 300°C in a furnace. The crucibles were then cooled in a desiccator, thus ensuring that no moisture increased in the dry weight measurements. One gram of sample was then put in the crucible and heated at $1,000^\circ\text{C}$ in the furnace for about an hour. The sample together with the crucible were then cooled in desiccator and weighted. The LOI was calculated using this formula:

$$\text{LOI} = \frac{(\text{mass of crucible+sample}) - (\text{mass of crucible+residue})}{(\text{mass of crucible+sample}) - (\text{mass of empty crucible})} \times 100\%$$

Trace and rare earth element contents of the samples in this study were made through quadrupole iCAP-Q Thermo Fisher Scientific ICP-

MS. Dried samples were dissolved with three acid leaching using nitric acid (ultrapure grade), formic acid (ultrapure grade), and perchloric acid (pro-analysis grade). Full suite of rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) as well as six other trace elements (V, Rb, Y, Ba, Th, and U) were analyzed. The CPSs (counts per second) of one blank and six levels of calibration solutions (0.1, 1, 5, 10, 25, and 50) were measured to produce the calibration curves of analyzed elements. Computer programme of the ICP-MS device transformed elements CPS of samples to concentrations using the previous calibration curves. AGV-2 and GBW 7112 were the two certified reference materials used in this study to certify the quality of measurement results. The geochemical analysis results are given in Table 2.

RESULT AND DISCUSSION

Mobilization Pattern of Major Elements and Heavy Metals

SiO_2 content of ultramafic rocks is generally less than 45% with high Mg value but low K content (Attoh *et al.*, 2006; Alam *et al.*, 2012). Si, Mg, and Fe oxides in the ultramafic rock laterites of Asera range in 23 - 37%, 9 - 22%, and 20 - 44% respectively. No other major element oxides exceed 1%, except Al_2O_3 with the content of 1 - 5% in the weathered ultramafic layers. The SiO_2 average in saprolites is 36% and it continuously decreases to 28%, 23.73%, and 23.37% in lower laterite, upper laterite, and top soil horizons respectively (Figure 3a). Similar progressive decreasing trends are shown on MgO and CaO which are declined to the average of 22.12% and 1.01% in layer 5 - 7, to 10.24% and 0.41% in layer 4, to 9.25% and 0.39% in layer 3, to less than 12% and 0.3% in layer 1 (Figures 3b and c). These declining patterns depict Si, Mg, and Ca characters as leaching elements during weathering (Sagapoa *et al.*, 2011).

In contrast, Fe, Al, and Ti show increasing pattern from the least to the most weathered layers (Figures 3d, e, and f respectively). Fe enrichment

