Development of Halloysite/Smectite Mixed Layer Mineral in Paleudult of Java Island

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Abstract

This study was initiated to investigate the development of unique kaolin/smectite mixed layer minerals in the Paleudult of Java Island. The present study was aimed to identify the kaolin minerals and to understand the development of the kaolin/smectite mixed layer. Clay fraction samples were collected from the Paleudult profile. Selective dissolutions using dithionite citrate bicarbonate, NaOH, and Na-citrate treatments were conducted on the clay fraction. The result showed that free iron oxide content increased with the depth. Halloysite which showed a 7.6 Å peak on the X-ray diffraction (XRD) was confirmed by the hot NaOH extraction. SiO_2/Al_2O_3 molar ratio from the hot-citrate extracts provided the halloysitic property only in the upper horizons. However, the peaks of 10-14 Å on the XRD collapse at 300°C following the hot citrate treatment suggesting that crystallinity of the halloysite mineral is weak. This halloysite mineral developed well in the upper horizons. The development of halloysite/smectite mixed layer is proposed in the four stages.

Key Words

Halloysite, development of halloysite/smectite mixed layer.

Introduction

Smectite minerals are found in several acidic soils such as Red-yellow Podzolic Soils in Java Island. The formation of smectite minerals in this area might be resulted from ejected materials from activities of several volcanoes in the past. These materials were then deposited in the sea and further weathering processes resulting smectite minerals. Geological processes might lead an uplift of the sea floor to be terrestrial and then developed soils. McDaniel (1995) reported the presence of beidellite in the E horizon in Spodosols that developed on volcanic ash in Northern Idaho.

Hydroxyl-Al interlayered vermiculite mineral was found in some Ultisols in Indonesia (Goenadi and Tan 1988; Supriyo *et al.* 1992). They described that this minerals showed 14.02 Å peak on the XRD on the Mg^{2+}-saturated clay and glycerol solvation, and the peak was gradually collapsed for K^+-saturated clay and following subsequent heating treatments. Rich (1960) mentioned the interlayering process of aluminum in the interlayer space of expansible 2:1 minerals. Transition of smectite to chlorite that resulted from geothermal alteration was reported by Robinson and de Zamora (1999). Kaolin/smectite mixed layer was identified in the clay fraction of the Paleudult developed on dacitic-andesitic tuffs from Jasinga Subdistrict Bogor Regency West Java Province Indonesia (Nurholis and Tokashiki 1998).

The objectives of the study were: (i) to identify the kaolin minerals in the kaolin/smectite mixed layer minerals, and (ii) to understand the development of this kaolin/smectite mixed layer minerals in the soil profile of the Paleudult.

Materails and Methods

The studied soils were the Paleudult, developed from volcanic materials, at Jasinga subdistrict, Bogor regency, West Java province. Five soil samples were collected from each horizon that developed in the soil profile. Soil texture was analyzed using mechanical analysis after oxidizing the organic matter using H_2O_2. The coarse and fine sand, silt and clay fractions were separated and collected for mineralogical studies. The fine sand fraction was then analyzed the primary mineral composition using XRD. The clay fraction was then pretreated using dihionite citrate bicarbonate (DCB) using Mehra and Jackson (1960) method. Formamide treatment was conducted to identify the kinds of kaolin minerals. Successive dissolutions were done to identify the properties and kinds of mineral that compose the clay specimens. Hot NaOH treatment was done on the DCB pretreated clay to extract kaolin mineral (Tokashiki *et al.* 1986). The extractable Si and Al elements were then determined using an inductively couple plasma spectrophotometer (ICPS). Sodium citrate treatment (Tamura 1958) was conducted on the residual clay after NaOH-DCB treatment. In the same way, the extractable Si and Al were then determined using ICPS. The residual clays were then analysed mineralogical properties using XRD.

Results

Lithologic discontinuity

Table 1 shows the primary minerals identified using XRD for fine sand and silt fractions. Integrated intensity of feldspar and amphibole increased with the depth, except feldspar decreased in B3 horizon, on the contrary quartz decreased with the depth. Based on the Goldich stability series, amphibole is more stable than feldspar. Feldspar was only detected in the A horizon. Feldspar was still detected in the 2B horizon. Anatase was detected in the silt fraction in all horizons and it showed increase with the depth. Free iron oxides slightly increased from the surface horizon to B3 horizon, and slightly increased in 2B horizon. According to the results it can be stated that the soil profile exhibited lithologic discontinuities, as there was a different in the mineralogical composition in the fine sand fraction.

