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MINERALOGICAL AND CHEMICAL PROPERTIES OF MANGANESE NODULES IN JAVA SOILS DEVELOPED FROM DIFFERENT PARENT MATERIALS

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ABSTRACT

Manganese nodules were found in Java soils which is located in the humid tropical region and influenced by volcanic environment. The objective of this research was to study the mineralogy of the soil manganese nodules developed in the different parent materials. Both samples of manganese nodule and soil were collected from soil profiles developed from limestone (Semanu), tuff-agglomerate (Patuk), and tuff (Cikopomayak). Mineral composition of the manganese nodule was identified with combination of successive selective dissolution and X-ray diffraction. The predominant soil clay mineral in all samples was kaolinite; while in Semanu soil there was also intergrade mineral (Vt-Ch); and vermiculite, illite and Vt-Ch were also identified in Cikopomayak soil. In the manganese nodules, manganese-oxide minerals were almost amorphous minerals and iron-oxide minerals were goethite. Birnessite was only present in Semanu, and Mn was concentrated 23 times in this sample. Some heavy metals were also enriched from the soil to manganese nodule. As for the similarity in the mineralogy of layer silicate on both manganese nodule and soil, it was suggested that the manganese nodules were developed in the soil.

Key words: Birnessite, enrichment, different parent materials, goethite, Mn-nodule.

INTRODUCTION

Java Island, as a part of Indonesian archipelago, is annually influenced by the northeastern and south-western monsoons alternately from the China and Australian continents, respectively. As the result, there are dry season in April-September and wet season in October-March in this area. Physiographically, the Java Island is occupied with volcanoes and mountains. Topography may play a role on the mean annual temperature and rainfall; that on the 100 m elevation higher, the mean annual temperature decreases 0.6°C; and the annual rainfall increases as the elevation increase.

Development of soils in Java Island was influenced by the activities of several volcanoes in the past and present (Van Schuylenborgh, 1957; Tan and Troth, 1982; Goenadi and Tan, 1989). In general, development of soils in the high elevation may result in the Andosols, and in the slope area in Latosols and Podzolic soils. The development of

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Vertisols from andesitic volcanic material in this island was reported by Subagyo (1983). Dudal and Soepraptohardjo (1960) reported the genetic relationship between Latosols and Andosols and roughly plotted the both soils in Java Island. Recently, studies on some Andosols and Latosols from this island by Supriyo et al. (1992) showed that these soils had light clay texture; strong to weak acidic reactions; low in exchangeable bases and base saturation; the main minerals of silt fraction were quartz and cristobalite (Andosols) and quartz and magnetite (Latosols); and the minerals of the clay fraction were kaolinite, halloysite, smectite and some gibbsite (Andosols) and kaolinite and goethite (Latosols). Beside the volcanic soils, there are also some soils developed on limestone. There are some tertiary and quaternary limestone facies in the Central Java (Rahardjo et al., 1977). On the other hand, Van Schuylenborgh (1957) reported some black concretions of manganese-iron in the Bg horizon of Red-Yellow Podzolic soils developed from acidic tuff. Subagyo (1983) also reported the occurrence of Mn-stain in the 2B horizon of Typic Pelludert developed from andesitic volcanic material. However, there was not report on the mineralogy of manganese-nodule in the soil profiles from Java Island.

There were several studies on mineralogical and chemical properties of the Mn-nodules developed in soils of Okinawa (Japan), Australia, America, and Europe (Taylor et al., 1964; Tokashiki et al., 1986; Uzochukwu and Dixon, 1986; McKenzie, 1989; Tokashiki, 1993 and 1994). They have been reported that there is a few knowledge in the soil Mn-oxide minerals, because the soil Mn-oxide minerals do not give a sharp peak on the X-ray diffraction, few in content, and there is also the overlapping peak with the associated minerals. McKenzie (1989) reviewed characteristics of Mn-oxides and hydroxides in soils and assessed the analytical method, chemical properties and the development of Mn concretion. Tokashiki et al (1986) and Tokashiki (1993) reported that lithiophorite and birnessite were found in the Mn nodules of Okinawa soils developed on the limestone. Lithiophorite, birnessite, hollandite, and todorokite were also found in Mn nodule of some Australian volcanic soils (Taylor et al., 1964). Therefore, this study was aimed (i) to investigate the mineralogical properties and chemical compositions of manganese nodules developed in soils of Java Island with different in parent materials, and (ii) to preliminary assess the formation of Mn-nodule in these soils.

