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Thermal and Infrared Studies of Garnierite from the Soroako Nickeliferous Laterite Deposit, Sulawesi, Indonesia

Analisis Termal dan Inframerah Garnierit dari Endapan Laterit Nikel Saroako, Sulawesi, Indonesia

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Abstract

Mineralogical characterization of some garnierite samples from Soroako have been conducted using X-ray diffraction, thermal analysis, and infrared spectroscopy methods. XRD patterns reveal the samples mainly containing the mixture of kerolite (talc-like phase) and serpentine with minor smectite, sepiolite, and silica. Thermal analyses of garnierite samples indicated by DTA curves are in good agreement with patterns that have been reported in literature. Three endothermic peaks normally occur in the ranges between 58º C and <800º C illustrating three steps of weight losses: adsorbed, bound, and hydroxyl/crystal water. One additional weight loss in low temperature region of sepiolite is corresponding to the lost of zeolitic water. Infrared spectra appeared in 3800 - 3200 cm^{-1} region generally exhibit broad absorption bands, indicating low crystallinities of studied samples and can be assigned to the presence of hydroxyl group bonded to octahedral coordination mainly Mg atom. The bands observed at 1660 cm^{-1}, 1639 cm^{-1}, 1637 cm^{-1}, and 1633 cm^{-1} in all samples indicate water molecules. FTIR spectra displaying the strong bands at 1045 cm^{-1}, 1038 cm^{-1}, and 1036 cm^{-1} could be related to the presence of Si-O-Si bonds linking to tetrahedral coordination. The strong absorption bands appeared at 511 cm^{-1}, 505 cm^{-1}, 499 cm^{-1}, and 496 cm^{-1} in respective samples are attributed to divalent cation bonds (*e.g*. Mg, Ni-O). Both TG/DTA and FTIR seem to be the powerful tool in diagnosing the crystal chemistry of garnierite which is mainly composed of phyllosilicate minerals.

Keywords: infrared, thermal analysis, kerolite, sepiolite

Sari

Penentuan karakter mineralogi percontoh garnierit Soroako telah dilakukan dengan menggunakan metode difraktometri sinar X, analisis termal, dan spektroskopi inframerah. Pola XRD menunjukkan percontoh mengandung campuran kerolit dan serpentin dengan sedikit smektit, sepiolit, dan silika. Analisis termal yang ditunjukkan oleh kurva DTA sesuai dengan pola-pola yang dilaporkan dalam literatur. Tiga puncak kurva endotermik yang terdapat pada kisaran termperatur antara 58º C dan <800º C menggambarkan tiga tahap kehilangan berat: air permukaan, air molekul, dan air kristal. Satu tambahan kehilangan berat di daerah temperatur rendah pada sepiolit berhubungan dengan air zeolitik. Spektra inframerah pada daerah 800 - 3200 cm^{-1} yang umumnya memperlihatkan serapan lebar, menandakan kristalinitas rendah dan berkaitan dengan keberadaan kelompok hidroksil serta terikat dengan koordinasi oktahedra, terutama atom Mg. Pita-pita yang diamati pada 1660 cm^{-1}, 1639 cm^{-1}, 1637 cm^{-1}, dan 1633 cm^{-1} untuk semua percontoh menunjukkan molekul air. Spektra FTIR yang menggambarkan pita kuat pada 1045 cm^{-1}, 1038 cm^{-1}, dan 1036 cm^{-1} dapat dikaitkan dengan kehadiran ikatan Si-O-Si yang bertautan dengan koordinasi tetrahedra. Pita-pita serapan kuat pada 505 cm^{-1}, 499 cm^{-1}, dan 496 cm^{-1} pada masing-masing percontoh berkaitan dengan ikatan kation divalen (Mg-O, Ni-O). Tampak bahwa baik TG/DTA maupun FTIR merupakan alat yang ampuh dalam mendiagnosis kimia kristal garnierit yang terutama disusun oleh mineral filosilikat.

