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Research Article
Chemical Characteristics and Morphology of Amorphous Materials Derived from Different Parent Materials from Central Java, Indonesia

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Abstract

Background and Objective: The lack of information concerning morphology and chemical characteristics of different amorphous materials still there, particularly from Indonesian Andisols. This study was conducted to find out the soil chemical properties, amorphous materials content, infrared spectral characteristics and morphology of amorphous materials derived from different parent materials. **Materials and Methods:** Three soil samples were collected from B horizon from Mt. Merapi which has an and esitic volcanic ash and Mt. Slamet which has a basaltic volcanic ash (1 soil sample and 1 sediment sample). Soil and sediment samples were analyzed for soil chemical properties such as pH-H_2O, pH-KCl, pH-NaF, C-org, CEC, SO_4, P retention and F reactivity, Fe-Al-Si with selective dissolution (NH_4-oxalate pH3, Nap-pyrophosphate and DCB), IR spectral characteristics and TEM image. **Results:** The content of allophane, imogolite, ferrihydrite and Al/Si ratio from Mt. Merapi were obtained at range of 15.2-27.3, 2.4-6.8, 0.04-0.06 and 1.14-1.39%, respectively. While soil samples from Mt. Slamet were obtained at range of 15.8-40.5, 0.6-25.6, 0.1-0.6 and 0.1-1.71%, respectively. Infrared spectral characteristics of clay from Mt. Merapi and Mt. Slamet were observed that absorption band peaks appeared at three mean areas, namely: 3433-3456/3417-3456, 1635/1627 and 972-1010/972-987 cm^{-1}, respectively. Allophane possess hollow sphere morphology with a diameter of 2.9-5.0 nm for samples from Mt. Merapi and 3.5-5.4 nm for samples from Mt. Slamet. While imogolite shaped like a long tubes with length of 536-1100 nm for samples from Mt. Merapi and 50-150 nm for Mt. Slamet. **Conclusion:** In average the content of allophane and imogolite in the soils from Mt. Merapi were higher than from Mt. Slamet, except for clay sediment sample. This sample contains more than 66% of amorphous minerals. Very surprisingly the soil samples from Mt. Merapi are found to contain imogolites of up to 1100 nm length, meaning these are the longest ever immogolites compared to anywhere else.

Key words: Flour reactivity, infrared specral, TEM image, allophane, imogolite, ferrihydrite

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Indonesia has approximately 400 volcanoes, of which 129 are active[1]. Volcanoes activity produces pyroclastic materials which are the parent materials of volcanic soils. Generally, soils formed from volcanic materials characterized by high amount of allophane, an amorphous aluminosilicate, that can configure a complexed bond with organic materials[2].

Mt. Merapi and Mt. Slamet are two active volcanoes located at the Central Java, Indonesia, which have height (m) about 2,968 and 3,428 above sea level, respectively[3,4]. The formation of both volcanoes are related to the subduction of the Indian oceanic plate beneath the Java arc[5,6,7].

The surrounding mountains have some kind of soil developed from volcanic ash, one of them is Andisols that are widespread in Indonesia[8,9]. Volcanic ash derived from different sources has different characteristic based on parent material. Volcanic ash derived from Mt. Merapi could be classified as basaltic andesite, due to the amount of SiO_2 range between 53.5-58%. Primary minerals found on Mount Merapi after erupting in 2010 were dominated by 49% volcanic glass, 26% labradorite and a bit of bitownit hiperstein, hornblande and opak[10,11]. Volcanic ash derived from Mt. Slamet could be classifed as basaltic andesite, due to SiO_2 content at range 45-53.5%. Primary mineral in Mt. Slamet were dominated by 32-34% phenocryst content, 19-22% plagioclase, 7-8% olivine and 4-5% Ca clinopyroxene[10,12].

Andisol has several characteristics, one of which is the high content in amorphous minerals[13]. The dominant clay minerals in andisol are allophane, imogolite and ferrihydrite. These are described by term such as spherical, tubular and gel-like. Their crystallinity has been described as amorphous, poorly crystalline, noncrystalline and short range order[14].

Andisol properties related to the nature and behavior of Al and Si or Fe active consisting of amorphous minerals such as allophane, imogolite and ferrihydrite[13]. Allophane an amorphous mineral, are the most reactive than imogolite and ferrihydrite because it has a surface that is very broad and there are many active functional groups such as silanol (Si-OH) and aluminol (Al-OH)[15]. Allophane and imogolite are naturally occurring aluminum silicate soil constituents with nano-ball and nano-tube morphology[16]. Allophane have hydrous aluminosilicate clays with Al/Si molar ratio between 1,0-2,0[13].

This study was conducted to find out the soil chemical properties, amorphous materials content, infrared spectral characteristics and morphology of amorphous materials derived from different parent materials.

MATERIALS AND METHODS

Study area: The study area was conducted at Mt. Merapi and Mt. Slamet located at Central Java province, Indonesia (Fig. 1). The study was conducted from January-December, 2016. Soil samples derived from basaltic andesite (intermediete) were collected from three location, namely: a) Turgo area located at old Merapi formation (Pleistocene), b) Kalitengah Lor area located at young Merapi formation (Holocene) and c) Kinahrejo area, located at young Merapi formation (Holocene). Whereas, soil samples derived from basalt are collected from two locations at Mt. Slamet, namely: a) Ketengerarea located under secondary forest and b) hot spring outlet (named: pancuran 7) as clay sediment. The both locations located at old Slamet formation (Pleistocene).