MATERIALS AND METHODS

Manganese nodules and the soil of horizon in which the Mn-nodule developed were collected form three locations with different in parent materials (Figure 1 and Table 1). There were Typic Eutrorthox from Patuk (developed from tertiary tuff-agglomerate), Typic Paleudult from Cikopomayak (developed from quaternary andesito-dacitic tuff in the Pleistocene), and Typic Pelludert from Semanu (developed from tertiary limestone within the range from middle Miocene to lower Pliocene) (Van Bemmelen, 1949; Rahardjo et al., 1977; Goenadi and Tan, 1989). The first two soils were characterized with the acidic in nature and developed on the slope land, while the last soil was in alkaline and developed on the basin of depression area.

Particle size distribution and soil texture were analyzed with pipette method as follows. 10 g of the air dry soil with diameter of >2.0 mm was digested with H₂O₂ to decompose



FIG. 1. Locations of Patuk, Semanu and Cikopomayak in Java Island.

organic matter. Then the coarse sand fraction was separated with passing to 0.2 mm diameter wire screen. After that the suspension was treated with ultrasonic wave and adjusted the pH 10 with NaOH addition. The silt and clay fractions were determined with the pipette method. Then the silt and clay fractions were separated with several times syphoning, and both silt and clay fractions were collected, respectively, for the next analysis. The pH(H₂O) of soil suspension was measured on the 1:2.5 soil and water ratio with pH-meter.

Sample	Longitude	Latitude	Parent material	US Soil Taxonomy	
Patuk Semanu Cikopomayak	110°30′ 110°37′ 106°27′	7° 55'S 8°01'S 6°29'S	Tertiary agglomerate Tertiary limestone facies Quaternary Andesito- dacitic tuff [†]	Typic Eutrorthox Typic Pelludert Typic Paleudult	

TABLE 1. Location, parent material, and soil classification of the studied soils

[†]Goenadi and Tan (1989).

Each aliquot of the Mn-nodule and the air dried soil (<2.0 mm) were ground with agate mortar and passed on the 0.25 mm diameter wire screen to make powder for chemical analysis. And then the clay fraction of Mn-nodule was collected with the following procedure. The suspension of the Mn-nodule was made by adding distilled water to the powder. Then this suspension was treated with ultrasonic wave and the pH was adjusted to 10 with the same procedure to the soil texture analysis. The clay fraction was syphoned after the coarser fractions were settled.

Total analysis of the soil and Mn-nodule was conducted with open digestion system (Yamasaki, 1995) as follows. 1.00 g sample with < 0.25 mm diameter was placed into 50 mL teflon beaker, which was placed in aluminum holder, and then it was added with concentrate solution of the mix HClO and HNO₃ (1:1). Then it was heated on the hot plate for 3 hours with capped by teflon watch. Then the cap was opened and continued by heating to evaporate the solution. Then it was cooled and added with HClO and HF and heated and then cooled again. The treatments were repeated for three times with the same sequences, and the materials became crystal. Then, it was added with HCl and closed with teflon watch and heated for one hour. Finally it was added with distilled water and heated for 30 min. The solution was adjust to 100 mL and kept in 100 mL polyethylene bottle in room temperature, and then the 15 dissolved elements (Fe, Al, Mn, Ca, Mg, K, Na, P, V, Ba, Sr, Cu, Zn, Cr, and Co) were measured with inductively coupled plasma atomic emission spectrometry (ICP-AES).