Kata kunci: *inframerah, analisis termal, kerolit, sepiolit*

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Introduction

Garnierite was firstly discovered in New Caledonia by Jules Garner, a French mining engineer in 1865 (Pelletier, 1996). The term of garnierite is referred to a green coloured material with high nickel grade. However, until recently this term has not been approved by the Commission of New Mineral and Mineral Name (CNMMN) of The International Mineral Association (IMA) (Proenza *et al*., 2008). The nomenclature of garnierite was provided for the first time by Faust (1966) and the later examination regarding its use was reviewed by Brindley & Hang (1973), and Brindley & Maksimovic (1974). According to these authors, the term of "garnierite" can be applied in a general sense covering the mixture of hydrous Ni-Mg sheet silicate with 1:1 layer (7Å) and 2:1 layer with 10Å basal spacing. Recent study of garnierite from Goro nickel laterite deposits, New Caledonia, was reported by Wells *et al*. (2009), while the garnierite from Falcondo mine of Dominican Republic was studied in more detailed by Tauler *et al*. (2009). It is generally agreed that garnierite constitutes at least one or combination of the following mineral series: talc-wilemseite, kerolite-pimelite, lizardite-nepouite, chrysotile-pecoraite, chlorite-nimite, Ni-smectite, and sepiolite-falcondoite.

Although nickel laterite deposit of Soroako has been exploited for nearly about 40 years, the information about garnierite mineralogy of this deposit is poorly understood. Study on garnierite mineralogy by X-ray diffraction technique does not always provide good results because this material is very fine-grained in size, poorly crystalline order, and especially frequent occurrence as intimate mixture of two or more components. Additional techniques such as thermal and FTIR seem to be the power tools in the characterization of garnierite. The present paper deals with analyses of some garnierite samples from Soroako using the combination of XRD, Thermal, and FTIR methods.

Materials And Methods

Four samples used in this study were collected from saprolite horizons in the Soroako mining district, Sulawesi (Figure 1). Two of them were taken from west block and two other samples derived from Petea mine. Field description and mode of occurrence of

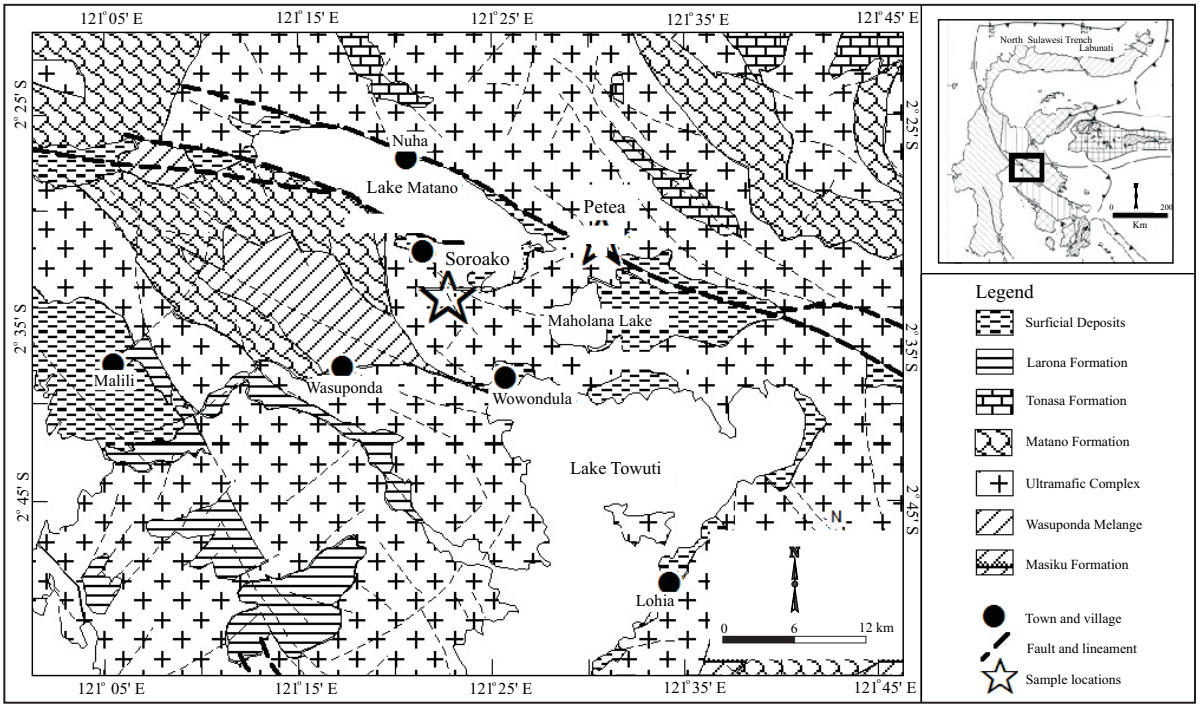


Figure 1. Simplified regional geologic map of Soroako area and sample location.