Table 2. Geochemical Compositional Variation in the Studied Area

	UMK 53-1	UMK 53-2	UMK 53-3	UMK 53-4	UMK 53-5	UMK 53-6	UMK 53-7	UMK 154
SiO ₂	23.37	36.14	23.73	28.30	34.43	37.33	36.60	39.41
Si	10.98	16.99	11.15	13.30	16.18	17.55	17.20	18.13
Al ₂ O ₃	4.71	4.31	4.81	4.67	1.72	1.95	1.73	0.98
Al	2.59	2.37	2.65	2.57	0.95	1.07	0.95	0.63
Fe ₂ O _{3T}	42.39	31.36	43.83	39.47	22.37	23.07	20.68	8.70
Fe	29.67	21.95	30.68	27.63	15.66	16.15	14.48	7.35
CaO	0.27	2.60	0.39	0.41	0.89	1.09	1.06	0.75
Ca	0.19	1.15	0.28	0.30	0.64	0.78	0.76	1.23
MgO	11.51	9.64	9.25	10.24	22.68	22.02	21.66	37.39
Mg	6.91	6.38	5.55	6.14	13.61	13.21	13.00	26.06
NiO	0.90	0.31	1.15	1.27	1.44	1.31	1.33	0.33
Ni	0.71	0.25	0.99	1.00	1.14	1.03	1.05	0.30
Cr ₂ O ₃	1.55	0.78	1.33	1.15	0.68	0.67	0.64	0.34
Cr	1.07	0.54	0.92	0.79	0.47	0.46	0.44	0.2505
TiO ₂	0.07	0.02	0.06	0.05	0.02	0.02	0.02	0.01
Ti	0.0274	0.0101	0.0231	0.0207	0.0079	0.0077	0.0081	0.0141
SO ₃	0.05	0.05	0.04	0.04	n.d.	0.02	0.01	0.02
P ₂ O ₅	0.05	0.03	0.04	0.03	0.01	0.01	0.01	n.d.
MnO	0.69	0.28	0.86	0.82	0.28	0.26	0.24	0.13
LOI	14.25	14.39	14.32	13.37	15.41	12.16	15.96	11.88
Total	99.83	99.92	99.80	99.82	99.93	99.91	99.95	99.94
V (ppm)	201.35	40.29	132.08	129.02	93.95	79.91	100.45	78.82
Rb	75.25	74.89	75.02	72.92	72.29	71.60	72.96	73.05
Y	3.20	2.32	4.36	4.04	0.97	0.64	0.45	0.27
Ba	44.24	24.09	48.97	56.27	39.84	31.02	34.53	28.46
La	2.21	2.01	2.72	2.60	0.74	0.40	0.31	0.32
Ce	2.68	1.32	2.75	2.54	1.21	0.67	0.70	0.72
Pr	0.46	0.37	0.53	0.50	0.12	0.08	0.06	0.07
Nd	1.55	1.25	3.17	1.76	0.40	0.26	0.21	0.22
Sm	0.29	0.23	0.34	0.34	0.07	0.05	0.04	0.05
Eu	0.05	0.04	0.07	0.07	0.01	0.00	0.00	0.01
Gd	0.37	0.29	0.45	0.42	0.12	0.07	0.09	0.06
Tb	0.06	0.05	0.08	0.07	0.02	0.01	0.01	0.02
Dy	0.39	0.30	0.46	0.44	0.12	0.09	0.07	0.07
Ho	0.10	0.08	0.12	0.12	0.03	0.02	0.02	0.02
Er	0.32	0.25	0.39	0.37	0.10	0.08	0.06	0.06
Tm	0.05	0.04	0.06	0.06	0.02	0.02	0.01	0.02
Yb	0.36	0.27	0.42	0.40	0.12	0.11	0.10	0.07
Lu	0.07	0.05	0.08	0.08	0.02	0.02	0.02	0.02
Th	0.31	0.14	0.38	0.43	0.06	0.02	0.05	0.50
U	0.37	0.35	0.39	0.38	0.34	0.34	0.35	0.36
∑REE	8.96	6.54	11.65	9.76	3.09	1.90	1.71	1.74
∑REE+Y	12.15	8.85	16.01	13.80	4.06	2.53	2.16	2.01
Ce/Ce*	0.62	0.35	0.53	0.51	0.90	0.86	1.17	0.62
Eu/Eu*	0.50	0.48	0.56	0.56	0.41	0.25	0.13	0.50

K₂O and Na₂O are not listed because the value is relatively very low.

Element Mobilization During Weathering Process of Ultramafic Complex
in North Konawe Regency, Southeast Sulawesi Based on A Profile from Asera (R. Irzon and B. Abdullah)