The studied area was described in detail as present in Table 1.

Sample preparation and soil analysis: Soil samples were collected from the andisol B horizon and immediately put in the polyethylene bag and tied tightly. Measurements were done on air-dried soils samples passed through a 2.0 mm sieve prior to analysis and results are expessed on air-dried soil basis. Soil reaction (pH) was measured in H_2O and 1M KCl to solution ratio 1:5 and 1:50 for 1M NaF[17], C-org was determined by Walkey-Black wet combustion method[18], cation exchange capacity (CEC) with 1 M NH_4Cl [19], P-retention[20] and fluoride reactivity (FR) consumed for back titration[21].

Clay collection: Clay (<2 μm) collection was done by applying a pipette method. First step, removing the organic matter with peroxide (H_2O_2) 30%, ultrasonic tool (20 kHz) also used to maximize soil colloids dispersed so that the fraction of sand, silt and clay were completely separate. The suspension was transfered quatitatviely to a 1 L polythene bottle. Dispersing agent about 20 mL was added and shaked overnight (16 h) on reciprocating shaker with speed of 125 strokes min^{-1}. The suspension was poured to a 1000 mL sedimentation cylinder and added water untill the mark. The cylinder was covered with a tight-fitting rubber bung and mixed the suspension by inverting the cylinder carefully 15 times [22]. Aliquots of these clay suspensions were washed with water until the clays dispersed again (5-10 times), the fine (<0.5 μm) clays were collected by centrifugation. Aliquot was transfered to a porcelain cup and heated at 40°C in the oven untill dry or freeze-drying.

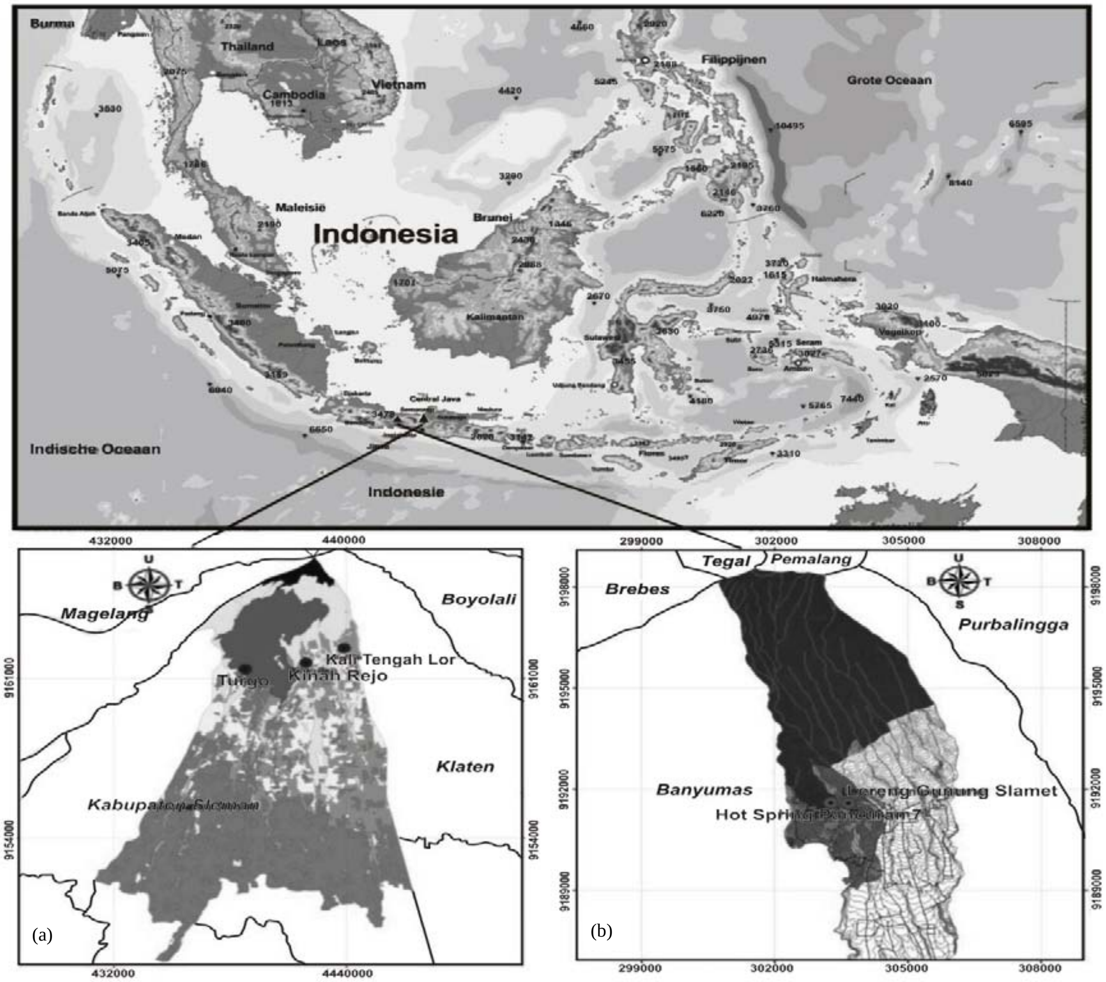

Fig. 1(a-b): Studied areas of (a) Mt. Merapi dan and (b) Mt. Slamet located in Central Java Indonesia