these samples were reported by Sufriadin *et al*. (2010). After being dryed at 100°C for 1 hour, samples were ground with agate mortar and vibrating mill, followed by screening to 100# (< 0.15 mm). Samples were analyzed using XRD, DT/TGA, and FTIR.

X-ray diffraction (XRD) analysis was performed by a Rigaku RINT 2000 X-ray diffractometer with Cu-Kα radiation (λ=1.541) at 40 kV and 20 mA. The patterns of diffraction were obtained by scanning random powder mounts from 2 - 65º 2θ, scanning step at 0.02º, and counting time of 2º/minute. For clay analysis, three times scanning from 2 to 40º 2θ were employed including air-dry, ethylene glycol salvation, and heating to 550º C. Phase identification and semi-quantitative proportion of minerals contained in the samples were executed by MATCH 1.10 programme.

Differential thermal analysis (DTA) was conducted by a simultaneous differential thermal analyzer SSC/5200 SII-SEIKO Instrument at The Centre for Advanced Instrumental Analysis, Engineering Faculty, Kyushu University. Data were collected in an air atmosphere with a flow rate at 20 mL/min, temperature range from 27º to 1000º C, and heating rate of 10 °C/min. A Sample was placed in a platinum crucible and the calcined Al_2O_3 was used as inert substance.

Infrared spectra of garnierite samples were recorded by means of JUSCO FTIR spectrometer. This analysis was conducted at Mineral Processing Laboratory, Department of Earth Resource Engineering, Kyushu University. KBr pressed disc (the mixture of about 2 g powder sample and 200 g KBr) was prepared. The disc was scanned under absorbance mode within the range frequencies of 4000 - 400 cm^{-1}. Spectral manipulations including smoothing, baseline correction, and curve fitting were performed by an Essential FTIR 1.50 programme.

Results And Discussion

X-Ray Diffraction

Results of XRD analysis reveal some variations of garnierite mineralogy (Table 1). However, the majority of studied samples comprise essentially the binary mixture of ~10Å (talc-like mineral) and ~7Å (serpentine-like phase), sepiolite, and smectite. The samples also contain minor amount of primary mineral mainly pyroxene, quartz or amorphous silica, and iron oxide.

Garnierite samples analyzed from west block include the mixture of talc- and serpentine-like phases (± quartz/smectite). The basal reflections with broad lines in the range of 9.13Å to 10.62Å showed a better match to kerolite-pimelite series, a hydrated talc with general formula $Mg_3Si_4O_{10}(OH)_2.nH_2O$ (Figure 2). The terms of kerolite-pimelite series can be applied for a series of Mg-Ni hydrous silicates that are characterized by the similarity of talc composition and structure. Highly disordered and non swelling stacking of the layer is typical of this material (Brindley *et al.,* 1979). According to Springer (1974) the shift in basal spacing (002) of talc from 9.3Å to 10Å which normally observed for this kind of materials might be attributed to the effects of additional water molecules in its structure.

The 7Å phase (serpentine-like mineral) detected in samples is indicated by the presence of strongly basal reflection at 7.35Å (Figure 2). Further reflec-

Table 1. Mineralogical Composition of Garnierite Samples analyzed by XRD

Minerals/ phases	Sample			
	KR1	AN4	PG3	PG4
Kerolite-pimellite	++	-	-	+++
Lizardite/chrysotile	+++	+	-	++
Smectite	-	+++	-	-
Sepiolite-falcondoite	-	-	+++	-
Quartz/silica	-	-	+	+
Pyroxene	-	+	-	-
Iron oxides	+	-	-	-

