MINERALOGY, GEOCHEMISTRY, AND LEACHING BEHAVIOR
OF THE SOROAKO NICKELIFEROUS LATERITE DEPOSITS,
SULAWESI, INDONESIA

SUMMARY

By

Sufriadin
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Graduate Program of Geological Engineering
Faculty of Engineering, Gadjah Mada University
Yogyakarta

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1. Introduction

About 70% of world land-based nickel resources are contained in lateritic ores, however, they only account for about 40% of global nickel production. Indonesia is the world’s second largest nickel producer (232 kt pa) behind Russia. Soroako laterite deposits are the most important Ni resources from Indonesia and they have been mined by PT. Vale Indonesia to produce nickel matte (av. 78% Ni plus 22% S). Two ore types have been mined in the Soroako deposits on the basis of their serpentinization degree of protolith. In general, the west ore type is characterized by higher in Ni, S/M ratio and olivine content than that of east ore type. For an efficient smelting operation, the ores must meet constraints of S/M ratio (1.95 - 2.15), Fe content (20 – 23 wt %), olivine (<22 %), and Ni (> 1.50 wt %). The strong increase in production of east ore type has led to continuous depletion of the ore reserves. Hence, a new mine area has been developed to find the east ore type which is located at Petea block.

There is a tendency in industry for treatment the laterite ore by acid leaching technology (Gupta, 2003) due to high energy demand of smelting process. The advantages of leaching are operate on low temperature and elements such as Ni, Co, Fe, and Mg can be recovered simultaneously (Liu at al, 2009). PT. Vale Indonesia has been commissioning the intensive studies in the recovery of Ni and Co from laterite ores by means of pressure acid leaching (PAL) process. However, no information about the leaching test on these ores has been published to date.

Some studies have been conducted in the Soroako nickeliferous laterite deposits. Golightly (1979a; 1979b) described the deposits with the focus on the discrimination between the deposits those developed over unserpentinized ultramafic rocks in the western half and those developed over ultramafic bedrock with medium to highly serpentinized degree in the eastern half of the Soroako area. A further review by Golightly (1981) suggested that garnierite tends to well developed on unserpentinized peridotite as compared to those on serpentinized ultramafic protolith. However, formation mechanism and mineralogy of garnierite is not yet fully understood.
Despite various studies have been performed on this deposit, the investigation focusing on the relationship between nature of protolith including serpentinization degree and variation of mineralogy and Ni content of the overlying laterite deposit is still needed to improve a better understanding on the evolution of minerals and elemental behavior with special emphasis on the Ni cycles in weathering profiles. Mineralogical and chemical analyses including textural features of garnierites are crucial because those data are very useful in assessing the origin and factors responsible for the formation of garnierite.

Leaching study is also very important because the future trend of Ni and (Co) recovery from laterite ores will be relied on the hydrometallurgical process. Therefore, leaching test should be done to find out a better insight about dissolution behaviour of minerals and leaching rates of metals. This information is fundamental for the future plan process if leaching technology is the main option. Because the mineralogy and chemistry of laterite deposit is sensitive for leaching process, it is expected that Ni laterite genesis is a key factor in the resulting the differences mineralogical and chemical characteristics which in turn, have different responses on the leachability of these ores during acid treatment. An understanding on the relationship of ultramafic bedrocks and the overlying mineralogy, textures, and grades of nickeliferous laterite deposits may have important hydrometallurgical implication for ore processing.

The ultimate aim of the current study is to assess the role of protolith for development of overlying nickeliferous laterite deposits derived by intensive chemical weathering of peridotite with different serpentinization degree. The specific objectives are: (1) to describe petrological and geochemical signatures of ultramafic rocks in the two blocks, (2) to determine mineralogical distribution and elemental behavior throughout the selected profiles during chemical weathering, (3) to establish the nickel cycle in the weathering profiles with related to supergene process of Ni, (4) to assess the origin of Ni-Mg hydrous silicate ore (garnierite) constrained by textural, chemical and mineral variety and (5) to investigate the impact of mineralogical composition of the saprolitic nickel ores in terms of their dissolution behaviour and metal leaching under sulfuric acid.
2. Methods

This study is focused on the mineralogy and geochemistry with subsequent leaching of Ni laterite deposits of the two different blocks from Soroako, South Sulawesi. Samples were collected from these two blocks including bedrocks, garnierites and lateritic soils. Laboratory works include mineralogical and geochemical analyses, and leaching experiment. Mineralogical characterization of samples was conducted using optical microscopy and X-ray diffraction analysis (Rigaku RINT-2100). Some garnierite and saprolitic Ni ores samples were also analyzed by means of thermal analysis (SSC/5200 SII-SEIKO Instrument) and FTIR spectroscopy (JUSCO), whereas the geochemical analyses include X-ray fluorescence spectrometry (Rigaku RIX-3100) and SEM-EDX. These works were done at Laboratory of Economic Geology, Department of Earth Resources Engineering and The Centre for Advanced Instrumental Analysis, Faculty of Engineering, Kyushu University, Japan.

Mineral chemistry analysis of some bedrocks and garnierite samples were conducted using electron probe microanalysis (EPMA) after microscopically localized of the mineral target under polished thin sections using JEOL Superprobe JXA - 8800R Electron Microprobe Analyzer situated at Department of Earth Science and Technology, Akita University, Japan.

The leaching experiment of saprolite samples under sulfuric acid at atmospheric pressure condition was conducted in batch reactor using magnetic stirrer model REXIM-RSH at Laboratory of Economic Geology, Department of Earth Resources Engineering, Kyushu University. Reaction time (30, 60, 90, 120, 150, and 180 minutes) was set as variable. At the end of leaching, residues were separated from the leached solution using a 0.45 μm membrane filter. After drying, the solid residues were analyzed using XRD for mineralogical identification. One solid residue from each sample was also analyzed by FTIR and SEM-EDX. Chemical composition of ore samples and leached solutions were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, VISTA-MPX, Seiko Instrument Inc.) at Mineral Processing Laboratory, Department of Earth Resources Engineering, Kyushu University.
3. Results

3.1 Petrology and Geochemistry of Ultramafic Bedrocks

Ultramafic bedrocks at Soroako west block are commonly composed of peridotites which characterized by very low to unserpentinization degree. Mineral compositions were dominated by olivine (75 - 95 vol %) with subordinate orthopyroxene (<15 %) and locally clinopyroxene (<5 %) and spinel (<4 %). Nearly all analyzed samples are grouped as harzburgite according to the classification of Streckeisen (1976). The olivines were microscopically characterized by well developed irregular cracks with slight alteration and also show corrosion on the margin which is known as “iddingsite”. Kink bands and undulose extinction also occur. Orthopyroxenes show anhedral to subhedral; whereas clinopyroxenes were minimal and commonly occurs as exsolution lamellae in orthopyroxenes. Some fractures in olivine and orthopyroxene have been filled by secondary phases that might have been formed during the initial stage of weathering. Spinel generally occurs in the studied samples which is commonly present as inclusion in olivine and locally in orthopyroxene.

In contrast, the bedrocks at Pejeka block are commonly constituted the ultramafic rocks with medium to high degree serpentinization (> 50 % by volume) and this has modified the original mineral and texture. Serpentine textures in studied samples can be distinguished into two types: pseudomorphic and non-pseudomorphic. Pseudomorphic texture occurred when the olivine crystals were replaced by serpentine forming mesh texture; while replacement of pyroxene by serpentine has produced bastite texture, where the original crystal shape was still preserved. Non-pseudomorphic texture is characterized by the presence of late serpentine veins that have penetrated either serpentinized olivine or serpentinized pyroxene. Spinel, in some cases, shows alteration mainly along the cracks or the margin of crystals possibly during serpentinization.

It is appeared that serpentinization of olivine is more extensive than pyroxene. Serpentinization is also responsible in generating the formation of fine-grained with disseminated magnetite crystals that was observed within or along the margins and the center of serpentine veins and pyroxene cleavages.
Whole-rock chemical analyses of ultramafic rocks show that unserpentinized harzburgite and dunite samples from west block contain higher in SiO$_2$ (mean 43.1 wt%) and MgO (mean 45.3 wt%) as compared to those serpentinized rocks from Petea block with MgO (ave. 40.9 wt%) and SiO$_2$ (ave. 37.5 wt%). Relative depletion of these elements from Petea block is a consequence of water introduction during serpentinization. Average moisture content from Petea samples is about 12.1 wt% indicating strongly serpentinized protolith. The elements such as FeO, Cr, Ni, and Co also show higher concentration in the west block samples than Petea block. However Al$_2$O$_3$ content of bedrock from west block samples is lower than Petea samples.

Binary plot between MgO and SiO$_2$, Al$_2$O$_3$ and CaO shows inverse correlation for west block samples; whereas relation between MgO and SiO$_2$, Al$_2$O$_3$ and CaO for Petea samples displays no significant correlation. The higher Ni content (av. 0.36 wt%) of bedrock samples from west block reflects the domination of forsteritic olivine. With the exception of Al and Ti, generally, some major and minor elements have been lost in some extent during serpentinization of ultramafic rock.