The mineralogical properties of fine-sand and silt fractions were determined with XRD from 60° to 2° 2 θ (Brindley and Brown, 1980). In this study, the XRD was conducted in 30 kV, 10 mA, 2°/min, and Cu K α as source of X-ray. The mineralogical properties, especially the phyllosilicates, of the DCB-pretreated clay fraction of soil and Mn-nodule were also determined with XRD after saturation with Mg²⁺-and glycerol solvation, and saturation with K⁺ and subsequential heating (Mehra and Jackson, 1960; Wada, 1966). Formamide treatment was done to differentiate kaolinite from halloysite by addition of a few drops of formamide on the clay specimen and allowed for 10 min, then it was X-rayed (Ross et al., 1983). Semiquantitative analysis of the detected minerals were done by measuring the intensity of the first peak of mineral.

Determination of mineral compositions in the Mn-nodule was conducted with combination of successive selective dissolution and XRD methods (Tokashiki, 1994) as follows. 5 units of 10 mL teflon centrifuge tube were filled with 10 mL of colloid containing 50 mg of clay fraction of Mn-nodule. All of these were centrifuged and the supernatant was discarded, then the one unit of residue was X-rayed and the 4 others were followed by 5 M NaOH treatment on the boiled water bath for an hour. After finished, centrifugation was done, the extractable elements (in the supernatant) were measured with ICP-AES, one unit residue was X-rayed, and the 3 others were then treated with hydroxyl-amine hydro-chloride (HAHC) treatment at 25°C. With the same to the previous step, the extractable elements of one unit were measured and the residue was X-rayed, and the 2 others were then treated with HAHC treatment at 60°C. One unit of extractable elements was measured and the residue was X-rayed, and finally DCB-treatment was conducted on the last one residue. Then the residue was X-rayed, and the extractable elements were measured. The determination of the mineral compositions was based on the position of peak which destroyed, and the kind and content of element which extracted on the certain step of dissolution.

RESULTS AND DISCUSSION

The Mn-nodule and soil of Patuk sample

Soil sample from Patuk was predominated with clay fraction and acidic in nature (Table 2). The Mn concentration was found as a soft black stain on the soil ped surface. An interesting phenomenon is that the position of Mn-nodule of this sample is shallow (35–50 cm depth) and the soil is developed on the slope-land. This Mn-nodule was developed in volcanic soil and was found in the B horizon (Table 2). The occurrence of manganiferous concretion on or near surface of Oxisols derived from volcanic parent material in Hawaii was also reported by Glasby et al. (1979).

Table 3 shows the contents of the 15 elements in the soil and Mn-nodule. In this sample, Fe, Mn, P, V, Ba, Cu, Zn, and Cr contents of Mn-nodule were higher than those of soil. Uzochukwu and Jackson (1986) postulated that Co, Li, Zn, Ba, and Cu might had been trapped during the formation of Mn minerals. McKenzie (1989) reported that Mn, Cu, Co, Ni, Pb, Cr, and V were generally enriched in Mn-nodule from the surrounding soil. The Mn-enrichment in this sample was 2.5 times, however the content of Co was very low in soil and nodule of this sample. Al, Ca, and Mg contents in the Mn-nodule in this sample was lower than in soil, although these elements were abundant in soil.

Figure 2 shows the XRD pattern of the mineralogical component of the fine-sand fraction. The detected minerals of this fraction were magnetite (2.54 Å), quartz (3.35 Å),

Sample	Soil Color	Depth	Horizon	pH(H ₂ O)	c. sand	f. and	Silt	Clay	Texture [†]
		-cm-				%_			
Patuk	2.5YR4/8	35-50	B(Mn)	5.45	8.8	3.9	13.6	73.6	HC
Semanu	10YR2/1	23-50	A(cnMn)	7.55	1.8	5.2	13.3	79.7	HC
Cikopomayak	5YR6/6	137–150	B(cnMn)	4.79	15.0	32.4	18.0	34.7	LiC

TABLE 2. Morphological properties, pH and particle size distribution of studied soil

[†]HC: heavy clay; LiC: light clay.