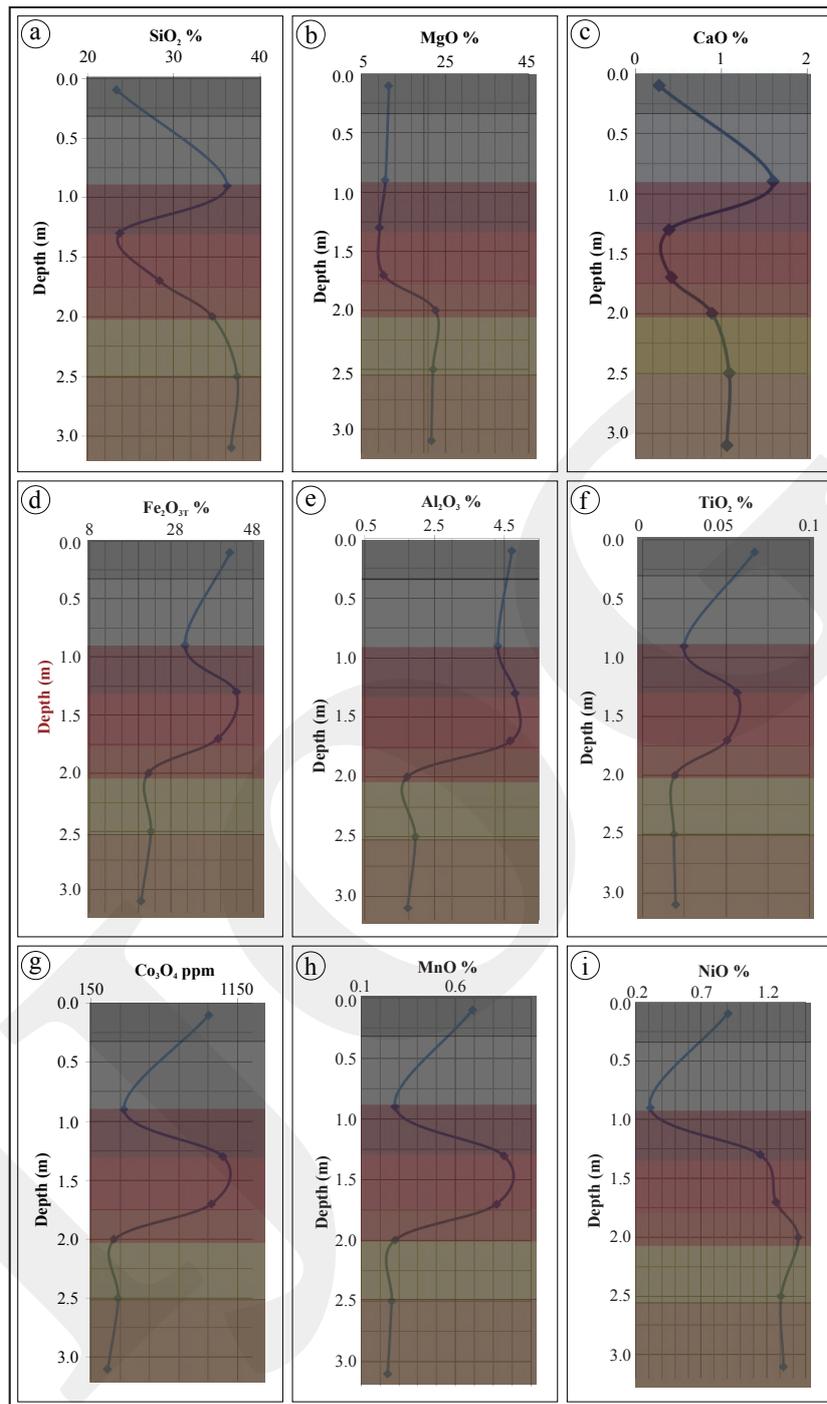


Figure 3. Element mobilizations of the studied profile: a) SiO_2 ; b) MgO ; c) CaO ; d) Fe_2O_{3T} ; e) Al_2O_3 ; f) TiO_2 ; g) Co_3O_4 ; h) MnO ; and i) NiO_2 .

is more than twice from less than 15% in lower saprolite to more than 30% in upper laterite (Table 2). Moreover, Al and Ti contents in layer 3 are almost three times larger than layer 7, 0.95% to 2.65% and 81 ppm to 231 ppm respectively. The three major elements are residually concentrated

in weathering process (Sagapoa *et al.*, 2011). Al and Ti enrichment in the profile could be due to the coupled alteration of silicate minerals (feldspars and ferromagnesian) and the formation of Al and Ti-bearing minerals (Calagari *et al.*, 2015). Heavy economic metals of Cr, Mn, and Co in the studied

UMK 53 depict the same rising pattern bottom up to reach 0.9%, 0.66%, and 770 ppm respectively in dark-red laterite layer. Co and Mn are concentrated in the laterite part of the profiles which are poorly protected against erosion and mechanical transportation as shown in Figures 3g and h.