EPMA results of olivines in dunite and harzburgite from west block reveals NiO content ranging from 0.3 to 0.5 wt%. Theoretically forsterite has Ni concentration up to 0.5 wt% (Ottenello, 1997). Orthopyroxene contains low NiO (0.04 – 0.15 %) and clinopyroxene has very low NiO (<0.04 %). Microprobe results of serpentines from Petea block show fully serpentinized rocks tend to be higher in NiO (up to 3 wt%). In contrast, serpentine mesh, vein, and bastite derived from serpentinized harzburgite samples show low NiO concentration (<0.2 wt%). Spinel shows different NiO between core (0.01 %) and rim (0.21%). It is shown that serpentinization of dunite, resulting in fully serpentinized rock, has been accompanied by nickel enrichment. This feature is attributable to the higher content of Ni in original olivine as principal constituents of dunite. Conversely, serpentinization of harzburgite has led to slight depletion in nickel. Spinel shows an indication of Ni enrichment during serpentinization, however it only occurs as accessory mineral in the protolith.
3.2 Mineralogy and geochemistry of Ni laterite deposits

3.2.1 Weathering profiles

Soroako west block: In general, lateritic soil profiles studied at the Soroako west block show various thickness and can be distinguished into different horizons from bottom to the top on the basis of their physical appearance, texture, mineralogy, and chemistry. The lowest horizon is covered by the parent rocks that are mainly composed of unserpentinized peridotite which display greenish gray, medium to coarse grained textures and massive. The incipient weathering has led to corrosion of the rock surface in which changes of the color into the brownish yellow upward forming rocky saprolites. The boundaries between bedrock and overlying saprolite horizons are very irregular and gradual. Saprolite horizon is characterized by greenish brown to yellowish in color, fine to coarse grained and porous. Saprolite still contains peridotite boulders or cores stones and shows rounded textures and various in size. Toward the upper profile, locally the color is dark grey to black with very soft but it is gradually changed into light yellow to light brown forming limonite zones. At the top profiles, the zone exhibits relatively reddish to dark brown with indurated materials that is collectively termed as red limonite zone.

Mineralogical composition determined by XRD shows that the parent rock contains predominantly olivine with minor enstatite and trace diopside and spinel. At the upper bedrock, where the weathering is active, mineralogy of materials is composed of saponite, talc and locally amphibole. At the lower saprolite zone, the primary minerals were progressively decomposed into smectite, talc, secondary serpentine, quartz and goethite. At the upper saprolite, the mineralogy remain consists of goethite, quartz with minor talc, serpentine, and trace amounts of smectite. The subzone between saprolite in the lower and limonite in the upper profile is composed of lithiophorite or asbolane, Mn-rich poorly crystalline minerals. At this zone, smectite and serpentine are removed but talc is still preserved. At the limonite zone, with exception of talc, all sheet silicate phases have been transformed into goethite. Hence goethite is predominant mineral
occurring in the upper profile. Talc still appears to accompany goethite up to the upper yellow limonite horizon, but at the top of profile, talc is also decomposed and is replaced by goethite forming red limonite zone. Hematite might also be present in small amounts in top of profile. The broad diffraction lines of all observed peaks reflect that goethite and hematite are poorly crystalline materials. Hematite very rarely occurs as a sole oxide in lateritic soil but it is usually associated with goethite (Cornell and Schwertmann, 2003).

Lithogeochemical variation diagram of major and some trace elements through the studied weathering profiles in the Soroako west block shows that MgO, SiO₂, and CaO are strongly depleted from bottom to the top of profiles. In contrast, FeO, Al₂O₃ and TiO₂ strongly increased. Meanwhile, MnO content is low in bedrock and the highest concentration is located in the limonite zone but slightly decreases toward the top of profile. The concentration of Cr shows increasing from bedrock upward while Co tends to have similar trend with MnO and reach maximum at saprolite – limonite interface. Vanadium has low content at bedrock and it steadily increases upward. Nickel content is low in the protolith (0.27 – 0.34 %) but it dramatically increases at saprolite horizon (up to 4.2 %). However, it decreases again toward the top of profile.

**Petea Block.** The weathering sequences in the profiles from Petea block are developed on the strongly serpentinized peridotites. In general, three zones can be discriminated in the full profiles on the basis of their physical appearances from bottom to the top are bedrock or blue zone followed by saprolite zone in the middle and limonite zone in the upper profile. The boundaries between zones are relatively easy to discern but they show very irregular in nature. The bedrocks zone is characterized by fine grained texture and light to dark grey, greenish to light yellow in color, depending on degree of serpentinization and the types of serpentine minerals present. Saprolite overlaying the bedrock shows fine grained texture, greenish yellow to light brown, porous and soft materials. They show relatively homogenous earthy masses. Complete chemical weathering of saprolite has led to the formation of yellowish brown materials in the upper profile forming limonite zone. The thickness of limonite horizon is generally lower than
underlying saprolite zone. Red limonite zone on top of profile overlaying the limonite zone exhibit dark to reddish brown with medium soft and locally indurated materials.

Results of XRD analysis show that the primary serpentine, most likely lizardite, is predominant mineral present in the bedrock. It is associated with minor enstatite and trace amounts of diopside and magnetite. Amphibole and chlorite is also detected in bedrocks. Progressive chemical weathering results in alteration of primary minerals into secondary phases such as smectite, serpentine and iron oxides. In contrast, serpentine in weathering front is relatively conserved so that it becomes predominant mineral occurring in the saprolite zone. In the limonite zone, serpentine and smectite have been destroyed when the weathering is completed. Both minerals might be transformed into goethite therefore goethite becomes dominant in the limonite zone. Quartz also occurs in limonite zone as residual material or it may precipitate as the result of silica saturation of groundwater due to the evaporation mainly in dry season (Taylor and Eggleton, 2001). In the red limonite, goethite is dominant with trace maghemite.

Chemical variations with depth of major and some trace elements in the studied profiles at Petea block reveal that MgO has strongly decreased toward the top of profiles. SiO$_2$ has similar behaviour with MgO but silica may be present in the upper part leading to the relatively higher SiO$_2$ content as compared to the west block profiles. The concentration of FeO shows strongly increased upward that has opposite trend with SiO$_2$ along the profile reflecting the immobility of iron during chemical weathering. Al$_2$O$_3$ diagram also show similar pattern with FeO which increases upward in to limonite. MnO and Cr increases from bedrock and attain maximum values at lower limonite zones. Co also shows the maximum concentration in limonite as compared to the protolith. Nickel concentrations attain the maximum values about 2.4 wt% in the coarse saprolite as compared to only about 0.2 wt% in the bedrock. Toward the limonite zone, Ni gradually decreases down to 1 wt% in the red limonite zone. V concentration is very low (in ppm level) but it show steadily increasing in the profile upward. The differences in concentration factor between Ni and Co of the profile indicate that eventually those elements differ in mobility during chemical weathering of ultramafic rocks.
3.2.2 Weathering indices and mass balance calculations

Weathering indices calculation show that Ruxton Ratio (RU) values of bedrock sample in a profile from west block (SL) was higher than bedrock sample in a profile from Petea block (PL). This was due to the slightly lower silica and higher alumina in bedrock of PL profile which was likely induced by the introduction of water during serpentinization process that predates weathering. RPI and JE show relatively similar values in the bedrocks of both profiles. The intense chemical weathering has led to mobilization of silica keeping alumina as immobile component. It is generally shown that all calculated weathering indices of PL profile have higher values than those of SL profile especially in weathered materials, suggesting that mobile behavior of silica is more extreme at the SL profile. RPI graphic in the upper PL profile show zigzag patterns implying that retention of silica in the weathering zones of PL profile due to the slow dissolution rate of serpentine. During progressive weathering, SiO$_2$ is leached out faster in SL profile than in PL profile. Alternatively, divalent iron is more mobile during serpeninization, leading to slight reduction of total iron containing in bedrock in the PL profile from Petea block.

All weathering indices considered in this study show negative trends toward the limonite zones indicating relative immobility of Al$_2$O$_3$ in the weathering profile and significant loss of mobile element. It is also shown that bulk density values are minimal occurring in the saprolite-limonite interface but increase toward the top of profile, implying that the profiles have collapsed.

The intense weathering of ultramafic rocks leads to strongly loss of mobile elements (e.g. Si) and leaving immobile components such as Al, Fe, and Ti. Olivine and pyroxene which contain Si in the west block protolith leaches out more rapidly than does serpentine in Petea bedrock. On the contrary, Al, Fe, and Ti in both protolith have left as immobile elements in the weathering zones. In weathering profile developed over ultramafic rocks, Al$_2$O$_3$ released from the alteration of primary silicates (e.g. pyroxene), serpentine and spinel is immobile, being precipitated in secondary phases such as clays or incorporated into goethite structures. Similarly, the iron is considered to be immobile component due to the
retention of Fe in secondary phases mainly goethite (Price and Velbel, 2003). It is apparent that different degree serpentinization of protolith has impact on the resultant weathering rate of ultramafic rocks over the two blocks. Generally, the increase of weathering indices and bulk density with depth indicates that the application of mobile to immobile oxides ratio is best candidates in characterizing the weathering profile as suggested by Duzgoren-Aydin et al. (2002). However, the application of weathering indices involving alumina and titania in the weathering study of ultramafic rock has drawback due to the low content of these elements in such rocks.