Element	Patuk			Semanu			Cikopomayak		
	Soil	Nodule	Enrich. [†]	Soil	Nodule	Enrich. [†]	Soil	Nodule	Enrich. [†]
	ppm			ppm			ppm		
Fe ($\times 10^{3}$)	102.5	239.3	2.3	97.2	135.6	1.4	90.5	264.4	2.9
Al $(\times 10^3)$	148.7	121.9	_	121.5	72.5	-	67.5	50.5	-
$Mn(\times 10^{3})$	1.6	4.0	2.5	5.9	137.5	23.2	4.1	8.4	2.1
$Ca(\times 10^{3})$	1.1	0.6	_	9.3	24.6	2.6	0.2	0.1	-
$Mg(\times 10^{3})$	2.0	1.2	-	2.6	1.6	-	1.8	1.6	-
ĸ	493.0	329.0	-	682.0	760.0	1.1	3697.0	3096.0	-
Na	142.0	129.0		668.0	1275.0	1.9	600.0	660.0	1.1
Р	263.0	715.0	2.7	259.0	344.0	1.3	173.0	443.0	2.6
v	294.0	725.0	2.5	286.0	555.0	1.9	210.0	300.0	1.4
Ba	222.0	386.0	1.7	632.0	15670.0	24.8	650.0	1049.0	1.6
Sr	15.0	9.0	_	38.0	96.0	2.5	15.0	15.0	-
Cu	146.0	249.0	1.7	90.0	190.0	2.1	26.0	31.0	1.2
Zn	77.0	83.0	1.1	62.0	86.0	1.4	47.0	71.0	1.5
Cr	11.0	25.0	2.3	41.0	5.0	-	57.0	63.0	1.1
Co	tr		-	29.0	638.0	22.0	51.0	111.0	2.2

TABLE 3. Total analysis of soil, nodule and the enrichment values of each element

[†]Enrich. is enrichment = ppm of element in nodule/ppm of element in soil.

cristobalite (4.06 Å) and gibbsite (4.85 Å). These minerals were also almost detected in the silt fraction (Figure 3) except manganite. In addition serpentine (2.52 Å), mica (4.47 Å), goethite (4.18 Å), and anatase (3.52 Å) were detected in the silt fraction, which were not in fine-sand. This result indicated that there was few difference between the mineralogical component of fine-sand and silt fractions.

Figure 4a shows the XRD pattern of clay fraction of the Patuk soil after DCB pretreatment. There were two main peaks of 7.2 Å and 3.5 Å shown on Mg^{2+} and K^+ -clays. The formamide treatment did not expand the 7.2 Å peak to 10 Å. The behavior of the peaks of XRD under K⁺-saturation and subsequent heating up to 550°C suggested that the main mineral was kaolinite (Wada, 1966). There was not clear on the broad peak in the region of 10 Å and 14 Å under Mg^{2+} or K⁺- saturation. After the heating on the K⁺-saturation specimen to 550°C the weak broad peak from about 10 Å and 14 Å appeared suggesting as a vermiculite-chlorite intergrade mineral.

Phyllosilicates component in the clay fraction of the Mn-nodule were determined (Figure 4b). The results show that the clay mineralogy of the Mn nodule was similar to that of the soil (Figure 4a), and also the formamide treatment did not expand the 7.2 Å peak, that were predominated with kaolinite (7.2 Å). Vermiculite-chlorite intergrade mineral (10 Å and 14 Å) was detected, gibbsite (4.8 Å) was also detected in the nodule. An interesting phenomenon was on the gibbsite, that in the soil sample, it was found in the silt and fine sand fractions but was not detected in the clay fraction; then in the Mn nodule the gibbsite wad detected again. It is presumably occurred that gibbsite as a secondary mineral had developed, and the size had been $>2\mu$ m in the soil.