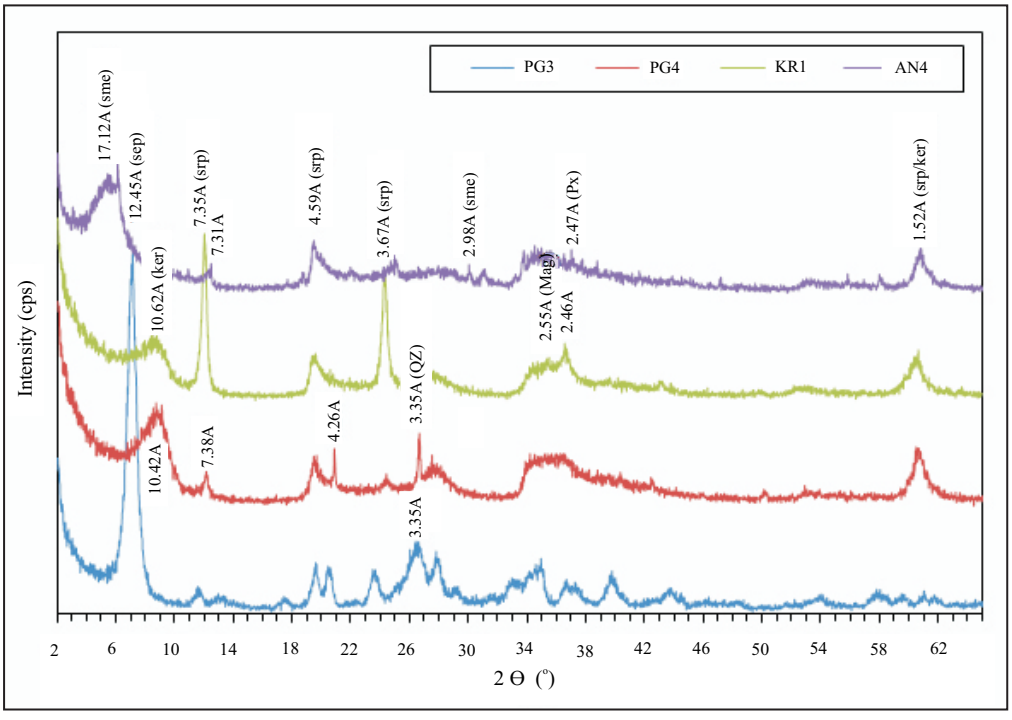


Figure 2. X-ray powder diffraction patterns of four garnierite samples from Soroako: sme smectite, sep sepiolite, ker kerolite, srp serpentine, px pyroxene, qz quartz, mag magnetite.

tion at 3.67Å is also a distinctive peak of serpentine, probably a lizardite and/or chrysotile end-members. Due to the similar peaks, it is usually not easy to discriminate serpentine species and generally the XRD patterns of these materials showing overlaping. Reflections at 17.12Å and 4.98Å found in sample AN4 (Figure 2) clearly indicate the presence of smectite.

Based on XRD analysis, two samples from Petea area (PG3 and PG4) contain significant amounts of sepiolite with small amounts of quartz and the mixture between kerolite and serpentine with minor amounts of quartz and trace iron oxide respectively.

The most intense reflection appeared at 12.48Å in sample PG3 (Figure 2) is a diagnostic peak of sepiolite, a phyllosilicate containing ribbons of 2:1 layer that has continuous two-dimensional tetrahedral but lacking continuous octahedral sheets (Jones and Galan, 1988). The peak at 3.35Å detected on this sample may indicate the presence of quartz. The peak of 10.48Å in the sample PG4 is the basal spacing of kerolite, while reflection at 7.38Å is better match for serpentine. The strong reflections at 4.26Å and 3.35Å on this sample clearly indicate the presence of quartz.

In order to clarify the evidence of sepiolite structure, one sample (PG3) was further analyzed on its structure under different treatments. Figure 3 displays diffraction patterns of oriented air-dried film (AD), ethylene glycol saturation (EG), and heated to 550°C (HT). It can be seen that reflection at ~11.75Å of oriented air dry sample slightly expanded to ~12.05Å of ethylene glycol solvation. This structure is similar to sepiolite as reported by Karakaya *et al*. (2004). The change in reflection at 3.34Å (air-dry) to 3.40Å (ethylene glycol) is also similar to the behaviour of sepiolite (Tauler *et al.,* 2009). The splitting of d spacing to be ~11.33Å and 8.75Å after heating to 550° C confirmed the formation of anhydrous sepiolite (Post *et al.,* 2007; Onal *et al.,* 2008).