Results of mass balance calculations for SL profile in the west block show that Si, Mg and Ca have strongly depleted at the saprolite zone (av. 80 %, 90% and 74% respectively) which correspond to the mass transfers of average about -456 kg Si, -726 kg Mg, and -8 kg Ca per cubic meter of weathered bedrock which is followed by the increase an average about 100 % Fe, 114% Mn, and 61% Co (i.e. +186 kg Fe, +3 kg Mn, and +0.2 kg Co per m³). The absolute enrichment of Ni is 467 % (+36 kg) was noted at the lower saprolite zone. At yellow limonite zone, the average depletion rate was 97% of Si (-560 kg) and 98% of Mg (-760 kg). Nearly all Si (100 %) and Mg (100 %) have been leached out from the top of profile which is corresponding to the losses about 576 kg Si and 774 kg Mg. The enrichment factor of Mn was strongly increased by about 646% (+19 kg/m³) and Co was about 865% (+3 kg/m³).

In the case of PL profile, transformation of 1 m³ of parent rock into the saprolitic materials leads to depletion an average 62% Si, and 90% Mg which is corresponding to the elimination about 270 kg Si and 518 kg Mg respectively. These losses were compensated by the enrichment about 208 % Fe (+ 244 kg), 125% Cr (+9 kg), and 288% Ni (+16 kg). At limonite zone, depletion has occurred about 71% of Si (-315 kg), 99% Mg (-575 kg) and 93% of Ca (-1 kg). Conversely, about 313 kg of Fe, 18 kg of Al, 10 kg of Cr and 6 kg of Ni have been gained during the limonitization process. The maximum gains of Mn and Co occurred in the limonite zone were about 892 % and 609 % which are corresponding to the gains of +17 kg Mn and +1.3 kg Co respectively.
3.2.3 Mineralogy and chemistry of “garnierite”

Garnierites at Soroako have generally been found to occur widely at the lower part of laterite profiles and they seem to have well developed on unserpentinized peridotites. Conversely, the garnierite occurrences at Petea block have only rarely been found where it is predominantly underlain by serpentinized ultramafic rocks. On the basis of field appearances, mode of occurrences of garnierites in the Soroako laterite deposits can be distinguished into three groups: (i) thin layers (~1 mm to <0.5 cm thick) of garnierite on fractures/joints or slickensided fault coating developed commonly on unserpentinized peridotites but also rarely occur on serpentinized protolith. (ii) vein-filling fractures occurring both in unserpentinized peridotite and slightly weathered serpentinized ultramafic protolith which is locally intercalated with quartz or silica. (iii) matrices and/or some clasts as components in the conglomeratic or brecciatic peridotites that are cemented by iron oxides.

Microscopic analysis reveals textural variation of garnierite samples which consist of concentric growth banding with colloform lamellae, triangular banding and relative parallel alternating light and dark bands. Another typical texture is fibrous aggregate material which commonly developed on sepiolite and is associated with silica. Mineralogical composition of garnierites from Soroako west block determined by XRD shows that the mixtures of talc- and serpentine-like phases are the major component with kerolite-pimellite series dominant talc-like phase. Other components such as talc-willemseite series and Ni-smectite are also present in minor amounts. On the other hand, garnierite samples from Petea block demonstrate the domination of sepiolite-falcondoite series with trace amounts of silica. Only few samples show the mixture between kerolite-pimellite series and Ni-serpentine with minor amounts of quartz.

There is a tendency of NiO enrichment occurring at the light bands compared to the dark bands as indicated by SEM/EDX data. However, the variation of NiO is not always due to the zoning but it is related to the way in which Ni-rich solutions were precipitated (Tauler et al., 2009).
SEM/EDX analysis reveals that variation of elemental composition mainly appears as the changes in SiO$_2$, MgO, and NiO concentrations. Al$_2$O$_3$ is present in very low content (< 0.1 wt%); whereas FeO has wide range compositions. Other major oxides such as TiO$_2$ and CaO and trace elements such as Cr and Co are below detection limit.

It is generally demonstrated that chemical composition of garnierites is dominated by Si, Mg, and Ni. Spot analyses along the traverse across a kerolite vein reveal that chemical change between Mg and Ni existed. The values of Si remained constant across the vein while Mg displays relative depletion at the core as compared to the edge. Conversely, Ni apfu is increased from the margin toward the center of the vein. Nickel enrichment over magnesium at the core likely reflects the changes in solution chemistry during neoformation of kerolite – pimellite series (Wells et al., 2009).

Chemical compositions of garnierite samples obtained by SEM/EDX and EPMA cover a wide range interval between kerolite-pimellite, talc-wilemseite, lizardite-nepouite and sepiolite-falcondoite solid solution series. The highly chemical variations of garnierite samples suggests a complex mechanism of dissolution-precipitation of minerals phases which is likely controlled by physicochemical condition of solution (Tauler et al., 2009).

It must be noted that structural formulae deviate greatly from formulae for ideal serpentine: Mg$_3$Si$_2$O$_5$(OH)$_4$, talc: Mg$_3$Si$_4$O$_{10}$(OH)$_2$, and sepiolite: Mg$_8$Si$_{12}$O$_{30}$(OH)$_{14}$(OH$_2$)$_4$.8(H$_2$O). Deviation from the calculated ideal structural formulae is likely caused by contamination in the case of spot analyses reported for serpentine by talc and vice versa in chemical analyses reported for kerolite by serpentine. Similarly, in the case of sepiolite-falcondoite, total tetrahedral cations must be 12 or less, therefore the excess of Si can be explained by the presence of amorphous silica intergrown with Ni-sepiolite. The excess of Si in the Ni-serpentine may be an indicative for the contamination of quartz or amorphous silica in intimate association with this phase. Hence, it would have overestimated the amount of Si more than two.
3.3 Leaching Behavior of Saprolitic Nickel Ores

Results of mineralogical characterization of two saprolite ores used in this leaching study reveal that west ore (WO) sample mainly contains olivine, quartz, talc-like phases (garnierite) with minor secondary serpentine, pyroxene and goethite. Meanwhile, mineralogical composition of east ore (EO) sample is dominated by lizardite-1M [(Mg,Fe)3Si2O5(OH)4], a serpentine end-member with subordinate chlorite [(Fe,Al)12(SiAl)8O20(OH)16], enstatite, amphibole, maghemite [γ-Fe2O3] and quartz.

Bulk chemical composition shows that WO sample contains higher SiO2 (49.2%) and MgO (23.2 %) than EO sample (38.9 % SiO2 and 15.5 % MgO). These are consistent with the higher proportion of quartz and olivine in WO samples. The presence of significant amounts of quartz is also indicated by FTIR spectra at 887 and 791 cm\(^{-1}\). In contrast, Fe\(_2\)O\(_3\) and Al\(_2\)O\(_3\) show higher in EO sample as compared to the WO sample. It is assumed that iron in sample EO is not only occurred in maghemite but it is likely also held in the crystal structures of serpentine/lizardite and chlorite. Similarly, Al might also be present as adsorbed or substituted element within goethite and serpentine structures. The Mn and Co are relatively similar for both ore samples, while Cr is higher in sample EO. Chromium is mainly present in spinel, lesser in goethite, and trace amounts in pyroxene. Nickel content is higher in WO sample than EO sample. Nickel is principally associated with talc-like phases and serpentine-like phase (garnierite) in WO sample; whereas residual serpentine/lizardite is the main Ni-bearing phase in EO sample.

3.3.1 Dissolution of ore minerals

Leaching experiment results indicate that olivine in WO samples was completely dissolved which is followed by secondary serpentine. The iron-oxides, enstatite and talc were hard to dissolve and quartz seems not dissolved at all. For EO sample, residual primary serpentine was readily dissolved in acid which was followed by chlorite; whereas maghemite, esntatite, amphibole, and quartz were difficult to dissolve.
Rapid dissolution of olivine in WO sample indicates significant release of magnesium and lesser iron into solution. Reaction of silicon is presumed to occur and it also enters the solution, whereas goethite dissolution liberates iron, aluminium and possibly some trace metals such as Ni, Co, and Mn. Serpentine-like phase (secondary serpentine) which is mainly associated with talc-like minerals (garnierite) releases magnesium and nickel as well. For east ore (EO) sample, dissolution of residual serpentine shows incongruent as much of metal cations released into solution and leaving silica residues. Dissolution of chlorite likely releases iron and aluminum to solution. Silicon reaction likely occurs and also enters to solution, while maghemite dissolution releases iron. It is predicted that both iron and aluminum leached can further hydrolyze, resulting in iron/alumina precipitates. Leaching of residual serpentine not only releases significant Ni but also it may result leach residues rich in silicon.