XRD pattern of the Patuk Mn-nodule under successive selective dissolution is shown in



FIG. 2. Mineral composition of the fine sand fraction. Cb:cristobalite; Fd:feldspar; Gb:gibbsite; Ge:goethite; Ma:magnetite; Qz:quartz

Figure 4c. On the untreated sample, Mn-nodule showed 7.2 Å, 4.8 Å, 4.18 Å, and 3.5 Å peaks. The 7.2 Å and 3.5 Å were probably the peaks of kaolin or birnessite (Tokashiki, 1994). However, the NaOH treatment resulted in collapses of 7.2 Å, 3.5 Å, and 4.8 Å peaks. Therefore the 7.2 Å and 3.5 Å peaks were kaolinite, and 4.8 Å was gibbsite (Tokashiki, 1994). The next HAHC treatments on 25°C and 60°C did not change the 4.18 Å peak, and finally the DCB treatment caused a collapse of this peak, and it was suggested as goethite. The content of the goethite in the clay fraction of Mn-nodule was 8.27% (Table 4). The successive dissolution treatment on the Mn-nodule did not result in the peak of Mn-oxide mineral. However, the Mn element was extractable with each extractant except for NaOH suggesting that the Mn-oxide was amorphous mineral. According to combination of the kind of elements (Al, Si, Fe and Mn) and these contents in the soluble extract (Table 4), and the XRD pattern in the residues after each treatment of the successive selective dissolution, we would like to approach the elements which



FIG. 3. Mineral composition of the silt fraction. At:anatase; Cb:cristobalite; Fd:feldspar; Gb:gibbsite; Ge:goethite; Ma:magnetite; Mc:mica; Qz:quartz; and Sp:Serpentine.

composed the Mn-nodule minerals. The NaOH treatment that was able to collapse the 7Å and 3.5Å, suggested that the dissolves Si and Al were originated from kaolinite. In addition, the 4.8Å peak was also collapsed on the NaOH treatment, it suggested that a part of Al was also from gibbsite (Figure 4c and Table 4).

The Mn-nodule and soil of Semanu sample

Semanu soil Mn-nodule was morphologically characterized with small ball in form and soft. This nodule was formed in the A horizon of Vertisol derived from limestone facies and heavy clay in texture and alkaline in nature (Table 2). Generally, there is a continuous

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FIG. 4. XRD pattern of the clay fraction of the Patuk sample. (a) in the soil, after DCB treatment.
(b) in the Mn-nodule after DCB. (c) in the Mn-nodule with successive selective dissolution.
A:Mg²⁺-saturation; B:glycerol solvation; C, D, E, and F:K⁺- air dry, 100°C, 300°C, and 550°C, respectively.

1: untreatment; 2: after NaOH treatment; 3: after HAHC (25°C) treatment; 4: after HAHC (60°C) treatment; and 5: after DCB treatment.

Sample	Element	Successive selective dissolution							
		NaOH	HAHC [†] (25°C)	HAHC [†] (60°C)	DCB				
		%%							
Patuk	Si	10.64	0.03	0.03	0.09				
	Al	11.38	10 ⁻³	0.01	0.35				
	Fe	0.03	0.08	0.25	8.27				
	Mn	0.00	0.29	0.04	0.02				
Semanu	Si	9.43	0.06	0.07	0.11				
	Al	8.05	10 ⁻³	0.01	0.11				
	Fe	0.05	0.02	1.15	5.67				
	Mn	0.00	9.61	0.80	0.09				
Cikopomayak	Si	4.02	0.05	0.03	0.19				
	Al	4.06	0.00	10 ⁻³	0.55				
	Fe	4×10^{-3}	0.06	0.54	17.00				
	Mn	0.00	2.07	0.31	0.06				

TABLE 4. The extractable Si, Al, Fe, and Mn on the successive selective dissolution

[†]HAHC: hydroxy amine hydrochloride.

self churning in Vertisol that might inhibit the formation of B horizon. Position of this Mn-nodule was different among soils. Although the position of Semanu sample is shallow (Table 2), the soil is developed in the basin of the depression zone of tertiary limestone and there is a distinct difference between dry and wet season in every year. This condition provides seasonally water-table fluctuation, and it might result in a continuous oxidation and reduction processes.