Table 1: Descriptions of studied area (Mt. Merapi and Mt. Slamet)

Descriptions	Locations				
	Mt. Merapi			Mt. Slamet	
Location	Turgo	Kalitengah Lor	Kinahrejo	Ketenger	Hot spring
Parent material	Volcanic basaltic-andesite ash	Volcanic andesite ash	Volcanic andesite ash	Volcanic basaltic ash	Volcanic basaltic ash
Volcano types	Stratovolcano	Stratovolcano	Stratovolcano	Stratovolcano	Stratovolcano
Topography	Hilly>30%	Hilly>30%	Hilly>30%	Hilly>30%	Hilly>30%
Sea level (m asl)	1120	1197	1155	843	780
Climate type*	Zone B wet (Q = 0,28)[1]			Zone C rather wet (Q = 0,34)[2]	
Time	Pleistocene	Holocene	Holocene	Pleistocene	Pleistocene
Vegetation	*Pinus merkusii* Waru (*Hibiscus tiliaceus*)	*Acacia decurents* Sengon (*Albizia chinensis*)	*Bambuseae*	*Agathis dammara* Puspa (*Scima wallichii* Mahoni (*Swietenia macrophylla*) pterydophyta	-
Soil sample	B Horizon	B Horizon	B Horizon	B Horizon	Sediment material

Selective dissolution: Clay fraction was subjected for Fe, Al and Si analysis with three selective dissolution methods, namely: Dithionite citrate bicarbonate (DCB), acid ammonium oxalate pH3 and Na-pyrophosphate. Ammonium oxalate which extract nanocrystalline (amorphous) inorganic forms of Al_o, Si_o and Fe_o[20], dithionite citrate bicarbonate (DCB)

Table 2: Chemical properties of andisols from Mt. Merapi and Mt. Slamet

Location	pH H_2O (1:5)	pH KCl (1:5)	pH NaF (1:50)	C-org (%)	CEC [cmol(+)kg^{-1}]	SO_4 (ppm)	P-Ret (%)	FR [cmol(+)kg^{-1}]
Mt. Merapi								
Turgo	6.4	5.7	10.2	1.1	8.41	73.9	47.42	752
Kalitengah Lor	6.4	5.8	10.8	2.09	11.04	180.8	65.76	349
Kinahrejo	6.4	5.7	10.4	0.80	8.41	0	77.43	537
Mt. Slamet								
Ketenger	6.8	5.9	11.2	5.06	31.36	656.4	99.59	752
Hot spring	7.8	7.2	9.4	0.87	32.74	714.7	83.40	155

CEC: Cation exchange capacity, P-Ret: Phosphate retention, FR: Flouride reactivity

extractable Al_d and Fe_d which represent finely divided minerals and amorphus forms of Al and Fe[23], pyrophosphate representating the organically complexed extractable Al_p, Si_p and Fe_p[20]. Al, Si and Fe from extract were quantified by atomic absorption spectrophotometry.

The Al/Si atomic ratio for allophane was estimated from $(Al_o\text{-}Al_p)/Si_o$values[24]. Calculation of the content of allophane, (allophane+imogolite), imogolite and ferrihydrite proposed with equation 1, 2, 3 respectively as follow[25]:

$$\text{Allofan (\%)} = \text{Si* \% (100/y)} \quad (1)$$

where, y is the % Si inside the allophane. The equation is y = 23.4-5.1x, where $x = (Al_o\text{-}Al_p)/Si_o$.

Calculation of allophane+imogolite:

$$\text{Allophane (\%)+Imogolite} = \text{Sio* (\%) 7.1} \quad (2)$$

$$\text{Imogolite (\%)} = \text{(Sio* \% 7.1)-Si* \% (100/y)} \quad (3)$$

Calculation of ferrihydrite according to Childs[26]:

$$\text{Ferrihydrite (\%)} = 1{,}7\text{* } Fe_o \quad (4)$$

Infrared spectral and morphological characteristics of clay fraction: FT-IR spectra were obtained on a IR Prestige-21 Shimadzu spectrometer for both aluminosilicate compounds by pressing a 1 mg dry sample into a spectral grade 200 mL KBr matrix with vibrating mill Shimadzu pressed using a hydraulic press. The resolution of each spectrum was 2 cm^{-1} and it was scanned 32 times. The spectrum electromagnetic will show in the wavelength between 2.5-50 µm and in the bandwidth between 4.000-250 cm^{-1}.

The particle size and morphology of composites were examined using Transmission Electron Microscopy (TEM)[27]. Specimen were tested in a JEOL JEM-1400 TEM.The specimen is cleaned with acetone by an ultrasonic cleaner, then slashed to 3 mm in size and 300 µm in thickness, put it on the grid inside the electron microscope at vacum condition. The specimen then shoot by an electron gun. An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen.