Dissolution rates of silicate minerals can be affected by its crystal structures, depending on degree of Si-O polymerization. On the basis of leaching studies in connection with silicate structure, it is inferred that dissolution rates of primary minerals would be in the reducing order: forsterite > enstatite > amphibole > quartz. For sheet silicates, it is shown that relatively higher dissolution rates of serpentine (Mg/Si=3/2) as compared to talc (Mg/Si=3/4) due to the easy access of acid in serpentine as compared to talc structures. This fact indicates that talc is more resistant to acid attack and dissolution rates is slower than other sheet silicate minerals including serpentine (Jurinski and Rimstidt, 2001; Okada et al., 2003).

Another factor that may affect the dissolution rates of silicate minerals is properties of metal cation in silicate structures (Terry, 1983). Silicon-oxygen bonds are much stronger than other metal cation-oxygen bonds. Hence the metal-oxygen bonds with lower valency states are more prone to acid attack. The extent of hydroxyl bonded to metal cations in phyllosilicate minerals may also increase dissolution rate due to their bond strength is weaker. It is suggested that, higher dissolution rates of serpentine as compared with talc could be related to the higher content of crystal water in serpentine structures (ideal value of 12.9 wt% H₂O) than in the normal talc (4.8 wt% H₂O).
Relative stability of silicates in acid is also related to polarising power of metal cation. This can be presented in ionic potential (ratio of ionic charge to ionic radius). Minerals with high ionic potential are inert to acid; whereas silicate cations with low ionic potential are readily soluble in acid (Terry, 1983). Rates of chemical reaction of minerals with acid are also affected by crystallinity, impurities, grain size, dislocation and porosity (Terry, 1983). Poorly ordered crystalline minerals would be more reactive than well crystalline phases. In the case of serpentine, weathering process has led to substitution of metals such as Fe, Al, and Ni for Mg in serpentine structures. Effect of these substitutions might cause octahedral shrinkage and tetrahedral expansion (Liu et al., 2009). This deformation might weaken the crystal stability thereby acid attack would be easier (Lander and Gilkes, 2007). It is suggested that rapid dissolution occurs preferentially for residual serpentine with higher iron content and low crystal order.

### 3.3.2 Leaching rates of metals

SEM/EDX results show that MgO and NiO are strongly depleted in solid residues during 2 hours leaching as compared with the original WO samples. Iron content show slight decreasing but SiO₂ is significantly increased. The strong increase of SiO₂ concentration in solid residues is consistent with the presence of quartz and/or unleached silica in solid residues as indicated by XRD patterns. Mostly Mg and Ni in solid residues were likely bonded to talc-like phase (garnierite) as this mineral was difficult to dissolve. Iron might be present in magnetite/goethite or alternatively held in unleached talc and enstatite structures. In the case of east ore (EO) sample from Petea block, the strongly depleted of MgO in solid residues along with undetected NiO by EDX indicates the fast dissolution rates of residual serpentine as the main component. Similarly, the significant reduction of FeO in solid residue suggests that this element is associated with serpentine or iron oxides as well. In contrast, the significant increasing of SiO₂ in solid residue is corresponding to the presence of unleached quartz and amorphous silica.
Distributions of leaching rates of metals demonstrated that there are slight variations of metal extractions from both ores throughout the time interval of experiment. This is likely influenced by the complexities of minerals in both ore samples. Leaching rates of Ni and Mg was higher from EO sample (58 % and 74 % respectively) which was achieved for 120 minutes reaction as compared to that from WO sample (47% and 59% respectively). Relatively higher of Ni and Mg that could be recovered from EO sample may be due to the fast dissolution of residual primary serpentine as the main component. Protonation is relatively easy in the serpentine structures as compared to the talc-like structures.

In contrast, the extraction rate of Fe (61 %) was higher from WO sample which could be reached at longer reaction time (150 minutes). In addition to goethite, Fe in WO sample is most likely present in divalent cation as as solid solution in the primary phases such as olivine; while in EO sample Fe mainly occur in serpentine and maghemite. Solubility of Fe$^{3+}$ is much lower than Fe$^{2+}$ (Cornell and Schwertmann, 2003). Leaching rates of Co (70 %) and Mn (65 %) were also higher from WO sample as compared to those from EO sample (i.e. 49 % and 58% respectively). It is inferred that Co-bearing Mn phase occurs and is masked with iron-oxides (goethite) in WO sample. Some Co and Mn were also expected to be solid solution with other divalent metals in octahedral structure of silicates. Cobalt and Mn have similar kinetic dissolution in acid solution, however, Georgiou and Papangelakis (2009) have found that cobalt is more rapidly liberated in aqueous phase as compared to manganese.

Both Al and Cr show slower leaching rates as indicated by maximum extractions of 12% for Al and 19 % for Cr from WO sample. Leaching rate of Al and Cr was 22 % and 12% respectively that could be reached from EO sample at for 120 minute reaction. The lower leaching rates of these two elements may be partly controlled by their mode of occurrence in the saprolite ore. Chromium mainly occurs as spinel group (spinel, chromite or magnetite). These phases were relatively resistant to acid, even after long periods of reaction (McDonald and Whittington, 2008). Aluminum is likely held in spinel or substitutes in part for Si in tetrahedral coordination or alternatively replaces for Fe in goethite structure.
4. Discussion

4.1 Nature of Ultramafic Rocks at Soroako: Their Relation to Nickeliferous Laterite Formation

Soroako West Block: Unserpentinized ultramafic protolith at Soroako west block consists mainly of harzburgite. However, dunite lenses are locally found as well. The rocks are essentially composed of olivines and minor orthopyroxenes with trace clinopyroxenes and spinels. Olivines are characterized by higher in Mg# (0.91 – 0.94) and NiO (0.30 - 0.50 wt%). With respect to the formation of nickeliferous laterite deposits, it has shown that higher Ni (0.27 – 0.36 wt%) of the bulk-rock compositions of ultramafic rocks from Soroako west block are most suitable as nickel source for high grade ore through supergene enrichment process in the weathering profile. The deposits at west block are unique as they have been formed by weathering of unserpentinized peridotite protolith resulting in silicate ore type. Forsteritic olivines, rich in Ni, which dominate mineralogical composition of peridotites at Soroako west block have significant roles in supplying Ni for development of the overlying laterite deposit. The presence of kink bands, undulose extinction and recrystallized olivine grains may promote dissolution rates during the chemical weathering. Microfractures developed in both olivines and pyroxenes can provide pathway for solutions to extensively chemical attack due to the increase of effective surface area of crystals (Eggleton, 1986). These evidences are indicated by the existence of weathering rims so called iddingsite and incipient secondary phases occurring primarily at olivines and lesser at pyroxene crystals.

Petea Block: Ultramafic rocks at Petea block are characterized by medium to strong serpentinization degree of dominated-harzburgites. Serpentinization involves the physical and chemical changes induced by hydration. This process has led to increase the rock volume that was marked by development of pseudomorphic textures such as mesh and bastite (Mevel, 2003; Lambiv Dzemua and Gleeson, 2012). The presence of magnetites that accompany serpentinization may indicate the higher oxygen fugacity of the system. Alteration of
orthopyroxene to serpentine produces significant amounts of SiO$_2$. This silica would react with MgO released by serpentinization of olivine leading to the formation of additional serpentine. The absence of brucite [Mg(OH)$_2$] in analyzed samples from Petea block may be due to the suppression of serpentine formation through SiO$_2$ – MgO reaction (Shervais et al., 2005; Frost and Beard, 2007).

Results of EPMA analysis reveals that serpentine in fully serpentinized ultramafic rock (dunite protolith) contains much higher NiO than those of partly serpentinized peridotite (harzburgite protolith). This is consistent with the elevated nickel content of original olivine (up to 0.5 wt% NiO) as compared to the original orthopyroxene (0.1 wt% NiO). It has shown that pervasive serpentinization of olivines and pyroxenes in some extent have led to redistribution of nickel and other mobile elements. Because Ni has intermediate mobility, some of this element would be readsorbed by fine grained serpentines that have previously replaced the original olivines. Dissolved Ni is also incorporated in serpentine mesh and is subsequently fixed with serpentine veins. It is apparent that Mg is strongly declined in the most analyzed components of serpentinite. This is might be caused by the higher mobility of Mg than that of Ni. Iron also seems to have been lost during hydration of olivine in which is enhanced by high water/rock ratio (Gahlan et al., 2006). Generally, nickel concentrations in decreasing order would be olivine relics, serpentine mesh, and serpentine vein.