The Mn-enrichment in Semanu Mn-nodule was 23.2 times than that in soil (Table 3). It was very high comparing with the Mn-enrichment in the Patuk sample. Barium also showed the similar phenomenon to Mn, that the enrichment in Mn-nodule was very high (24.8 times) in this sample. It presumably correlated with the parent material; that Semanu developed from tertiary limestone facies, and it was resulted from transgression of the sea. Three elements of Ca, K, and Sr were enriched in Mn-nodule of Semanu, while it was not shown in the Patuk sample. It was presumably influenced by the parent material, that the Semanu Vertisol was developed on the Limestone facies. Also it can be seen that the Ca content and the pH in Semanu soil was very high than the Patuk sample (Table 3). The enrichment of Cr in Mn-nodule occurred in Patuk (Table 3), however it was not shown in the Semanu sample. In this sample, Co was abundant and the enrichment of this element was very high (22.0 times). Burn and Burns (1975) and Burns (1976) reported that similar size of the ionic radii of Co³⁺ and Mn⁴⁺ suggests that some cobalt substitutes for Mn⁴⁺ ion in edge-shared (MnO₆) octahedral in many Mn(IV) axes mineral structure like Birnessite. Loganathan et al. (1977) reported that at pH values above 6, abrupt absorption increase in the sorption of Co^{2+} and Zn^{2+} in the hydrous manganese oxides were observed. Al and Mg contents in the Mn-nodule in this sample were also lower than in soil. McKenzie (1989) reported that Al and Li were higher in Lithiophorite, but low in Birnessite. The predominant mineral of the Semanu Mn nodule was birnessite (Figure 5c).

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FIG. 5. XRD pattern of the clay fraction of the Semanu sample. (a) in the soil, after DCB treatment. (b) in the Mn-nodule after DCB. (c) in the Mn-nodule with successive selective dissolution. The legend are same with figure 3.

The presence of Mn-nodule in the shallow depth of soil enable to cause some problems in soil fertility. Accumulation of Co in the Mn-nodule can lead to Co deficiency in pastures and to fixation of Co applied as fertilizer (McKenzie, 1989).

The XRD pattern of primary minerals in fine-sand fraction of the Semanu soil sample is shown in Figure 2. There were quartz, feldspar, goethite, cristobalite and magnetite present as the primary minerals. The detected minerals in the silt fraction are shown in Figure 3. It can be seen that the mineralogical components of the fine-sand and silt fractions were similar. Mica (4.47) was present in the silt fraction of this sample, but goethite was not. In the silt fraction, the peak intensity of feldspar decreased, however that of cristobalite increased.

Figure 5a. shows the XRD pattern of clay fraction of the Semanu soil after DCB pretreatment. There was a similar pattern on clay mineralogy between the Patuk and Semanu soils (Figure 4a. and 5a.). The clay mineralogy of the Semanu was also predominated with kaolinite (supported with the formamide test). Quartz (4.27 Å and 3.35 Å) was found in Semanu, while gibbsite was not present in this sample. Figure 5b also shows that the clay fraction of the Mn-nodule was predominated with kaolinite, and it was also confirmed with formamide test.

Untreated clay fraction of Semanu Mn-nodule gave broad-strong 7.5 Å peak, and weak broad peaks of 3.78 Å and 3.60 Å on the XRD (Figure 5c.). The NaOH treatment resulted in lowering and shifting of the 7.5 Å peak to 7.2 Å, shifting of broad peaks of 3.78 Å and 3.60 Å to 3.64 Å, and appearance of a weak peak of 4.18 Å. Tokashiki et al. (1986) reported that NaOH treatment was able to dissolve the kaolin mineral (7Å peak) which coincided the main peak of birnessite (7.27 Å). On the HAHC (25° C) treatment, the peaks of 7.2 Å and 3.64 Å disappeared, therefore these peaks were suggested as birnessite (Tokashiki, 1994). The remaining peak was 4.18 Å, and this peak was collapsed on the DCB treatment, and it was suggested as goethite.