RESULTS AND DISCUSSION

Soil chemical properties: Soil chemical properties are described in Table 2. Based on the criteria from Eviati and Sulaeman[17], that the soil reaction analyzed with water (pH H_2O) and potasium chloride (pH KCl) revealed that soil from Mt. Merapi was categorized as slightly acidic, while at Mt. Slamet ranged from netral - slightly (alkalis). As for the pH NaF at all locations> 9.4, it indicates an amorphous mineral present in the soil[28]. The content of total organic C from Mt. Merapi ranges from very low to moderate, while the C-organic from Mt. Slamet ranges from very low to high. Low cation exchange capacity of soil from Mt. Merapi observed at range of 8.41-11.04 cmol(-)kg^{-1}, while at Mt. Slamet> 31 cmol(-)kg^{-1}. The higher CEC of the soil from Mt. Slamet is probably related to parent material which is more base than soil from Mt. Merapi. Phosphate retention of soil from Mt. Slamet was higher than from Mt. Merapi. High fluoride reactivity (FR) of soil from Mt. Merapi was observed at range of 349-752 cmol kg^{-1}, while at Mt. Slamet varies about 155-752 cmol kg^{-1}. The lowest FR was obseved at clay sediment from hot spring outlet, this probably due to a high content in sulphate ion (Table 2).

Amorphous materials composition of clay fraction: Selective dissolution method applied to estimate some mineral forms such as crystaline, amorphous material and humic complexed form in the clay fraction (<0.5 µm). Elements such as Fe, Al and Si extracted with dithionite citrate bicarbonate (DCB) are denoted as Fe_d and Al_d, for ammonum oxalate pH3 are denoted as Fe_o, Al_o, Si_o and for Na-pyrophosphate are denoted as Fe_p, Al_p, Si_p, respectively. The result of analysis was presented in Table 3.

Based on the Table 3 revealed that the clay fraction composed by Fe_o, Al_o and Si_o forms are more dominant than

Table 3: Short range order minerals in the clay fraction from Mt. Merapi and Mt. Slamet

Location	Acid-oxalate (%) FeO	AlO	SiO	Pyrophosphate (%) FeP	AlP	SiP	DCB (%) FeD	AlD	Al/Si ratio	Alloph[a] (%)	Imogo[b] (%)	Ferrih[c] (%)	Alloph+ imogo (%)	Total amorphous material
Mt. Merapi														
Turgo	1.29	5.01	3.75	0.04	0.26	0.24	0	0.34	1.27	22.1	4.50	0.06	26.6	26.7
Kalitengah Lor	1.35	3.76	2.49	0.04	0.31	0.20	0	0.50	1.39	15.2	2.40	0.05	17.7	17.7
Kinahrejo	0.84	5.77	4.81	0.03	0.29	0.23	0	0.51	1.14	27.3	6.80	0.04	34.1	34.2
Mt. Slamet														
Ketenger	2.30	4.63	2.32	0.07	0.65	0.12	0	0.74	1.71	15.8	0.60	0.10	16.5	16.6
Hot spring	6.53	1.03	9.30	0.37	0.26	1.46	0.03	0.11	0.10	40.5	25.6	0.60	66.0	66.7

[a]Allophane, [b]Imogolite, [c]Ferrihydrite

Fe_p, Al_p, Si_p and Fe_d, except Al_d from hot spring sediment. Atomic Al/Si ratio of clay fraction from Mt. Slamet was higher than from Mt. Merapi, exept sample from hot spring very low. In general, allophane and imogolite content in the clay fraction from Mt. Merapi was higher than from Mt. Slamet, except for sample from hot spring sediment in which reach 40.5 and 26%, respctively. In contrast the ferrihydrite content in the sample of Mt. Merapi was lower than Mt. Slamet.

Infrared (IR) spectral characteristics: Infrared spectra is a two-dimensional picture which, as the x-axis is the wave number (frequency), while the y-axis is the intensity transmittance[29]. All of samples were analyzed using FTIR, shows a broad absorption in the OH-stretching to about 3500 cm^{-1} from water is absorbed which is the typical allophane. Infrared absorption spectra of clay fraction from five location samples are presented in the Fig. 2.

Analysis of clay morphology using TEM: Morphology of allophane and imogolite are presented at Fig. 3-7. The shape of allophane was spherules and imogolite is look like tube. These particles formed aggregates of various shapes and sizes, either by themselves or with other constituents[30].

Allophane appeared as fine, ring shaped particles with diameters 3.5-5.0 nm. The morphology of imogolite is very unique and comprises thin fibrous tubes with inside and outside diameters of approximately 1 and 2 nm[31].

Soil chemical properties

Soil reaction (pH): Soil reaction (pH) is an indication of acidity or alkalinity of soil and is measured in pH units. Soil pH is defined as the negative logarithm of the hydrogen ion concentration[32]. The amount of H^+ ions extracted with water are often expressed by actual acidity, while those extracted with KCl 1 N solution are often referred to as potential acidity. Levels of soil reactions are grouped into 3 categories: Acid, neutral and alkaline.

The higher pH value of soil samples from Mt. Slamet may be related to the more alkaline parent material of the soil from Mt. Merapi. In the range of pH 5.6-7, hydroxyl aluminum polymers predominate among acids soil components, exchangeable acidity is virtually absent and only none exchangeable and titratable acidity are present in measurable quantities[33]. Although potential acidity depends on the equilibrium pH of the soil suspension[34], exchangeable aluminium normally occurs in significant amounts only at soil pH values less than about 5.5.