Table 1. The primary minerals identified using XRD of the fine sand and silt fractions

Horizon	Fine sand			Silt		
	Feldspar	Amphibole	Quartz	Feldspar	Quartz	Antase
	Integrated intensity fraction*					
A	0.07		0.93	0.07	0.89	0.10
Bl	0.12	0.05	0.83		0.89	0.11
B2	0.23	0.05	0.72		0.86	0.14
B3	0.07	0.19	0.72		0.86	0.14
2B			1.00	0.12	0.71	0.17

*relative value among the detectable minerals

Halloysite/smectite miexed layers

Figure 1 shows the XRD pattern of the clay fraction of the soil A horizon as a representative result for five clay samples. The Mg saturated clay showed 15.9 Å and 7.6 Å peaks. NaOH treatment resulted in a collapse of the 7.6 Å peak. Glycerol solvation resulted in swelling the peak of 15.9 Å to 19.64 Å, whereas the 7.6 Å peak changed from a relatively sharp peak to a broad peak. K saturated clay showed a change in the 15.9 Å peak of the Mg saturated clay to a broading of the 12.1 Å peak accompanied with a continuous form between 7.6 Å and 12.1 Å. Formamide solvation resulted in a shift of the 7.6 Å peak to 9.72 Å. Accordingly, it is suggested that the 7.6 Å peak is halloysite.

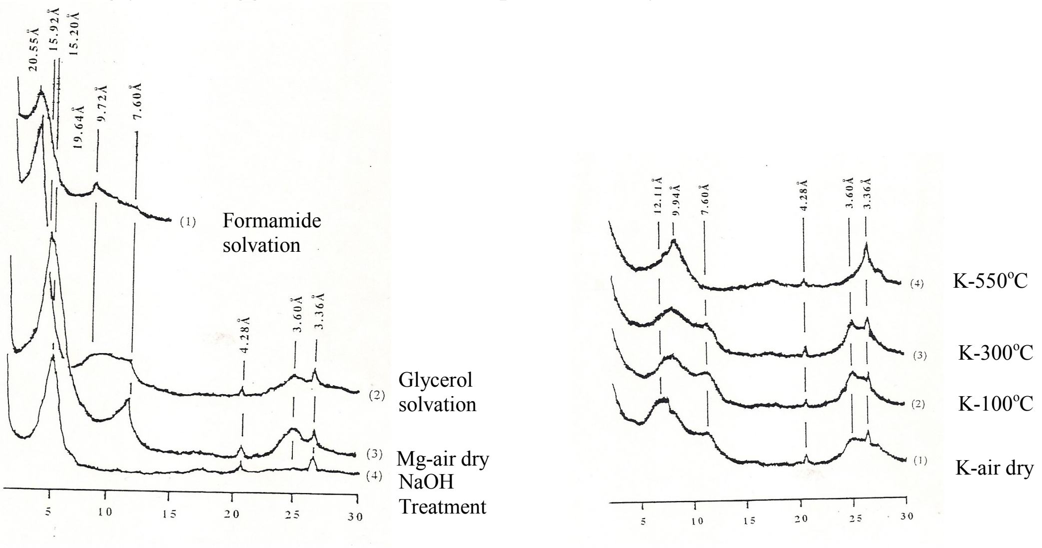

Figure 1. The XRD pattern of the clay fraction of the soil at A horizon

Development of the halloysite/smectite mixed layers

Table 2 shows the results of the successive dissolution using hot NaOH and hot citrate extraction. The hot-NaOH extraction resulted in the SiO_2/Al_2O_3 molar ratio of 2.29 for the A horizon and increased from A to B2 horizon and then decreased for the following B3 and 2B horizons. According to Tan and Troth (1982), the extracted material is kaolin minerals, and for the present study is halloysite. Prolonged hot-citrate extraction was successfully used to identify the interlayer materials in hydroxyl-Al interlayered vermiculite (Nurcholis 2003). The hot citrate extractable SiO_2 and Al_2O_3 resulted in the SiO_2/Al_2O_3 molar ratio of 2.83 for the A horizon, and the highest value was for the B2 horizon. The value of the SiO_2/Al_2O_3 molar ratio resulting from the hot citrate extraction is too high for halloysite. It is probably that prolonged hot citrate extraction also caused the destruction of the crystals of whole minerals. The lithologic discontinuity in the studied soil profile might also contribute to the variation in materials.

Table 2. Dissolution of silica and alumina and silica/alumina molar ratio by the NaOH treatment for the DCB pretreated clays

Horizon	NaOH extraction on the DCB pretreated clay			Hot-citrate extraction on the NaOH-DCB pretreated clay		
	Al_2O_3 mg/g	SiO_2	SiO_2/Al_2O_3 molar ratio	Al_2O_3 mg/g	SiO_2	SiO_2/Al_2O_3 molar ratio
A	58.75	79.37	2.29	1.93	3.22	2.83
Bl	67.71	90.91	2.28	1.49	2.08	2.36
B2	62.62	96.09	2.60	1.81	3.70	3.46
B3	67.17	96.09	2.43	1.54	2.95	3.25
2B	61.06	72.71	2.01	1.62	2.98	3.31

Conclusion

According to the results, it is possible to propose a mechanism of the development of halloysite/smectite mixed layer in four stages, as follows: the first stage is designated with the deposition of quaternary volcanic ash under the sea environment and it was diagenetically altered to smectite minerals. The second stage is gradual transgression of the sea, weathering and soil genesis processes. The third stage is Al-OH growth in the interlayer space of smectite mineral as hydroxyl-interlayered smectite. And the fourth stage is an inversion of a portion of the Si tetrahedral sheets of smectite mineral and halloysite which are then separated as free forms, and there is an arrangement of halloysite-smectite layers.

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