There was also a tendency in the relation between the amount of extractable Si and Al and the intensity of the 7 Å peak in the Mn nodule. There was very few extractable Fe and even no extractable Mn on the NaOH treatment. It was suggested that the extractable Fe was originated from amorphous Fe minerals. The HAHC $(25^{\circ}C)$ treatment also only dissolved few Si, Al, and Fe in this sample, and the extractable Si and Al were considered from amorphous silicate-layer minerals, and the Fe was from amorphous Fe minerals. In Semanu sample, the 7.2 Å peak (as the residual peak after NaOH treatment) was collapsed with the HAHC $(25^{\circ}C)$ treatment (Figure 5b.). It suggested that the dissolved Mn (9.61%) was from birnessite (Table 4). In the Patuk sample the extractable Mn was from amorphous Mn minerals. In the HAHC $(60^{\circ}C)$, like in the Patuk sample, there was extractable Fe which higher than Mn. There was no alteration on the XRD pattern in this treatment. It was suggested that all extractable elements were from amorphous mineral. The DCB extractable Fe was higher than the other elements (Table 4) and it was accompanied with a collapse on the 4.18 Å (goethite), and the content of this Fe oxide mineral was 5.67% in the clay fraction of Mn nodule.

The Mn-nodule and soil of Cikopomayak sample

The Mn-nodules of Cikopomayak was like the Patuk sample, it also developed on

volcanic soils and was found in the B horizon (Table 2). But the Cikopomayak nodule had developed becoming the large size with irregular shape nodule. The soil horizon, in which nodule was formed, had a light clay texture and acid in nature (Table 2).

Content of K in Cikopomayak Ultisol was very high (3697 ppm and 3096 ppm in soil and Mn-nodule, respectively) as compared with the other samples. It might be due to the fact that the Cikopomayak soil was developed on the youngest parent material as compared to the two other samples. There were also Al and Mg contents in the Mn-nodule that lower than in soil. Mn enrichment in Mn-nodule of this sample was similar to the Patuk sample. The enrichment of Cr in Mn-nodule which occurred in Patuk also in Cikopomayak, but did not in Semanu (Table 3). The content of Co in the Cikopomayak soil was higher than in the Semanu soil, but the enrichment of this element in the Mnnodule in the first soil was only 2.2 times. In general, there were similarities on the enrichment values in the Patuk and Cikopomayak samples, however there were some differences of enrichment values in Semanu sample (Table 3). It probably correlated with kind of parent material, that Patuk and Cikopomayak soils developed on the volcanic materials and Semanu soils from limestone.

Figure 2 shows the XRD pattern of primary minerals in fine-sand fraction. As for Patuk and Semanu soils, there were several kinds of primary minerals detected, however the Cikopomayak soil was predominated by Quartz and very few cristobalite. The similar pattern of XRD in fine-sand faction and silt fraction was also observed in Cikopomayak soil. The detected mineral in the silt fraction was only quartz (Figure 3). It is an interesting phenomenon in the Cikopomayak soil, as among the soil samples, this soil is developed on the youngest parent material. There are two probabilities that might be occurred: (i) The parent material is tuff that it is relatively weatherable, and or (ii) the main mineral is quartz that other minerals are shadowed by quartz and are not detectable with X-ray.

In the clay fraction of Cikopomayak soil, under Mg^{2+} and K^+ -saturations, there were sharp peaks of 7Å, 3.5Å and 3.35Å, and weak peaks of 14Å, 10Å, 5Å, 4.27Å, and 4.04Å (Figure 6a). According to the behavior of peaks of XRD on the glycerol solvation, subsequent heating, and formamide treatment, there were kaolinite (7Å and 3.5Å peaks); vermiculite, illite, and vermiculite-chlorite intergrade mineral (14Å, 10Å, and 5Å peaks); quartz (3.35Å and 4.27Å); and cristobalite (4.04Å) (Wada, 1966).

The XRD pattern of Mg^{2+} and K^+ -saturations on the clay fraction of Mn-nodule is shown in Figure 6b. The result showed that the clay mineralogy of all nodule samples was similar to that of the soils (Figure 4, 5, and 6), that were predominated with kaolinite (7.2 Å) (confirmed with formamide test). Vermiculite-chlorite intergrade mineral (10 Å and 14 Å) was also detected in Patuk and Cikopomayak nodule. Quartz was found in both Semanu and Cikopomayak nodules but was not in the Patuk nodules. Gibbsite (4.8 Å) was only detected in the Patuk nodule.