Andisols normaly possess a high content in amorphous minerals such as allophane, imogolite and ferrihydrite. Allophanic soils usually possess pH-H_2O values greater than 5 (pH values are in the range of 5-7) and the content of complexing organic compounds is low[35]. Allophanic soils are favored in base-rich parent materials (e.g. andesitic basalt, basalt) having colored volcanic glass and younger volcanic deposits. These condition favor higher pH values (pH>5), which promotes formation of Al-polymers relative to Al-humus complexes[36]. In this study, the pH NaF values at all locations >9.4, which suggests that amorphous material or active Al-OH groups are dominant in the soil exchange complexes. pH >9.4, is a strong indicator that short-range ordered materials dominate the exhchange complex[37]. The use of these ligand (F^-) to suspect the existence of a single OH group bonded with Al or Fe in allophane, imogolite or humus complexes Al/Fe.

In this case, pH NaF from Mt. Slamet higher than Mt. Merapi, except hot spring-Mt. Slamet. It is possible that some of the OH groups in aluminol (≡Al-OH) have been blocked by SO_4^{2-} which is mostly present in hot springs (Fig. 8).

C-organic: The results showed that the content of C-organic in Mt. Merapi is very low to moderate,this may related to recovery process of vegetations after eruption in 2010. Now the area is already overgrown with shrubs, grasses and accasia docuren. While sample from Ketenger-Mt. Slamet contain a higher organic matter than Mt. Slamet area, it is possible that the samples were taken from secondary forest with more plant population. The old leaves fall down to the soil surface will enrich the content of soil organic matter. The accumulation of

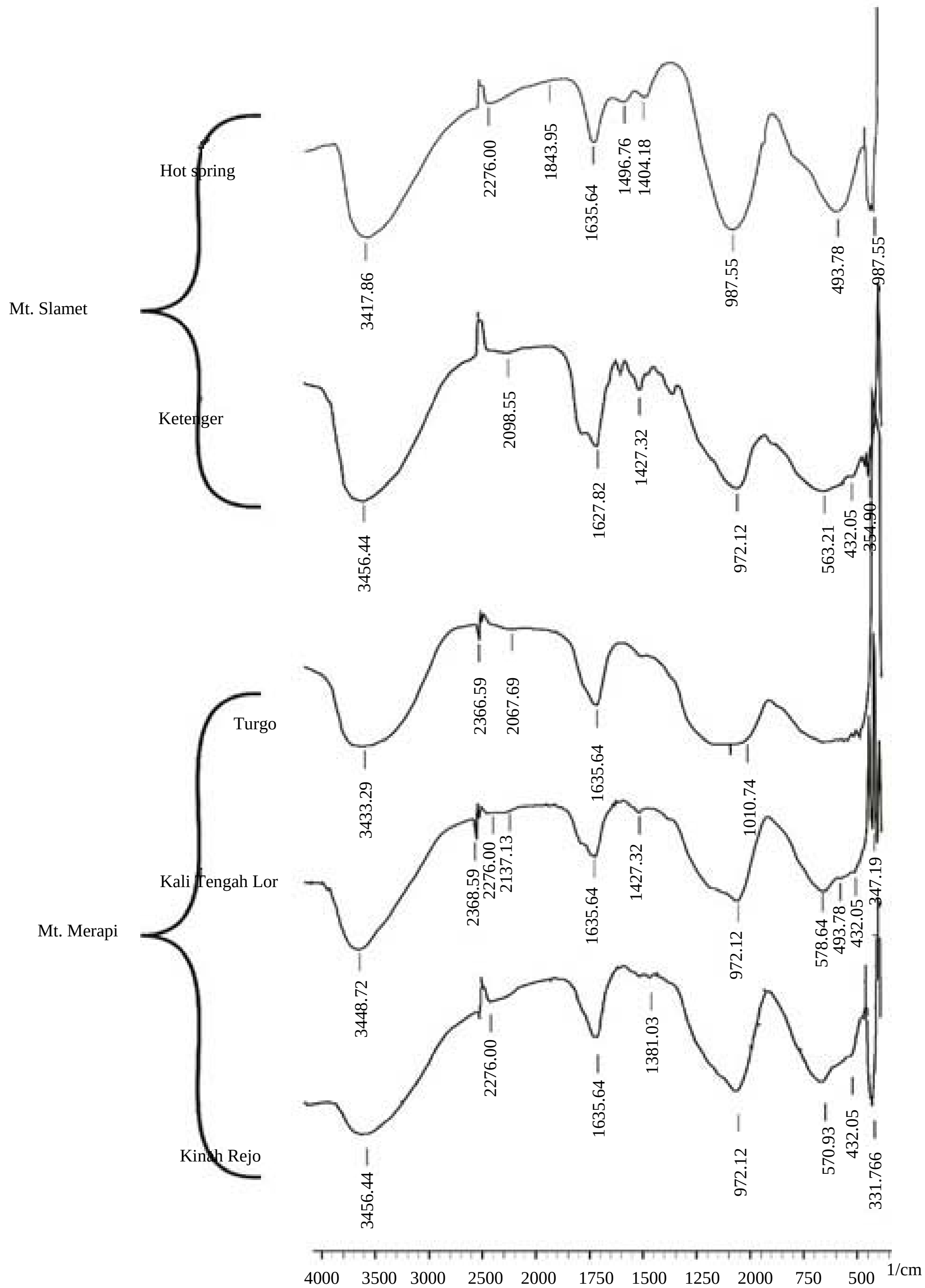

Fig. 2: Infrared absorption spectra of clay fraction from Mt. Merapi and Mt. Slamet

organic matter happens because the organic material strongly bound by allophane so that the process of decomposition is slower[39]. The low content of organic matter in the sample from the hot spring oulet because of the clay deposits carried by the flow of hot water and deposited on the outlet area.