Thermal Study

Thermal analysis was performed to confirm the behaviour of garnierite minerals under thermal treatment. One sample collected from each block was taken for analysis. Sample KR1 was chosen for thermal analysis representing garnierite from the

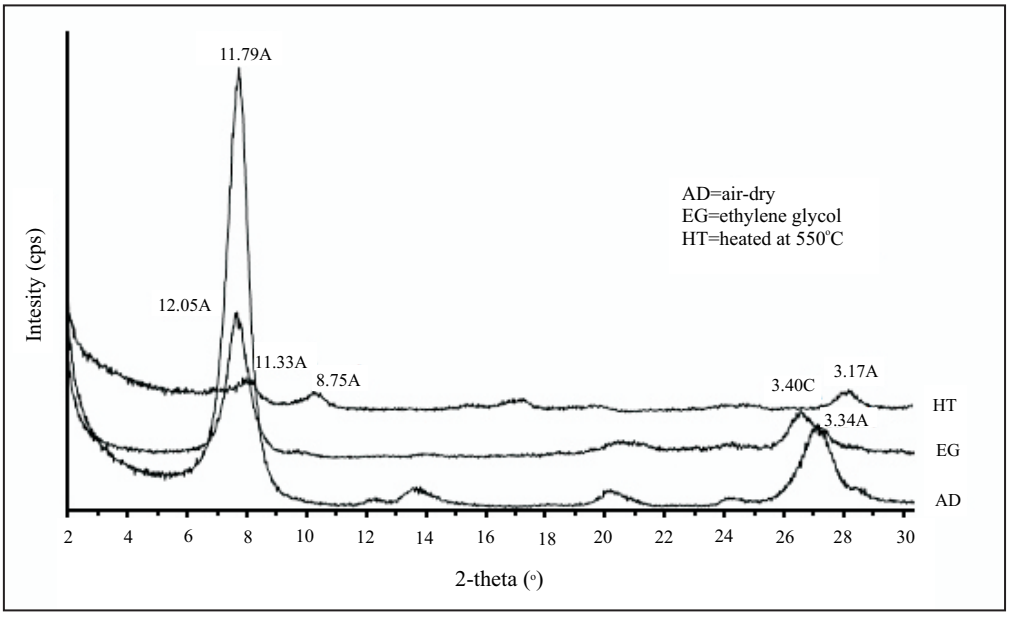


Figure 3. X-ray diffraction patterns of oriented mounts of sample PG3. AD: air-dry, EG: treated with ethylene glycol, HT: heated to 550°C.

west block, whereas sample PG3 that was predominantly composed of sepiolite with trace amounts of quartz was selected for thermal analysis representing Petea samples.

DTA curve of sample KR1 (solid line in Figure 4) displays three endothermic peaks at 58, 640, and 800°C. TG curve (dash line) in Figure 4 illustrates the weight losses in three steps. The low temperature