The untreated Mn-nodule of Cikopomayak sample showed 4.18 Å and 3.35 Å peaks (Figure 6c). The NaOH, HAHC (25°C and 60°C) treatments did not change both peaks. Finally, the DCB treatment was able to collapse 4.18 Å peak, however, there were sharp peaks of 10 Å and 5 Å shown, and the 3.35 Å peak intensity became higher. The 4.18 Å peak was goethite; 10 Å, 5 Å, and 3.35 Å were peaks of mica. It was suggested that Mn mineral which composed the Mn-nodule was amorphous mineral. In all Mn-nodule



FIG. 6. XRD pattern of the clay fraction of the Cikopomayak sample. (a) in the soil, after DCB treatment. (b) in the Mn-nodule after DCB. (c) in the Mn-nodule with successive selective dissolution.

The legend are same with figure 3.

samples, there was a tendency in the relation between the amount of extractable Si and Al and the intensity of the 7Å peak (Figure 4c. 5c. 6c. and Table 4). There was very few extractable Fe and even no extractable Mn on the NaOH treatment. It was suggested that the extractable Fe was originated from amorphous Fe minerals. The HAHC $(25^{\circ}C)$ treatment might dissolve few Si, Al, and Fe in almost samples, that these element were considered from amorphous minerals. In the DCB treatment, all samples showed a collapse of 4.18Å peak with accompanied with a lot of extractable Fe. It suggested that the extractable Fe was from goethite, and the content of goethite was 17.00% in the clay fraction of Mn nodule.

Similarity in the layer silicate minerals between soil and Mn-nodule

Finally, we would like to compare the mineralogical properties of the clay fraction of the Mn nodule and its surrounding soil. It is because we would like to preliminary assess the formation of Mn nodule in the soil. The question is whether the occurrence of Mnnodule in soil is the product of the pedogenesis, or this nodule has been present in the soil parent material. Table 5. shows the kinds of mineral and their contents on both Mn nodule and soil. In all samples, the predominant clay mineral of the soil and Mn-nodule was the same i.e., kaolinite. The difference was in the content of this mineral, that was a 10% decrease from soil to Mn nodule in Patuk sample, while an increase of kaolinite was observed in Semanu and Cikopomayak samples. It is suggested that kaolin mineral of Semanu and Cikopomayak nodules is enriched from their surrounding soil. As the Mn nodule developed, some elements and minerals of soil accompanied the Mn on the nucleation process of the Mn nodule. Gallaher et al. (1973) also reported similarity between the layer silicates of the Fe-Mn concretion and its surrounding soil. They suggested that minor constituents of soils material are embedded throughout concretion. Accordingly, we preliminary suggested that Mn nodule in the soil profile of the present study is developed in the soil as product of periodically alternation of oxidation and reduction. It is however, studies on the chemistry and mineralogy in soil profile, the Mnnodule and parent material are, indeed, needed to make clarification on the formation of

Sample	Kaolinite	Illite	Vermiculite	Vt-Ch	Cristobalite	Gibbsite	Quartz
				0/			
Patuk:				/0			
-Soil	100	_	_	tr	_		_
-Nodule	90	_	-	tr		10	_
Semanu:						10	
-Soil	81	-	_	19	_	_	_
-Nodule	100	_	-	_	_	_	_
Cikopomayak:							
-Soil	77	9	8	6	_	-	-
-Nodule	100	tr	-	-	tr	_	tr

TABLE 5. The mineralogical composition of the clay fraction of the soil and Mn nodule

Vt-Ch: vermiculite-chlorite intergrade mineral; tr:trace.

Mn-nodule in the soil. In addition, the several studies on the Mn-minerals in soil Mnnodule were conducted in detail in Okinawa and Australia. However, the soil Mn-minerals in Java Island which is located between both regions have not been studied. Although the number of sample used in the present study was small and thus can not be used to make a general description of the soil Mn-minerals in the Pacific region, we hope that this study will contribute to information on the soil Mn-minerals in Java Island.

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