Cation exchange capacity: Cation exchange capacity (CEC) of the soil is a general indicator of productivity potential for a soil. CEC is the capacity to absorb and exchanged the clay on the complex cation exchange is affected by the clay content, the type of clay and organic matter[40]. The results showed that CEC on Mt. Merapi is lower than

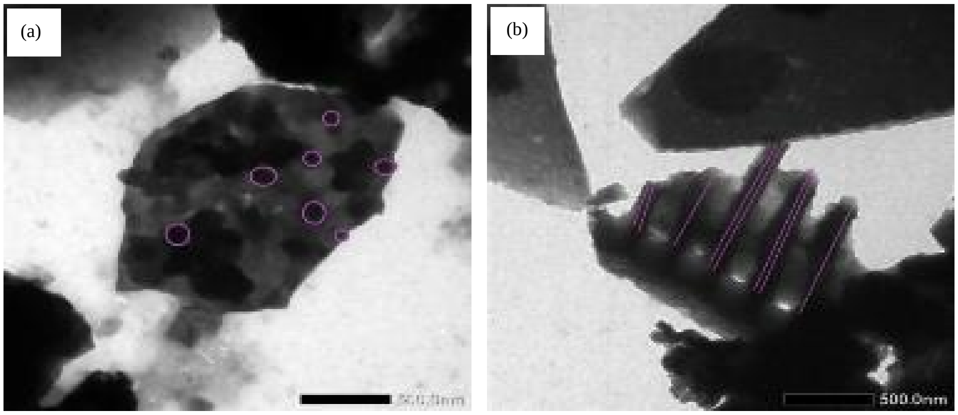

Fig. 3(a-b): TEM image from Turgo, Mt. Merapi (a) Allophane and (b) Imogolite

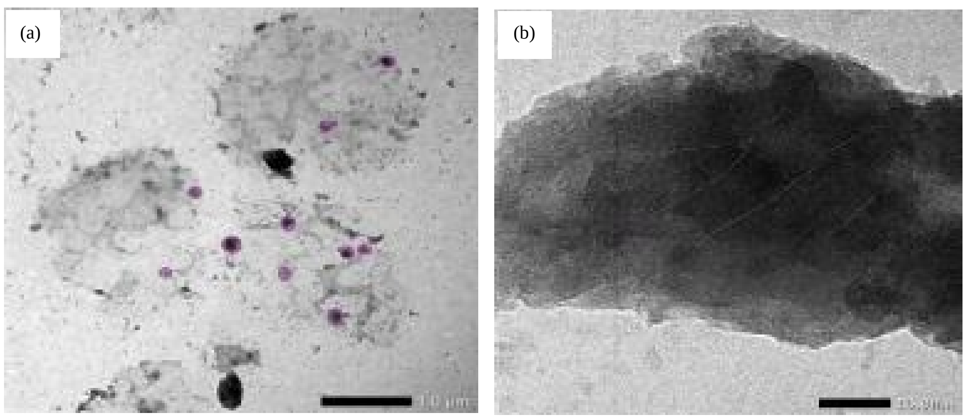

Fig. 4(a-b): TEM image from Kalitengah Lor, Mt. Merapi (a) Allophane and (b) Imogolite

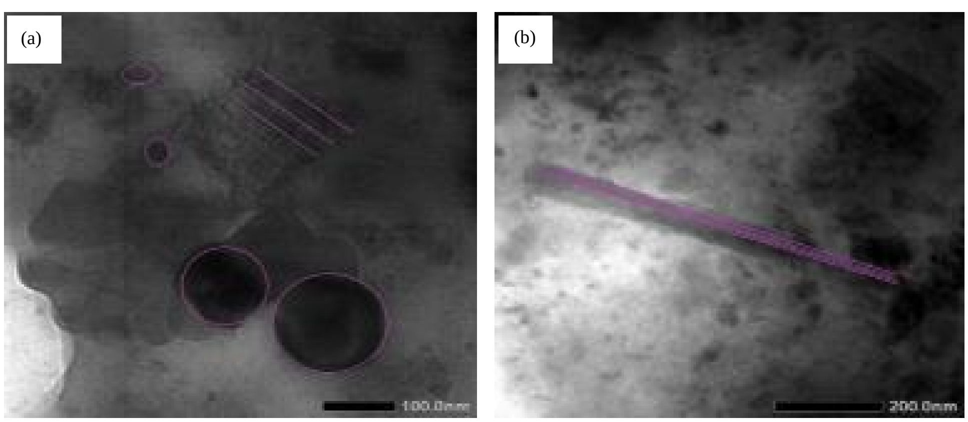

Fig. 5(a-b): TEM image from Kinahrejo, Mt. Merapi (a) Allophane and (b) Imogolite

Mt. Slamet. The high CEC is determined by the level of clay and organic matter present in the soil.