With respect to serpentinized harzburgite, Ni concentrations in bastite, mesh and vein are variable depending on its precursor mineral and textural context. Ideally, serpentine bastite should contain lower Ni than serpentine mesh. However, the anomalous value of Ni in the analyzed bastite from Petea samples indicates that it probably derives from adjacent Ni-rich olivines. Pyroxene bastite contains much lower Ni as compared to the assuming original pyroxene. Serpentine mesh and serpentine vein of altered harzburgite also contains lower Ni than those original minerals, implying that Ni was slightly lost during serpentinization. This was confirmed by Golightly (2010) who suggested that alteration of olivine to serpentine ± brucite reduces Ni grade from ~0.30 % in olivine to ~0.25 % in derived serpentine.
4.2 Mineralogical evolution in the laterite profile

Profiles at the Soroako West Block: During the early stage of weathering, olivine weathers first followed by enstatite and then diopside (Colin et al., 1990). Incongruent dissolution extends to epitaxial transformation of olivines to phyllosilicates mainly trioctahedral smectite (saponite) and iron oxy-hydroxides (e.g. goethite) under tropical weathering condition (Nahon et al., 1982; Eggleton, 1986). Weathering of olivine may also produce goethite without any formation of sheet silicates leaving behind free silica.

Rates of weathering of orthopyroxene and clinopyroxene differ as well in which the enstatite weathers two times faster than diopside (Colin et al., 1990). Weathering of enstatite can produce talc or serpentine (Eggleton, 1982; Wang et al., 2009) and amphibole, more likely actinolite or tremolite called “uralite” as suggested by Tardy (1997). Spinel is an assecory of mineral in peridotite. Despite relatively resistant to weathering process, however, under slightly oxidized conditions, spinel shows primary dissolution along the crack or the margin leading to the loss of Cr and Mg (Traore et al., 2008). Hydrolysis of chromian spinel initially occurs in the saprolite zone, producing Cr(OH)$_3$ which favor in the moist and slightly reduced conditions to maintain Fe$^{2+}$ ions in solution. This situation prevails in the middle zone of the profile or at saprolite – limonite interface. The Cr(OH)$_3$ produced can be adsorbed onto the surface of crystal structure of Fe- or Mn-oxihydroxides (Fendorf, 1995; Cooper, 2002).

In the lower saprolite, it is indicated that saponite is further transformed into dioctahedral smectite (e.g. Fe-rich montmorillonite) since the significant loss of Mg. The absence of nontronite may suggest that Si is also eventually leached out leaving behind Fe as residual materials. Smectite does not survive in longer wet condition as typical of humid tropical region (Ahmad, 2008) and is further changed into oxy-hydroxides minerals mainly goethite.

At the saprolite zone, secondary serpentine is also gradually dissolved leading to remove of Mg and leaving behind of silica. In contrast, talc is relatively undissolved and it survives up to lower limonite zone. Amphibole is departure to break down toward the upper profile. The disappearance of secondary silicates in
middle profile has increased the proportion of goethitic materials that maintain certain degree of original rock texture (Barros de Oleivera et al., 1992). Locally, precipitation of silica as amorphous or poorly crystallized products also likely occurs mainly within the cavities left by dissolution of primary hypgenous minerals (Colin et al., 1990).

When the most of soluble elements have been leached out, Ni is also more soluble in this environment and part of it moves downwards to accumulate at deeper zone of the profiles forming “garnierite”. This is possible because pH solutions increase to be more alkaline with depth (Taylor and Eggleton, 2001). A small amount of nickel retains in the ferruginous saprolite that constitutes oxidized or lateritic ore (Barros de Oleivera et al., 1992).

The last stage of weathering at the top of profile is characterized by the earthy yellow- to red-brown materials called limonite. The original textures are no longer preserved. All secondary silicates have been totally decomposed at this zone and they have been transformed into goethite. In time, the episodic desiccation result in dehydration of goethite and is ultimately transformed into hematite which covered the top of laterite profile (Figure 1).

**Figure 1** Schematic illustration of weathering profiles showing the different horizons and mineralogical evolution developed over unserpentinized ultramafic protolith in the Soroako west block.
The profiles at Petea Block: Bedrocks of laterite profiles in the Petea block are predominantly composed of primary serpentines and minor pyroxenes (i.e. enstatite) with trace amount of chlorite and magnetite. During the initial stage of chemical weathering, enstatite is firstly dissolved, resulting in secondary phases through one of the following sequential reaction (Noack et al., 1993):

1. Enstatite $\rightarrow$ Talc + (Quartz) + (Chlorite) $\rightarrow$ Goethite + Fe-hydroxides
2. Enstatite $\rightarrow$ Amorphous $\rightarrow$ Clay mineral $\rightarrow$ Fe-hydroxides

The absence of talc in the saprolite zone indicates that weathering of pyroxenes at Petea profiles tends to produce amorphous materials and smectite rather than talc (Eq.2). However, smectite is also not well evolved in the saprolite as has been confirmed by XRD analysis. This may be affected of local climate. Harder (1977) suggest that during wet season smectite cannot be formed because silica content of groundwater is very low. Amphiboles are likely the alteration products of pyroxenes or as residual material from precursor amphiboles at bedrock.

The intense chemical weathering has led to the transformation of magnetite into maghemite and goethite. This is possible because Fe$^{2+}$ contained in magnetite is totally oxidized into Fe$^{3+}$ (Cornell and Schwertmann, 2003). In contrast, serpentine remains unchanged during the supergene alteration so that it becomes predominant mineral occurring in the saprolite zone. Chlorite also seems to be resistant so that it remains appeared in the saprolite horizon. Progressive weathering results in increase the proportion of serpentine in the saprolite zone. Locally, serpentine is somewhat altered into smectite, but it was not longer preserved. Amphibole is further transformed into goethite at the limonite zone. It has also shown that chlorite is more stable than serpentine, especially in the lower limonite zone (Caillaud et al., 2004).

In the upper limonite, sheet silicate minerals such as serpentine and chlorite are unstable due to the groundwater condition is more acidic. At limonite zone, mostly secondary silicates were leached out so that goethite becomes dominant phase. Maghemite is likely stable up to the top of profile. Therefore red limonite zone is mainly constituted of goethite with lesser maghemite. Scheme depicting the mineralogical evolution of laterite profile at Petea block is given in Figure 2.
Figure 2 Schematic illustration showing the evolution of minerals in the weathering profile developed over serpentinized peridotite in Petaa block.

4.3 Elemental behavior during weathering

West block profiles: There is strong positive correlation between SiO₂ and MgO ($r = 0.854$) in the weathering profiles of west block, whereas the strong negative correlation of SiO₂ vs. FeO ($r = -0.98$) is indicated, implying the high immobility of iron in weathering profiles. The Fe³⁺ is only soluble under very acid condition, therefore when weathering solution is slightly neutralized, FeO(OH) is precipitated (Scott, 2008). Correlation of SiO₂ vs. Al₂O₃ and TiO₂ also show negative trend with $r = -0.84$ and $r = -0.79$ respectively; while SiO₂ vs. CaO shows positive relation ($r = 0.62$). Weathering indices and mass balance calculations show that SiO₂ was strongly leached out toward the top of profiles.

Aluminum shows positive correlation with other major oxides such as FeO, TiO₂ and MnO. Despite Al₂O₃ concentration reaches up to 7 wt% in the limonite zones, the amounts of Al are insufficient to form gibbsite [Al(OH)₃] and Al tends to incorporate into goethite structure where Al³⁺ ion can replace up to 33% Fe³⁺ in
goethite lattices (Cornell & Schwertmann, 2003). Weathering index calculation using Al₂O₃ and Fe-total as immobile component suggest that profile was collapsed as result of decreases in porosity and gravitational settling of the upper zone of profile. Titanium concentration is low with the maximum value of 0.2 %. This element might be carried by spinel or as solid solution with Si in tetrahedral sites of silicate minerals. In the weathering profile, Ti⁴⁺ ion (radius=0.61Å) may substitute for Fe³⁺ (radius=0.55Å) in goethite structures (Scott, 2008).

Manganese oxide (MnO) has negative correlation with SiO₂ but it shows positive trend with TiO₂, and FeO. Manganese concentrations of three studied profiles from the west block show elevated values between 1.9 and 3.8 wt% in the saprolite – limonite interface (transition zone) upward. Mass balance calculation reveals the enrichment of Mn about 645% occurring at the limonite zone. Manganese is presumably released from bedrock as Mn²⁺ and is oxidized into Mn⁴⁺ during weathering. It may also be leached from the near-surface limonite under low pH condition with high CO₂ activity (Marker et al., 1991). When Mn-bearing solutions reach the lower part of limonite zone, the increased pH due to hydrolysis of silicates are resultant of the oxidation of Mn²⁺ and/or precipitation of Mn oxides from colloidal solutions (Jenne, 1968; Marker et al. 1991).

Behaviour of Cr in weathering profiles of west block shows that Cr has good positive correlation with FeO (r=0.86) and Al₂O₃ (r=0.76), indicating the immobility of these elements at weathering profiles. Although Cr is commonly bound in spinel structures, however, if it remains in the trivalent state, Cr is insoluble and up to 6500 ppm and 3800 ppm may be incorporated into goethite and hematite (Scoot, 2008).