Such different patterns are shown in Ni fluctuation of the studied profile. Nickel decreases from lower saprolite (1.05%) to middle saprolite (1.03%), but then increases and reaches the top count in the upper saprolite (1.15%). Later, it continuously decreases in lower laterite (1%), upper laterite (0.9%), and soil (0.71%) (Figure 3i). The Mg distribution in bedrock and its weathered layers is related to Mg-Ni replacement process by an ionic exchange reaction such as: $\text{Mg-serpentine} + \text{Ni}^{2+} = \text{Ni-rich serpentine} + \text{Mg}^{2+}$ (Sagapoa *et al.*, 2011). Serpentinization was megascopically detected in the field work (Figure 2c). Moreover, Ni is not totally mobile and reacted with H_4SiO_2 to fill the pores in the weathered profiles (Purwanto and Agustini, 2014) to explain the Mg-Ni trend of UMK 53. Although Mg continuously decreases from saprolite to laterite, a highest Ni content is not detected in layer 3 nor layer 4 of laterites, because it was transported downward through the pores. Nickel, cobalt, and manganese may have been precipitated together as an oxidized concentration during weathering. After being co-precipitation of Ni-Co-Mn in earlier lateritization states, nickel then leached out of laterite concentrations and chiefly migrates to the saprolitic clay horizon of the profile at a later lateritization stage. Upper saprolite is the boundary layer between the laterite and saprolite horizons which is called transitional bedrock on nickel laterite study in Pakal Island (Purwanto and Agustini, 2014). Thus, it is relatively more clayish in comparison to the other saprolite layers. The Ni pattern is coherent with the lateritization process of ultramafic rocks in Solomon Island (Sagapoa *et al.*, 2011) and Goias, Brazil (Ratie *et al.*, 2015).

Mobilization of Large Ion Lithophile Elements (Rb, Ba, Sr, and U)

Cations are selectively leached or fixed in weathering profiles in relation to clay content. In

the UMK 53 profile, Ca composition gradually rises from the upper laterite (0.28%) to the lower saprolite (0.78%), whilst Rb and Ba reversely decline from the average of 74 ppm and 52 ppm in laterites to 72.8 ppm and 35.13 ppm in saprolites respectively (Figure 4). These patterns confirm that small cations, such as Ca, are selectively leached and weathered from weathering profiles, whereas cations with relatively large ion radii, such as Cs, Rb, and Ba, may be fixed by preferential exchange and adsorption on clays (Nyaikaru and Koeberl, 2001) as laterites are more clayey than saprolites.

Rare Earth Elements

Only small number of studies were conducted in correlation of REEs and strategic resource on ultramafic rocks as this kind of rock is not included in the seven strategic REE deposits of Castor and Hedrick (2006). The total amount of REE in studied lateritic samples ranges from 1.71 to 11.65 ppm which is very low and coherent with the previous conclusion. Although the studied profile is in the area of ultramafic complex (Rusmana *et al.*, 1993), the basement rock is not exposed in this site. Many studies were undertaken to confirm the use of REE for the basement rock, based only on the REE patterns of fresh rock up to the soil (Sagapoa *et al.*, 2011; Mustapha and Alhassan, 2012; Jianwu *et al.*, 2014). The mobilization of trace and rare earth elements in the profile contributes to our understanding of how these elements behave during weathering.

The profile in Asera indicates a gradual increase of total REE bottom to the top from lower saprolite to upper laterite (Figure 4). The total REE in the most weathered layer (11.65 ppm) is almost seven times higher than in the least weathered layer (1.71) (Table 2). The REE mobilization is related with the increasing of Fe and Mn content to the top of the profile, because REEs are mainly bound to both of the major elements (Marker and de Oliveira, 1994). These positive correlations of total REE-Fe and total REE-Mn are shown in Figure 5. The high degree of correlations in both bivariate diagrams of Fe *versus* ΣREE and Mn *versus* ΣREE is confirmed by the correlation coefficient values which are close to 1.