P-retention: High P retention is one of the unique properties of the soil andisol[21]. The soil taken from Mt. Merapi has P-retention that could be categorized into medium-high rate, while from Mt. Slamet categorized into high-very high rate. High P retention in andisol due to high content of the amorphous Al and Fe materials such as allophane, imogolite, aluminium hydroxide and ferrihydrite. The minerals possess

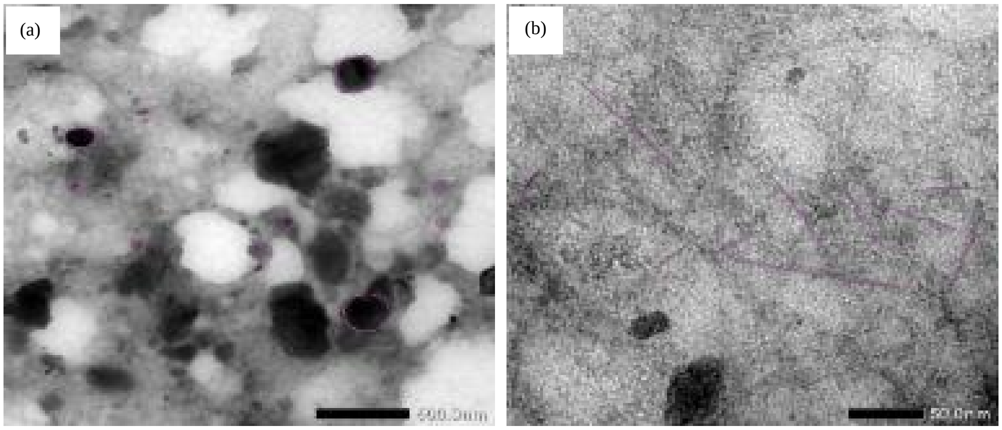

Fig. 6(a-b): TEM image from Ketenger, Mt. Slamet (a) Allophane and (b) Imogolite

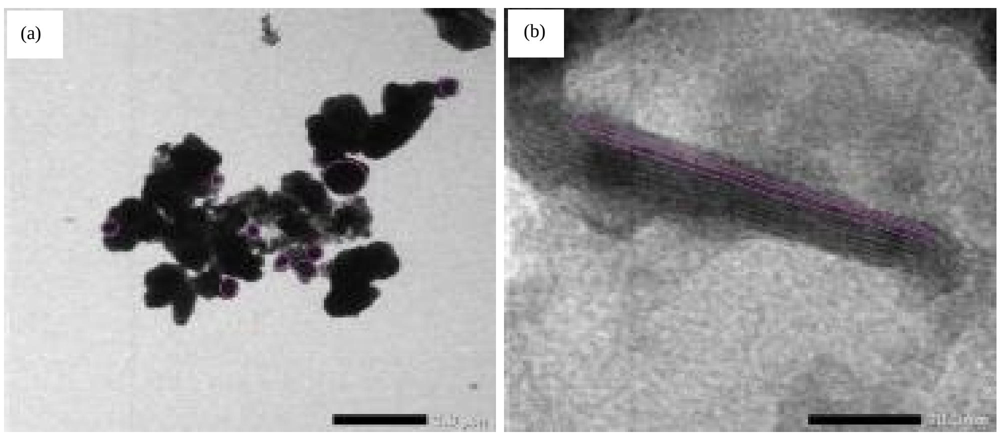

Fig. 7(a-b): TEM image from hot spring outlet, Mt. Slamet (a) Allophane and (b) Imogolite

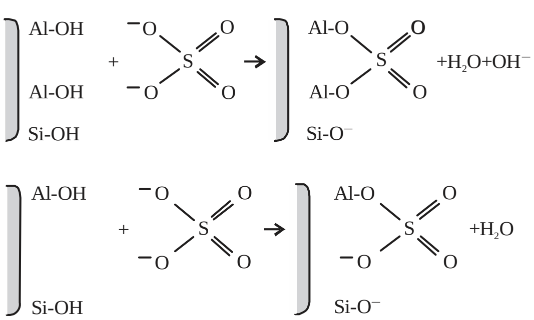

Fig. 8: Mechanisms of aluminol in allophane blocked by SO_4[38]

a high content in functional groups such as ≡Al-OH or ≡$Al\text{-}OH_2^+$ and ≡Fe-OH which has an important role in adsorbing phosphate ions. Aluminol and ferrol in the form of a hydroxyl anion singly bonded with Al/Fe are easily exchanged by phosphate ions through ligand exchange mechanism. Increasingly the number of groups aluminol in amorphous minerals such as allophane and imogolite, so the more phosphate adsorbed[39].

Flouride reactivity (FR): Fluoride reactivity of the soils from Mt. Merapi and Mt. Slamet varies between 349-752 cmol kg^{-1} and 155-752, respectively. The highest FR values were obtained on samples from Turgo-Mt. Merapi and Ketenger-Mt. Slamet of 752 cmol kg^{-1}, while the others were lower. The lowest FR values (155 cmol kg^{-1}) were obtained for clay sediment from hot spring outlet. It is possible that some of the OH groups in aluminol (≡Al-OH) and ferrol (≡Fe-OH) have been blocked by SO_4^{2-}, which is mostly present in hot spring outlet.