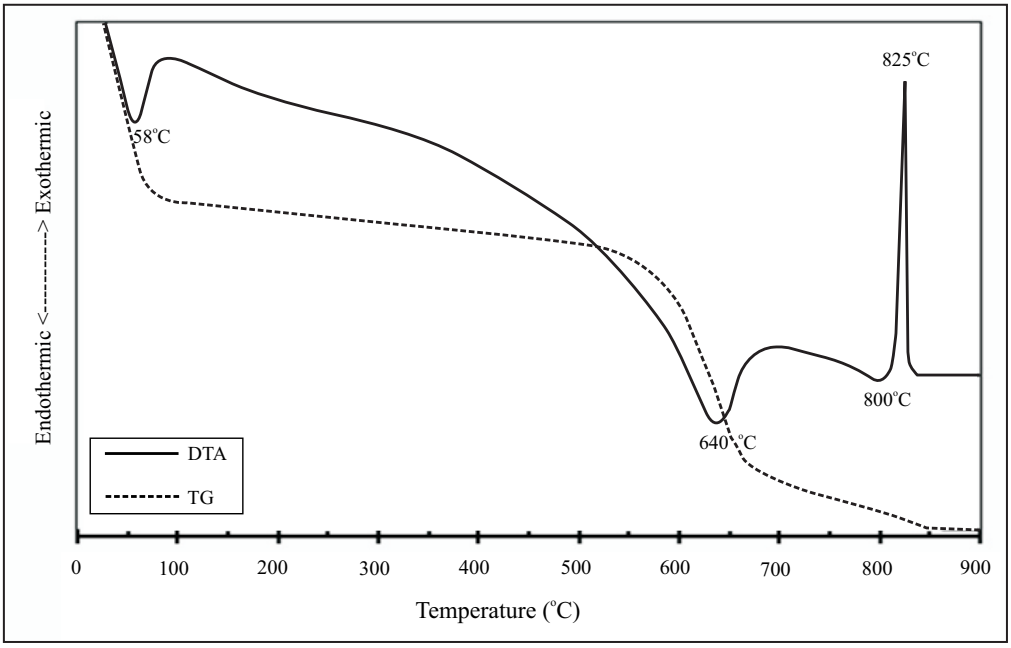


Figure 4. TG/DTA curve of sample KR1 collected from Soroako west block.

endothermic reaction occurred within the range between 30º and 100º C. If the total 10.7% of water content is assumed (LOI data), thus as much as 4.3% of weight loss is expected from this lower temperature region. This can be correlated to the elimination of adsorbed water. The second endothermic signal occurred in intermediate temperature region from 550º C to 700º C, corresponding to dehydroxilation process. This signal can be attributed to the liberation of about 5.3% bound or crystal water.

At 800º C, the completed weight loss is assigned to the elimination of 1.1% rest structural water. Above this temperature, DTA curve shows a sharp exothermic peak at 825º C indicating the completed recrystallisation. The pattern of DTA curve obtained is similar to DTA pattern of chrysotile (a serpentine end member having fibrous crystal) as reported by Vitti (2010).

Relatively higher adsorbed water that could be removed during low temperature reaction from this experiment might be due to the presence of additional water in structural surface of kerolite (Brindley *et al*., 1977).

After dehydroxilation process occuring above 800º C, the crystal structure of mineral collapsed and new phases, probably enstatite and amorphous silica might be formed (Wesolowsky, 1984). In case sample KR1 where the minerals are mainly composed of serpentine and kerolite, the possible chemical reaction during heat treatment of this sample over 800ºC is as follows:

$$\underset{\text{kerolite}}{Mg_6Si_8O_{20}(OH)_4.H_2O} + \underset{\text{serpentine}}{Mg_3Si_2O_5(OH)_4} \rightarrow$$

$$\underset{\text{enstatite}}{9MgSiO_3} + \underset{\text{amorphous silica}}{SiO_2} + 5H_2O \quad (T > 800^oC)$$

Result of thermal analysis for sample PG3 shows that four endothermic changes and one exothermic peak appeared during the experiment as depicted by DTA curve in Figure 5. TG curve of this sample (dashed line) shown in Figure 5 illustrates weight loss in four steps. The first lower temperature (27º C - 130º C) with sharply endothermic peak occurred at 75º C corresponding to the loss of adsorbed water and some zeolitic water. The second endothermic peak at 298º C is broad, extending from the region between 130º C and 320º C. This temperature range can be ascribed to the total liberation of zeolitic