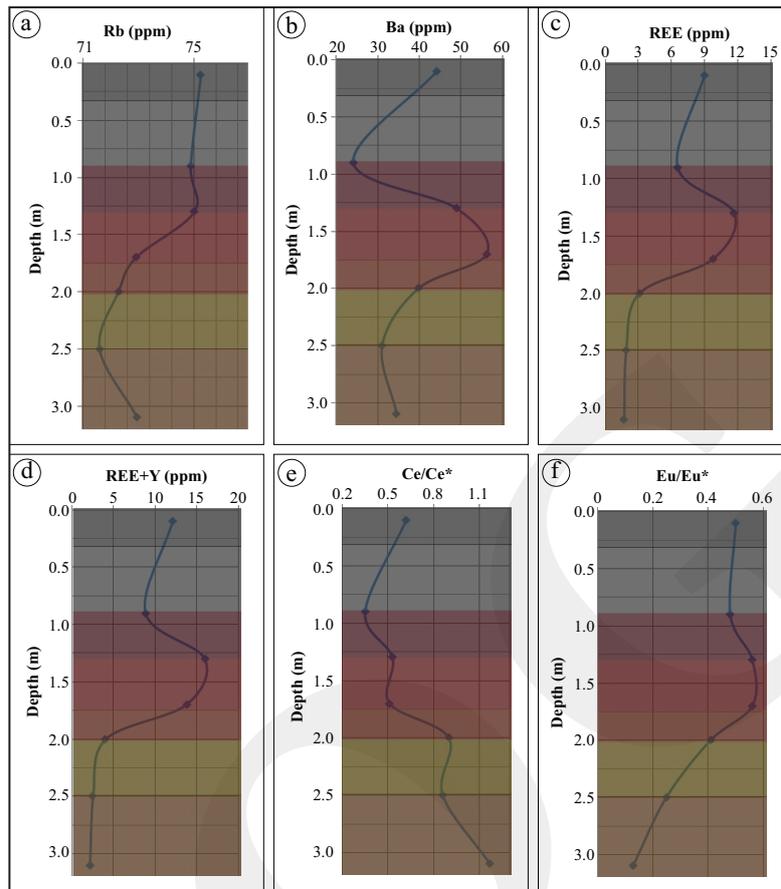


Figure 4. Trace elements and REE mobilizations of the studied profile: a) Rb; b) Ba; c) REE; d) REE+Y, e) Ce/Ce*; and f) Eu/Eu*.

REE values of samples in this study have been normalized to primitive mantle value (Sun and McDonough, 1989) to prevent the Oddo-Harkins effect. Downtrend of Ce anomaly from the lowest saprolite horizon to the top laterite is detected in studied profile (Figure 7). Cerium can occur in nature as trivalent as other REEs or as tetravalent in oxidizing condition. Ce is precipitated from solution in oxidizing condition from Ce^{3+} to Ce^{4+} as a very insoluble CeO_2 , and the solution consequently shows a negative anomaly (Braun *et al.*, 1990; Aide and Aide, 2012). In this study, Ce anomaly and Eu anomaly were calculated based on previous studies (Hren *et al.*, 2006; Mongelli *et al.*, 2015; Banakeng *et al.*, 2016; Yu *et al.*, 2017) in the following equations:

$$Ce/Ce^* = Ce_N / (La_N \times Pr_N)^{0.5} \dots\dots\dots 1)$$

$$Eu/Eu^* = Eu_N / (Sm_N \times Gd_N)^{0.5} \dots\dots\dots 2)$$

In UMK 53, the original Ce anomaly (Ce/Ce*) of 1.17 in layer 7 decreases to 0.88 (the average of layers 6 - 5) and 0.52 (the average of laterites) (Table 2 and Figure 4). The decrease of Ce/Ce* is related to oxidation of Ce along weathering process. Weathered rock REE deposit is a result of in-situ lateritic weathering on the host rock and easily recovered through ion-exchange mechanism which derived from direct cation-exchange reversible reactions at the permanent negative charge sites on the clayey minerals. The clay materials pick up REE+Y from aqueous solution through several processes including adsorption, the formation of surface solid solution, and surface precipitation (Piasecki and Sverjenski, 2008). This type of deposit leaves the tetravalent Ce as cerianite, whilst other trivalent REEs are transported upward to upper laterite (Papangelakis and Moldoveanu, 2014) in explaining negative cerium anomaly at the studied profile. The trivalent REEs are transported