Cobalt show very good correlation with MnO (r=0.90) and it concentrates at the lower limonite zone. This element is associated with asbolane or manganese wad. This was confirmed by mass balance results which show an enrichment of Co about 865%. The Co content in asbolane from Soroako laterite sample ranges from 0.3 to 3.1 wt% (Chen et al., 2004).
Petea block profiles: Major element distribution in the Petea profiles shows that MgO and SiO$_2$ have rapidly leached out during the first stages of weathering but their depletion show somewhat lower than that of west block. On the contrary, FeO, Al$_2$O$_3$ and MnO are residually concentrated in the weathering zone upward. The lower leaching rates of SiO$_2$ and MgO are possible because serpentines content of the bedrocks from Petea profiles have relatively lower dissolution rates than olivine and pyroxene. The strongly negative correlations is indicated by binary plots of SiO$_2$ vs. Al$_2$O$_3$ ($r = -0.96$), SiO$_2$ vs. FeO ($r = -0.96$) and SiO$_2$ vs. MnO ($r = -0.75$). Similar relations can be found between SiO$_2$ and other trace elements (Cr, Co and V) in the profiles. This confirms the different mobility of silica with respect to alumina, iron, manganese and other trace elements (Cr, Co, and V). Conversely, FeO has positive correlation with Al$_2$O$_3$, TiO$_2$, MnO and other trace elements (Ni, Cr, Co, Zn, and V). Overall, the values of correlation coefficient for trace elements show positive, indicating their similarity in mobile behaviour at weathering profiles.

The enrichment of Co occurs in the saprolite – limonite interface where Co content can reach up to 0.35 wt% as compared to bedrock ~0.01 wt%. At the weathering profile, Co is adsorbed by Mn$^{4+}$ colloids and/or incorporated into Mn oxi-hydroxides (Traore et al., 2008; Manceau et al., 1987) such as lithiophorite or asbolane. Precipitation of Co is more effective at higher pH, because solubility product of Co(OH)$_2$ is lower than that of Mn(OH)$_2$ and adsorbed Co becomes permanently fixed with aging (Lambiv Dzemua et al., 2012). This feature can explain the absolute enrichment of Co about +609% and enrichment factor for Mn is about +892%.

The overall studied profiles at Petea block show that trace element concentrations (Cr and Co) are slightly lower than that in west block profiles. This is likely due to the differences in: (a) concentrations of those elements in the protolith, (b) dissolution rates of minerals in the protolith as source for those elements, (c) mode of occurrence of these elements in minerals of the respective profiles.
4.4 Nickel cycle in the profiles

Soroako west block. The pathway of nickel is transferred and accumulated on the weathering profile is illustrated in Figure 3. Nickel is originally held in olivines structure and is released during first stage of chemical weathering, leading to increase the absolute abundance of Ni. Density of fractures may control the formation of Ni-rich secondary minerals on the saprolite horizon. Some Ni-bearing solutions derive from the overlying saprolite, moves downward and precipitates as fracture filling materials at the base profile in the form of Ni-rich silicate or garnierite. Some other Ni may be adsorbed onto amorphous iron hydroxides and trace amounts are fixed with residual talc and smectite. The combination of these materials form saprolite horizon with the bulk Ni content reaches up to 4.2 wt% and absolute enrichment reaches up to 467 %.

Progressive weathering results in destabilizing the Ni-bearing phases lead to remobilization of Ni in the limonite zone. Much of Ni is reprecipitated with Mn-oxides as neoformed minerals (e.g. asbolane, lithioporite) resulting in extreme Ni enrichment. However, Ni is not “permanently” fixed after adsorption of Mn-hydroxides, so that in time, Ni releases into solution where pH is drop. Recrystallization of ferrihydrite into goethite also releases Ni, leading to reduction of Ni content in the limonite zone.

Goethite contains low Ni at limonite, but it is important minerals in oxides ores because goethite is predominant constituent. Chen et al. (2004) reported that average content of goethite from Soroako sample is about 1.4 wt%. Relatively low Ni uptake in goethite structure is more likely caused by the differences of valence states between Ni$^{2+}$ and Fe$^{3+}$. Substitution of Ni leads to distortion of goethite, so that it is needed charge compensation by incorporation of other elements into the structure. At the red limonite Ni is strongly decreased with the value as low as 0.5 wt%. Continuous reduction of Ni might be due to dissolution and recrystallization of goethite. This leads to leaching of Ni due to lowering pH at near surface condition as common features of the humid tropical climates. Lander et al. (2009) also has postulated that some Ni is ejected from neo-formed hematite upon thermal transformation of goethite.
Figure 3 Schematic model illustrating the nickel cycle in weathering profiles at Soroako west block. Note: ▬ = approximate Ni content of minerals, ↔ = mineral transformation, ⇆ = Ni transfer.

Petrea block. The manner of nickel is transferred among the minerals in the Petrea block is illustrated in Figure 4. Nickel is mainly hosted in primary serpentine and trace amounts in chlorite, and pyroxenes. At the beginning weathering, serpentina remain unaffected but supergene nickel enrichment might occur through exchange reaction. In this process, some Mg$^{2+}$ ions are replaced by Ni$^{2+}$ (Golightly, 1981) in serpentine structures as the following reaction:

$$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Ni}^{2+}_{\text{aq}} \rightarrow [\text{Mg}_2\text{Ni}]\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Mg}^{2+}_{\text{aq}}$$

serpentine Ni-serpentine

Part of Ni is also incorporated into smectite, maghemite and iron-oxihydroxydes. These materials cumulatively form saprolite zone with the bulk Ni concentrations are within the range between 1.2 and 2.4 wt%. Mass balance calculation assuming constant volume shows an absolute enrichment of Ni in this zone about 460%.
Pelletier (1996) demonstrated that Ni grade of residual serpentine and iron oxihydroxydes can reach up to 5 wt% without any precipitation of garnierite. Recrystallization of limonite into goethite releases Ni into solution then it moves down through the profile which is readily saturated. If minerals at the saprolite are saturated, then garnierite may occur. However, garnierite in the Petea block is not well developed as compared to Soroako west block. This might be influenced by physicochemical properties of residual serpentine as host for Ni such as crystallinity and grain size. Lizardite crystals can accommodate the highest nickel content particularly in the smallest crystals. It is therefore suggested that serpentine in the weathering zone has important role acting as nickel trap and this might be responsible for the suppression of garnierite formation.

Mobilization of nickel requires a pathway where weathering solutions moves from a low pH in the overlying limonite down to the high pH environment. With continued weathering higher in the profile, above water table, Ni-rich serpentines lead to leaching Ni and precipitation of goethite and locally Mn-oxihydroxydes. These materials combine to form limonite zone dominated by goethite. Minor quantity of Ni is still retained in goethite and some other is adsorbed by Mn-oxides. Hence the bulk Ni content of limonite is slightly higher within the ranges between 1.0 and 1.5 wt% but it is appreciably lower than underlying saprolite.

Dissolved nickel further percolates downward with some other are incorporated or adsorbed onto maghemite, residual chlorite and poorly crystalline goethite located in the upper saprolite. Much of nickel is apparently reprecipitated in the lower profile to form garnierite or by substitution for Mg in the octahedral sites of residual primary serpentine producing the extreme nickel enrichment (Elias et al. 1981).

At the top profile (red limonite), Ni concentration is strongly depleted with the grade is generally in the range of 0.5 wt% to 1.0 wt %. Dissolution of iron oxides in the red limonite results in recrystallization of goethite followed by its thermal transformation into maghemite or hematite. At this zone, nickel is soluble at the acidic condition then is mobilized downward and precipitated in the lower profile when environment is mildly slightly alkaline.
Figure 4 Schematic model showing the Ni cycle in weathering profiles of Petea Block. Note: ● = estimated nickel proportion in minerals, ⇒ = nickel transfer, ⇀ = mineral transformation.

4. 5 The origin of Ni-Mg hydrous silicate ores (garnierite)

Soroako west block: Garnierite at west block commonly occurs at the base of profile in the form of vein filling fracture, slickenside fault coating, and clasts or matrices components of the breccias. The color of materials is generally medium green but locally pale green also occurs. They are clearly extensively developed on unserpentinized peridotites with highly fractured intensities. It is inferred that garnierites at Soroako west block have been precipitated at least in two generations; namely the early-formed garnierite and the late-formed garnierite.

The early-formed garnierite including vein-1 and fracture coating was derived from precipitation of Ni-rich solutions produced by both dissolution of primary magmatic minerals and leaching of other Ni-bearing phases from overlying weathering profile. However, tectonics reactivation in the region likely occur
leading to displacement of fractures resulting in the formation of slickensided faults. Tectonic process has also created blocks resulting in breccia zones with high fractions of open space as a site for garnierite precipitation (Golightly, 2010). The occurrence of matrices or clasts of garnierite higher in Ni grades as component within the breccias indicates that late-formed garnierite was related to the brecciation induced by hydrofracturing. Nickel supply could be originated from dissolution of early-formed phases plus other Ni-bearing phases overlying saprolite zone. The sequence of precipitation would be: garnierite Vein-I + slickensided fault coating \(\rightarrow\) garnierite Vein-II + matrices/clasts.