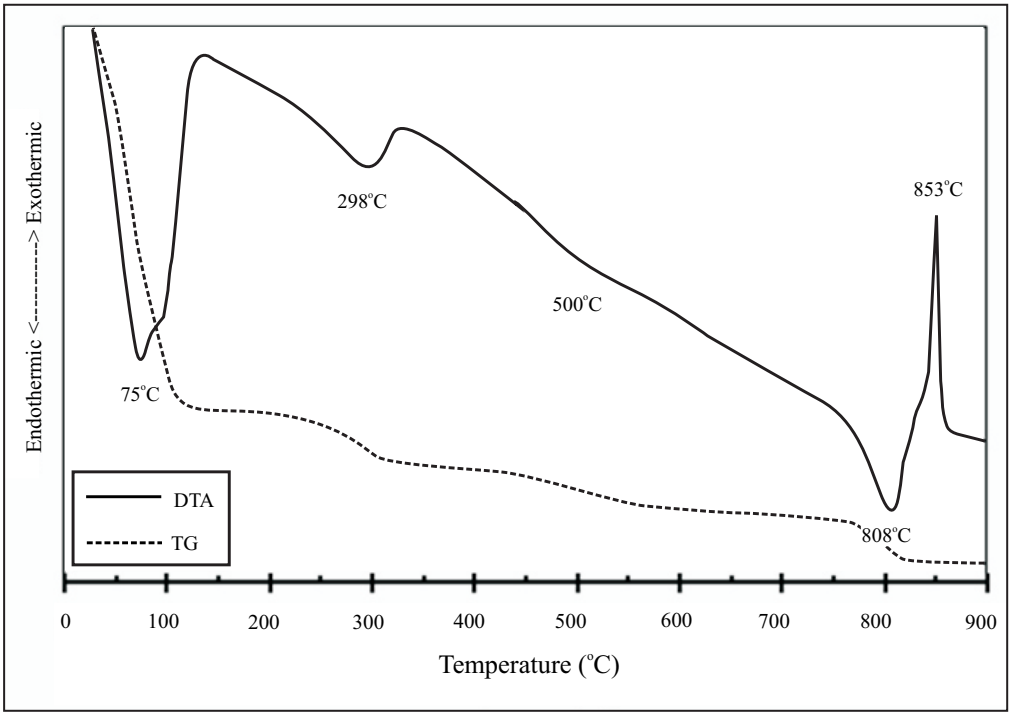


Figure 5. TG/DTA curves of sample PG3 collected from Petea Mine.

water. The third, a very weak endothermic peak took place at 500º C within the temperature range between 320º C and 750º C. This can be assigned to the lost of bound water. The last endothermic maximum occurred at 808º C, expanding from 750 to 820º C, corresponding to completed dehydroxilation of sepiolite.

An exothermic peak appeared at 853º C indicating the collapse of the crystal structure. In this last reaction, a new mineral was formed that had similar chemistry and structure with enstatite. The pattern of TG/DTA curve of this sample is consistent with a model for TG/DTA curve of sepiolite reported by Nagata *et al.* (1974). Similarly, Mitrovic *et al.* (1999) suggested that in the interval 350 - 450º C sepiolite anhydride was formed and channels in the sepiolite fibers were closed.

According to Frost and Ding (2003), four distinct weight losses may be observed with thermogravimetric and DTA curves of a sepiolite, consisting of two dehydration and other two dehydroxilation. Nagata *et al.* (1974) proposed a set of steps for sepiolite dehydration and dehydroxilation, corresponding to (i) the loss of adsorbed water, (ii) the loss of hydration water, (iii) the loss of coordination water, and (iv) the loss of water through dehydroxilation.

FTIR Study

Infrared spectrum analysis was intended to obtain an additional information about the crystal chemistry of garnierite mineralogy. Results of FTIR measurement of four garnierite samples show that two spectral regions could be identified. The first group occurred at 3800 – 3200 cm^{-1} and the second region was included in the bands at 1300 – 400 cm^{-1} (Figure 6).

Two samples (AN4 and KR1) which were collected from west block, on the basis of XRD examination, are predominantly composed of smectite and the mixture of serpentine-kerolite. The spectra in the 3800 – 3600 cm^{-1} region such as 3618 cm^{-1} and 3433 cm^{-1} appeared in the sample AN4 can be attributed to the inner and inner surface -OH stretching bands. The strong absorption band occurred at 1687 cm^{-1} in the sample KR1 likely correspond to hydroxyls bonded to magnesium atom. The wide absorption bands near 3400 cm^{-1} region (3438 cm^{-1} or 3433 cm^{-1} respectively) found in both samples can be assigned to water stretching vibration (Frost *et al*., 2001) or