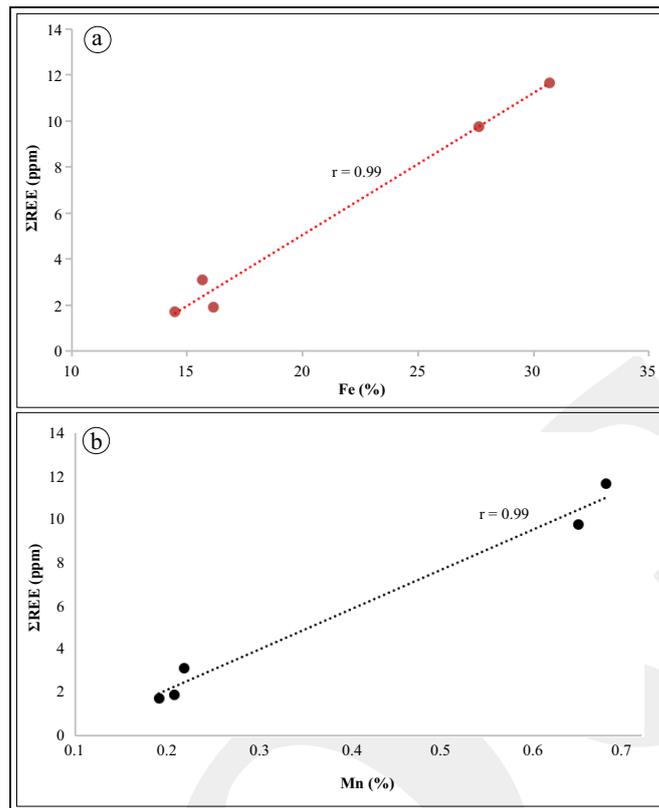


Figure 5. Bivariate plots of a) Fe versus total REE, and b) Mn versus total REE from layer 3 to layer 7 of UMK 53.

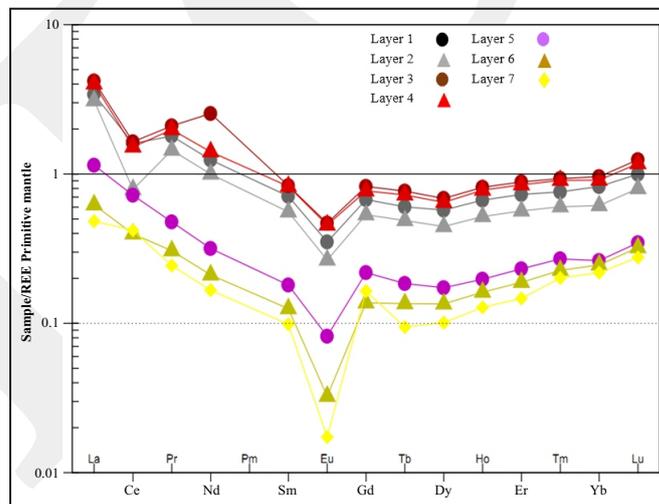


Figure 6. REE spider diagram of seven layers in the studied profile from North Konawe Regency. The sample values are normalized to primitive mantle of Sun and McDonough (1989).

above to upper laterite, but some of tetravalent oxidized Ce is left gradually as cerianite that is impossible to be recovered by ion exchange leaching (Papangelakis and Moldoveanu, 2014).

Eu positive and/or negative anomalies on weathering products are usually interpreted as

being inherited from igneous source rocks (Nyai-karu and Koeberl, 2001). Eu positive anomalies were found within ultramafic rocks in Dixcove Greenstone Belt, Ghana (Attoh *et al.*, 2006), Buck Creek Complex (Berger *et al.*, 2001), Victoria Land, Antarctica (Cottle and Cooper, 2006),



Figure 7. A photograph indicating a secondary input in the studied profile. Ultramafic pebbles (in circles) were mechanically transported and inserted into the studied profile.

Eastern Pontides, Turkey (Eyuboglu *et al.*, 2010), and southern Ethiopia (Yibas *et al.*, 2003), whilst negative ones were detected in Tamil Nadu, India (Dar *et al.*, 2014), Fiskenaesset, West Greenland (Fowler *et al.*, 1983), and Guangxi, China (Zhou *et al.*, 2004). Moreover, both Eu negative and positive anomalies were noticed in ultramafic unit from Yarlung-Zangbo, Tibet (Xia *et al.*, 2003). It can be concluded that Eu anomaly does not depend on the rock classification, but it is related to rock tendency to plagioclase separation of magma from its plagioclase crystals produces Eu negative anomaly, whilst accumulation of plagioclase crystals before solidification in the magma displays a relatively positive Eu anomaly (Xia *et al.*, 2002; Eyuboglu *et al.*, 2010; Dar *et al.*, 2014). Eu negative anomalies in all lateritic layers of this profile indicate that the fresh rock most probably also held the same anomaly and experienced plagioclase separation from its origin magma. Unlike the other lanthanides which are trivalent, Eu can exist in the reduced (2^+) state for Eu under reducing conditions and Ce in the