Textural evidences obtained from microscopic and SEM analyses (e.g. colloform banding, fibrous aggregates), coupled with poorly crystallized materials as indicated by X-ray diffractograms, suggest that garnierites have been precipitated from colloidal suspension with low temperature condition (Brindley \textit{et al.}, 1977). The results of mineralogical analyses reveal that garnierites at Soroako west block were principally composed of the mixtures between kerolite-pimellite and lizardite-nepouite series with lesser talc-willemseite and Ni-rich smectite. Variations of mineralogy observed may indicate the episodic changes in chemistry of solution particularly activities of Si, Mg, and lesser Al (Golightly, 1981). The 2:1 layer silicates (talc-like phases) are preferentially precipitated over the 1:1 layer silicates (serpentine-like phase) where Si activity is higher than Mg but Al activity is low (Birsoy, 2002). The presence of discrete magnetite crystals in association with garnierite indicates that iron is not accommodated in garnierite minerals. Alternatively, the absence of iron in garnierites can be explained by the condition of their formation because iron is not soluble under oxidizing condition. Garnierite may precipitates at ambient temperature from solution with higher oxygen fugacity (Pelletier, 1996; Song \textit{et al.}, 1995). Precipitation of garnierite is possible in the lower profile due to the changes in pH of solution. At the upper profile, weathering solution is slightly acidic (pH<7). However at the lower profile, the pH of solution is slightly alkaline (pH>7) due to the rock-water interaction (Taylor and Eggleton, 2001).
The occurrence of quartz replacement may result from periodic dry-wet condition or from retarded drainage in a more acid environment (Golightly, 1981). During the dry season in the humid tropical climates with minimum rainfall, silica concentrations are very high (Harder, 1977). Formation of quartz in the weathering profiles possibly occurs from colloidal silica → opal → chalcedony → macrocrystalline quartz (Zeissink, 1969).

**Petea Block:** Garnierites from Petea block are characterized by mm to cm thick of discontinuous veining. Their occurrences are rare and generally hosted in slightly weathered serpentinitized peridotite. Mineralogical composition of garnierite samples shows that sepiolite-falcondoite series are the main phase with minor quantity of lizardite-nepouite and kerolite-pimellite series. Quartz is commonly associated with Ni-korolite; while sepiolite-falcondoite has been found to be associated with amorphous silica rather than quartz. This indicates that sepiolite may form in more alkaline environmental condition with pH (~8.0 to ~9.5), high (Mg+Si)/Al ratio and low $\rho$CO$_2$ (Birsoy, 2002; Galan and Pozo, 2011). According to Yalcin and Bozkaya (2004) sepiolite can be formed directly from solution produced by dissolution of serpentines in the presence of amorphous silica with lower Al activity as the following reaction:

$$8\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{H}_4\text{SiO}_4 \rightarrow \text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH}_2)_4.8\text{H}_2\text{O}$$

*serpentine* \(\rightarrow\) *sepiolite*

Sepiolite showing fibrous aggregates morphology and kerolite displaying banding are typical of crack seal crystallization. Microscopic and EPMA analyses of a garnierite vein hosted in serpentinite indicate that this banded vein can be regarded as material that formed through crack seal process (Ramsay, 1980). This is considered the evidence of episodic crack opening driven by oscillation in fluid pressure (Wiltschko and Morse, 2001). Pressure solution is the process where the minerals dissolve as result of the pressure externally applied to them. Minerals under pressure are more susceptible to dissolve than unstressed minerals (Cluzel and Vigier, 2008). Transport of materials from dissolution sites to precipitation sites may take place through diffusion (Bons and Jessel, 1997). Materials precipitated in veins are due to variation of chemical activity of solution that can
be attributed to changes of temperature, fluid pressure, and differential stress (Andreani et al., 2004). Chemical weathering of ultramafic rocks leads to release Ni ion into solution. Because Ni cannot move away from its original location, then it is needed a way to enhance mobilization process toward the precipitation sites (Cluzel and Vigier, 2008).

It is shown that precipitation was commenced from the center of the vein and crack-seal process propagates at both sides toward the wall rock. This is a typical of antitaxial vein (Passchier and Trouw, 2000; van der Pluijm and Marshak (2004). The increments of cracking occur at the boundaries between bands or fibres and the vein walls possibly because the bonds are weakest. The fractures filled and matrices supported materials require active crack opening to allow the distinct phases to be precipitated within the open spaces (Cluzel and Vigier, 2008). Microanalysis across a kerolite banded vein reveals that Ni concentration decreases; while Mg increases from the center toward the margin of vein. This evidence is opposite with previous study of serpentine banded vein by Andreani et al. (2004) who found that chemical compositions of different bands were relatively constant.

In general, the scarcity of garnierites occurring at Petea block as compared to the west block may in part be controlled by different physico-chemical properties of ultramafic protolith and their weathering products. Peridotites at Soroaoko west block are unserpentinized and these rocks are characterized by medium to coarse grained and massive. However, their higher fracture intensities are prone to weathering thereby releases Ni into solution. The fractures are also acting as pathways to allow the rapid percolation of Ni-saturated solution downward and precipitate at the base to form Ni-hydrous silicate veins where condition becomes slightly alkaline.

On the contrary, the bedrocks at Petea block are typically consisted of the highly serpentinized peridotites with fine-grained texture. The rocks are characterized by well crystallized lizardite. However, the intense weathering of serpentine has led to formation of saprolite which is primarily composed of poorly crystallized, residual serpentine. According to Pelletier (1996) saprolite derived
from serpentinized peridotite shows a better cohesion than unserpentinzed rocks. These properties may preclude precipitation of garnierite because Ni\(^{2+}\) in weathering solution is readily adsorbed onto crystal surfaces or substituted for Mg\(^{2+}\) ions in octahedral sites of serpentine structures.

In summary, garnierites in the Soroako were formed by both precipitation of Ni-bearing solution as open space filling (mainly for west block) and crack seal process (mainly for Petea Block). Despite the mechanism of garnierite formation is actually complex, however, Gali et al. (2012) suggested that two main temporal and spatial trends were related to the supergene process of nickel, *i.e.* the leaching of Ni from iron oxihydroxides in the limonite horizon by meteoric waters and the repeated cycle of dissolution of Ni-poor phyllosilicates followed by equilibrium precipitation of Ni-rich phyllosilicates. The poor mobility of silica leads to increase the activity in time and reaching saturation level in the profile. The precipitation of Ni ore is then typified by a succession of mineral phases progressively enriched in Ni with more Si. Therefore, the sequence of precipitation would be: Ni-serpentine --- Ni-kerolite --- Ni-sepiolite like minerals.

### 4.6 Comparisons with other Ni-laterite deposits

Soroako laterite deposits represent the nickel ores which formed by intensive chemical weathering of ultramafic rocks in the humid tropical rainforest climate with the mean annual rainfall reach up to 2900 mm/year and an average temperature about 24 °C. The economic grade of Ni is predominantly hosted by silicate phases prevailing the deposit described as Ni-silicate ore (A type) according to definition of Brand et al. (1998). With respect to the protolith and climate history, Soroako nickeliferous laterite deposits are comparable with the deposits of New Caledonia (Troly et al., 1979) and Cerro Matoso, Colombia (Gleeson et al., 2004). All these deposits have been formed by weathering of ultramafic cumulates derived from the lower sequence of ophiolite complex that has been obducted onto the land since the Upper Miocene time.

Other deposits such as Murin-Murin and Kalgoorlie of Western Australia (Wells and Butt, 2006; Elias et al., 1981) and Niquelandia, Brazil (Colin et al.,
1990) are typical of clay silicate deposits with intermediate Ni grades. This deposit is developed over Archean komatiitic serpentinitized peridotite massifs and the highest Ni concentration occurs at smectite zone having the values up to 2.5%. In the Jacuba, Niquelandia of Brazil, nickel laterite profiles are formed by weathering of pyroxenites in which smectite developed over pyroxenites is acting as nickel trap where Ni laterally migrates from adjacent dunite and harzburgite weathering.

The oxides ore type is generally lower Ni grade than other two said classes. Examples of this type of deposits can be found in the Moa Bay of Cuba (Roque-Rossel et al, 2010); Goro of New Caledonia (Freyssinet et al., 2005); Greenvale of Queensland (Zeissink, 1969) and Cawse of Australia (Freyssinet et al., 2005) and Caldag in Turkey (Thorne et al., 2009).