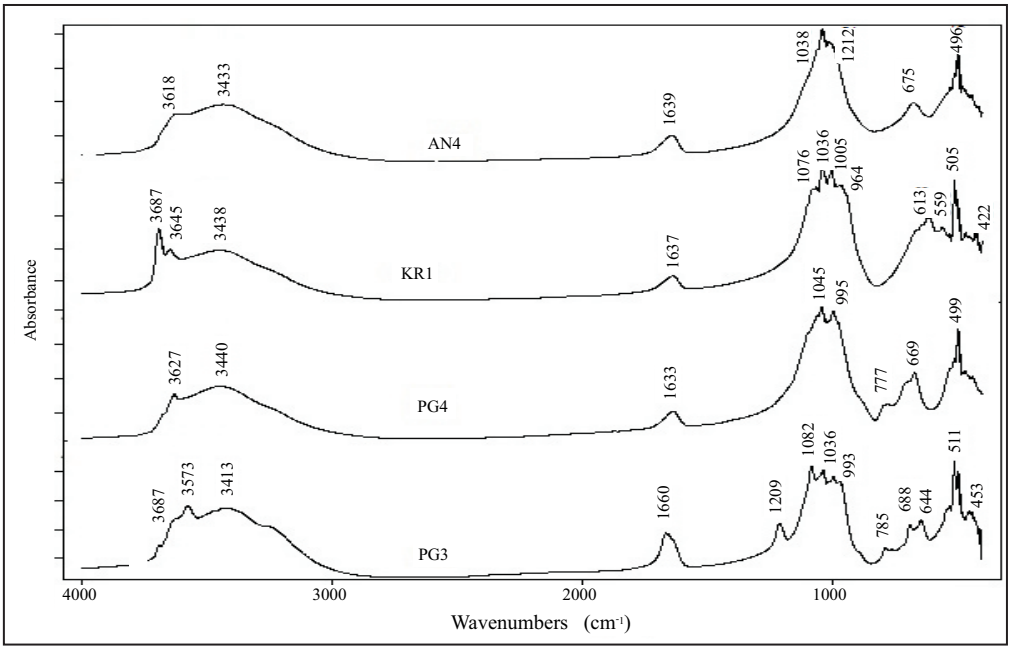


Figure 6. FTIR spectra of four garnierite samples from Soroako nickeliferous laterite deposit. Sample KR1 and AN4 collected from west block; whereas PG3 and PG4 taken from Petea mine.

are normally reported as due to hydroxyl bonded to trivalent cations (Fuchs *et al*., 1998). The bands at 1637 cm^{-1} and 1639 cm^{-1} which were observed in both samples are due to OH bending vibration. The spectra in 1100 – 800 cm^{-1} region that appeared strongly at 1036 cm^{-1} (sample KR1) and 1038 cm^{-1} (sample AN4) are related to the vibration of different Si-O bonds in tetrahedron (Fuchs *et al*., 1998). The strong absorption bands appeared at 505 cm^{-1} in the sample KR1 and 496 cm^{-1} in the sample AN4 respectively, can be assigned to (Mg,Ni)-O stretching vibration.

Other two samples (PG4 and PG3), according to XRD examination are mainly composed of serpentine-kerolite mixture and sepiolite and respectively. Similarly with two samples that previously described, the spectra at 3627 cm^{-1} (PG4) and 3687 cm-1 (PG3) are related to Mg-OH stretching vibration. The excess of water in kerolite structure is attributed to the wide absorption bands observed near 3400 cm^{-1}. While the occurrence of band at 777 cm^{-1} indicates the present of poorly crystalline silica in this sample. The strong band at 499 cm^{-1} is usually reported as O-Si-O bending vibration. The presence of band about 3573 cm^{-1} in sample PG3 is related to OH-stretching of coordinated water in sepiolite structures. Relatively strong band at 1660 cm-1 in sample PG3 is assigned to the zeolitic water in the channel of sepiolite (Frost *et al*., 2001).

Conclusions

XRD, thermal, and FTIR studies of some garnierite samples from Soroako nickeliferous laterite deposit have been carried out in order to improve a better understanding about garnierite mineralogy. Some conclusions that can be drawn from this study are as follows:

The patterns of XRD traces for all studied samples generally show broad reflections indicating a low temperature formation in oxidised environment.

TG/DTA curves of analyzed samples clearly exhibit the consistency with XRD data regarding the accuracy of mineralogy such as the presence of mixture between talc-like phase and serpentine-like mineral in the west block and sepiolite in Petea area.

Results of FTIR analysis for all samples show similarity bands at 3800 - 3200 cm^{-1} region and about 1640 cm^{-1} indicating the typical of hydrous minerals.

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