oxidized (4^+) state for Ce under oxidizing conditions (Al-Khirbash *et al.*, 2013). Eu anomaly in Asera profile depicts increasing pattern bottom up: 0.13 in lower saprolite, 0.25 in mid saprolite, 0.41 in upper saprolite, and constant of 0.56 in laterites (Table 2 and Figure 4). The Eu anomaly pattern informs more oxidizing condition along lateritization to prevent Eu reduction to Eu^{2+} , and confirms the previous Ce anomaly descending trend.

Colluvium Provenance

Element mobilization by weathering process of ultramafic rock in the studied laterite profile depicts anomaly. Fe, Al, Ti, and heavy metals show relatively elevation from relatively fresh rock upward to top soil layer, whilst Si, Mg, and Ca with contradictive trends in a progressive weathering (Sagapoa *et al.*, 2011; Ratie *et al.*, 2015). However, element compositions in layer 2 show anomaly. As described in Table 1, the layer 2 was built of soil as the latest result of weathering layer and unknown rock fragments to conclude that UMK 53 profile experienced secondary input from different sources, other than weathering result of ultramafic rock. The secondary input of the profile is shown in Figure 7.

UMK 53 is basically surrounded by ultramafic complex and alluvium. Pandua Formation which consists of conglomerate, sandstone, and claystone is located more than 9 km southeastern of the studied profile, whilst metasandstone, quartzite, shale, phyllite, limestone, and siltstone of Meluhu Formation occur more than 10 km southward (Rusmana *et al.*, 1993). Based on morphology, this profile is very unlikely to be influenced by alluvium, because it is located in a higher region than the Quaternary rock unit. Layer 2 is mainly composed of SiO_2 (36%), Fe_2O_{3T} (31%), and MgO (10.6%). The SiO_2 composition of layer 2 is 36%, much lower than 45% as a typical of ultramafic rock. The Mg content of colluvium rock fragments plus soil in layer 2 from Asera (6.38%) is much lower than the ultramafic bedrock from Tinangea (10.95 - 13.44%), South Konawe Regency, whilst Fe_2O_{3T} (31.36%) is much higher in the range of 29.38 - 31.54% (Syafrizal *et al.*, 2011). The relatively anomalies of magnesium and iron

content are related to soil fraction in this layer as more weathered laterite than layer 3. It can be concluded that the rock fragments in layer 2 are the mechanically transported ultramafic pebbles around UMK 53.

CONCLUSIONS

Chemical weathering is an important process that causes geochemical redistribution of elements. The study of laterite profile of weathered ultramafic rock shows that Si, Mg, and Co are leached during lateritization, whilst Fe, Al, and Ti are relatively enriched. The heavy economic metals of Cr, Mn, and Ca show increasing patterns upward to be concentrated in the upper dark-red laterite layer. Ni distribution along the profile shows that the metal is not concentrated in the most weathered layer, because of the influence of Mg mobilization. Small cations, such as Ca, are selectively leached and weathered from weathering profiles, whereas cations with relatively large ion radii, such as Cs, Rb, and Ba, are associated with more clayey layer. The REE mobilization is concomitant with the increasing of Fe and Mn content to the top of the profile. In weathering process, REE solution is transported upwards to upper laterite, but some of the oxidized Ce is left gradually as cerianite to set up Ce negative anomaly. Eu negative anomalies in the seven weathered layers of this profile indicate that the fresh ultramafic rock would also be characterized by Eu negative anomaly. The Eu anomaly trend informs more oxidizing condition along lateritization process. Element mobilization patterns depict that UMK 53 profile experienced secondary input from another source besides weathering result of the parent ultramafic rock. Rock fragments in layer 2 were originated from ultramafic complex based on morphology condition and the geochemistry characters.

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