4.7 Implication for hydrometallurgical processing

Although no commercial plant has been established to process the Soroako Ni laterite ores by means of hydrometallurgy to date, however, results of leaching experiment highlight some insight if leaching process is the choice for the future laterite ore treatment. For west ore (WO) sample, the complete dissolution of olivine leads to increasing Mg ions concentration in pregnant solutions. Despite all Ni was thought to have leached out from olivine structure, however, the highly leached magnesium is not favorable due to the more acid consumption (Whittington and Muir, 2000). Results of leaching experiment also reveal that west ore sample has low Ni recovery as compared to the east ore sample. The existence of kerolite (talc-like phase) as the primary Ni-host might be one factor for the low Ni extraction. Soler et al. (2008) suggest that dissolution rate of garnierite is incongruent at more acid condition indicating faster dissolution rate of serpentine than talc. The differences in mineral structure between serpentine-like phase (1:1 layer) and kerolite (2:1 layer) coupled with higher hydroxyl bonds of serpentine were the main reason for lower overall Ni recovery from west ore (WO) sample. The presence of undissolved minerals might not be indicative to affect Ni leaching but the potential of waste products should be accounted for.
In the case of east ore (EO) sample from Petea block, the high dissolution rates of residual serpentines results in co-extraction of Ni with Mg and Fe and production of amorphous silica. This is likely because H$_2$SO$_4$ concentration used in experiment was too high (~3M). In practice, formation of amorphous silica can have serious problem in further separating of metals from leached solution (Terry, 1983) because it may reduce filterability of slurry thereby a large quantity of water is required to attain satisfactory recoveries. However, residues of amorphous silica are easily pulverized and very reactive as compared to the crystalline silica. Therefore, this is potential as raw materials for the production of silicon carbide (Hirasawa and Horita, 1987). It is suggested that saprolitic ores from Petea block seem to have good potential for the future Ni extraction using atmospheric pressure leaching process.

The main constraint in application of acid technology at atmospheric pressure for recovering the Ni and Co from the high magnesium saprolitic ore is the large amounts of acid requirement. However, recent development in leaching technology (McDonald and Whittington, 2008a) indicates that reactive saprolitic laterite ore with higher magnesia can be used in second leaching stage to neutralize acidic liquor produced by the HPAL process.

Results of leaching studies should be a key in understanding of the future potential process for development of Ni extraction technologies from laterite ores. Because kinetics and mechanism of leaching of minerals within the ores are various, more efforts are needed to enhance the Ni extractions selectively by modifying the leach conditions (e.g. dilute acid) with various temperatures.

In summary, the low nickel recovery achieved from saprolitic ore of two blocks combined with co-dissolution of magnesium and iron may limit the application of sulfuric acid-based technology at atmospheric pressure. However with performed in conjunction with high pressure acid leach (HPAL), atmospheric leach (AL) seems to have promising due to effectively consumes acid. Mineralogy and reactivity of ore is very critical for high Ni extraction (McDonald and Whittington, 2008a). Hence, without suitable initial mineralogy studies, leach results are potentially subject to misinterpretation.
5. Conclusions and Future Outlook

5.1 Conclusions

The mineralogical and geochemical characteristics of the Soroako nickeliferous laterite deposits are the results of a complex interplay between geology and climate variables. The presence of suitable ultramafic protolith is primary controlling factor on the formation of economically important nickel laterite deposits. The following conclusions are comparison of nickel laterite deposits formed over unserpentinized vs. serpentinized peridotite:

1. Petrology and mineralogy unserpentinized ultramafic rocks at Soroako west block are characterized by variably fractured harzburgite and minor dunite containing predominantly olivines (>70 vol %) and higher in NiO. These rocks are the most suitable for the formation of economic grade nickel laterite ores. Conversely, peridotite in the Petea block is predominantly composed of serpentine (>60 vol %) showing pseudomorphic mesh texture after olivines and locally bastite after pyroxenes. Serpentinization process predated weathering has led to obliterate the original rock textures and slightly lost in nickel.

2. Distribution of minerals in the weathering profiles of unserpentinized rocks from west block contain secondary phases mainly goethite and “garnierite”; whereas the weathering of serpentinized peridotite at the Petea block results in the formation of saprolite zone which is mainly composed of residual serpentine. The complete weathering in the two blocks has led to the formation limonite zone in the upper profile which is predominantly composed of goethite. Distributions of elements in the weathering profiles of two block shows that Mg and Si were strongly depleted from the profile upward but Si was leached out faster from west block than from the Petea block profiles. Enrichment of Co and Mn occur at the lower limonite; while Fe, Al, Ti and Cr are residually concentrated on the upper limonite zones.

3. The supergene process of Ni assuming constant volume indicates two mechanisms of Ni enrichment in weathering solution, i.e. leaching of Ni from the upper portions of limonite zone by meteoric water and repeated cycle of
congruent dissolution of Ni-bearing primary minerals. At Soroako west block, Ni precipitation is mainly taking place at weathering front by reaction with silica and magnesium forming secondary Ni-hydrate phyllosilicates described as “garnierite”. In contrast, enrichment of Ni in the Petea block mainly takes place through the “exchange reaction” where Ni substitutes for Mg in octahedral sites of residual serpentine.

4. Garnierites were found more extensive at west block and they occur in the lower profile of the two blocks. The origin of garnierite may prevail one or two pathways, i.e. open fracture filling which is mainly developed on unserpentinized peridotite of the west block and crack-seal process which is found in serpentinized rocks of Petea block. Garnierites at west block are mainly composed of kerolite-pimellite with minor lizardite-nepouite, talc-wilemseite and Ni-smectite; whereas at Petea block, garnierite contains principally sepiolite-falcondoite with lesser kerolite-pimelite and lizardite-nepouite solid solution series. Variation of mineralogy and texture may reflect the episodic changes of solution chemistry. Garnierite precipitation occurs initially from solution with lower Si/Ni+Mg followed by higher Si/Ni+Mg ratio and Ni tends to increase toward the center of materials.

5. Leaching behaviour of saprolitic Ni ores from two blocks suggest that the presence of 2:1 layer silicates (talc-like phase) as the principal Ni-bearing mineral in the west ore and residual serpentine (1:1 layer silicates) in the Petea ore as the main Ni hosted could be accounted for different leaching rates. Extraction of Ni from Petea ore was higher than from west block, although generally leaching rates from both ores are still low. Co-dissolution of nickel with magnesium and iron indicates that leaching was not selective due to the strong proton attack for these reactive elements. With respect to hydrometallurgical process, this condition is not favorable due to high acid consumption. Dissolution of residual serpentine in the Petea ore was also result the formation of amorphous silica, which in practice, may inhibit further separation of valuable metals from pregnant solution.
5.2 Future Outlooks

The results of this work suggest some interesting points to be offered for the future investigations as follows:

1. Relation between bedrock jointing and development of nickel laterite deposits as hypothesized by Golightly (1981). Fracture spacing or fracture density of bedrocks can affect the rates and depth of laterite development. It is interesting and possible to measure the fracture density in the mine face before rehabilitation; while drilling record can be accessed. Soroako west block is the best sites for testing of this idea.

2. Further experimental leaching should be conducted for saprolite ore using dilute sulfuric acid to suppress leaching of undesirable elements mainly Mg and Fe. Other leaching parameters such as temperature, solid-liquid ratio and agitation speed should be considered in order to determine the optimum leaching condition. It is also interesting to carry out leaching study in the recovery of Ni from saprolite ore using chloride-based technology. Despite HCl is more expensive than H\textsubscript{2}SO\textsubscript{4}, however, previous studies demonstrated that Ni recovery was more effective by using chloride acid than sulphuric acid with the advantages that include low reagent requirement and magnesium can be recovered as by product. Bioleaching should also be considered to extract metals from laterite ore, because leaching with organic acids offer new green and clean technology with lower cost and lower energy demand than conventional processes.

3. It is highly suggested to perform the multiscale analyses for both original laterite ore samples and solid residues using novel technologies (e.g. QEM-SCAN, EPMA and LA-ICP-MS). This information is very important to improve a better understanding on the relationship between mineralogy, textures, grades and metal recoveries. The automated quantitative means for ore characterization is essential in optimizing extraction and processing methods.
References


A. Personal

Name: Sufriadin
Place/Date of Birth: Enrekang/17th August, 1966
Sex: Male
Nationality: Indonesian
Off. Reg. Number: 196608172000121001
Rank: III-C
Employment: Lecturer
Institution: Hasanuddin University
Faculty/Department: Engineering Faculty/Mining Engineering
Office Address: Jl. Perintis Kemerdekaan KM.10 Tamalanrea, Makassar 90245; Tel/fax.+62 0411 580202
Email Address: sufriadin_as@yahoo_com
Home Address: Jl. Gn. Lompobattang 206A Makassar 90114
Phone, mobile: (062)- 0411-322356; 081342760137
Spouse: Warzukni Wagimin, SE
Children: 1. Nurul Muslimah
          2. Muh. Zahran Mubarok
          3. Muh. Zahir Makhsum

B. Tertiary Education

2008 – 2013: PhD Program in Geology, Graduate Program of Geological Engineering, Faculty of Engineering, Gadjah Mada University.
             Thesis title: Mineralogy, geochemistry, and leaching behavior of the Soroako nickeliferous laterite deposits, South Sulawesi, Indonesia.

1999 – 2002: Master Program in Coal Science and Technology, Graduate Program of Mining Engineering, Bandung Institute of Technology.

             Thesis title: Geology and study of landslide at Kulinjang area, Enrekang regency of South Sulawesi, Indonesia.

C. Publications