Soil minerals containing high single-binding OH-functional groups are allophane, imogolite and ferrihydrite. Soil reactivity was measured using F^- anion to exchange the OH bound by Al and Fe. The more the amount of OH^- being released by minerals the more the amount of acid solution needed to neutralize OH^-. The mechanism of the OH^- and F^- exchange reactions can be written as follows:

$$\equiv S\text{-}OH+F^- \equiv S\text{-}F^-+OH^-$$

Amorphous minerals composition: The three selective dissolution procedure provide a basis for approximate differentation of the forms of Fe, Al and Si. Dithionate-citrate-bicarbonate (DCB) removes crystalline (free) inorganic Fe and Al oxide. Ammonium oxalate pH$\pm$3 dissolves amorphous (active) inorganic Fe, Al and Si. Sodium pyrophosphate extracts organic-complexed Fe and Al. Based on Table 3 indicated that Fe_d present in the all soil samples is very low (0-0.3%). Al_d in the soil from Mt. Slamet higher than from Mt. Merapi, except for clay sediment from hot spring outlet. However, the clay sediment contains higher FeO, SiO, FeP and SiP than the soil samples from Mt. Merapi and Mt. Slamet. Generally, the content of Fe, Al and Si extracted by NH_4-oxalate pH3 was higher than that extracted by Na-pyrophosphate.

The content of allophane and imogolite in the soil samples from Mt. Merapi were obtained at range of 15.2-27.3 and 2.4-6.8%, while from Mt. Slamet at range of 15.8-40.5 and 0.6-25.6%, respectively. The highest content of allophane and imogolite were found in the clay sediment from hot spring area. The allophane structure is much more ambiguous, especially because of its chemical composition variability. Indeed, different allophane structures have been determined according to the chemical compotion (atomic ratio Al/Si)[27]. The ratio $(Al_o\text{-}Al_p)/Si_o$ was used for estimating the Al/Si ratio of allophane and imogolite[25]. In this study, clay fraction from Mt. Merapi have Al/Si ratio 1.14, 1.27, 1.39 while Mt. Slamet have Al/Si ratio 1.71 and 0.1. Ferrihydrite presented in the samples from Mt. Slamet was higher than soil samples from Mt. Merapi. Ferrihydrite is an iron oxide which has a high capability in binding water molecules (water holding Fe-oxide). Ferrihydrite contains many monodentate OH groups, so easily to form a complex ligands with organic compounds[41].

Infrared spectral characteristics of clay fraction: Infrared spectrum analysis showed that allophane has three main areas, ie: 2700-3500, 1400-1800 and 650-1200 cm^{-1}. The first area, absorption band region one and two showed OH (width) and bend vibration of Si-OH, Al-OH and OH structure of the adsorbed water. In the hydroxyls stretch region (3000-3500 cm^{-1}), spectra are dominated by intense structure less absorption due to H-bonded species[42]. The second area show the number 2276, 2368 and 2098 cm^{-1} causes vibration bond Si-O-Al. Vibration deformation H-O-H in absorbing water appears at 1630-1640 cm^{-1}. Absorption of third region is Si-OH or Al-OH (vibration width) portion of vibration changes into Si-OH or Al-OH. Generally range from 1100-1000 cm^{-1} for Si-rich allophane were detected from Turgo, Mt. Merapi (1010 cm^{-1}). The vibration bands at 972 cm^{-1} was related to the Si-O-Al vibrations. The band at 500-300 cm^{-1} was assigned to the Al octahedral and probably arise from an octahedral sheet similar to the gibbsitic sheet present in imogolite[42] were detected from all locations (Fig. 2).

Table 4: Diameter of allophane and length of imogolite

Location	Total samples	Diameter allophane (nm)	Length imogolite (nm)
Mt. Merapi			
a. Turgo	10	3.6-4.9	536-1100
b. Kalitengah lor	9	2.9-5.0	Unmeasured
c. Kinahrejo	7	3-5.0	800-1000
Mt. Slamet			
a. Ketenger	10	3.9-5.4	50-150
b. Hot spring	10	3.5-5.0	80-120

Transmission electron micrographs of clay fraction: The transmission electron micrographsare presented in Fig. 3-7. In this study, clay samples from five locations showed a ring shaped particle dan a thin fibrous tubes. Ring shaped particle is allophane, often descibed as hollow sphere[43,44]. Allophane is a clay-size mineral of widespread occurrence involcanic ash soilswith shape like a hollow ball (nano ball)[43,45]. Table 4 presents diameter of allophane and length of imogolite from five locations. The unit particle of allophane is a hollow spherule with an external diameter at range of 2.9-5.0 nm for samples from Mt. Merapi and 3.5-5.4 nm for samples from Mt. Slamet. The thin fibrous tubes often referred imogolite morphology is shaped like a long tube (nano tube)[46]. Imogolites are single-walled aluminosilicate nanotubes ($Al_2SiO_2H_4$) of 2-3 nm in diameter[44]. Imogolite is easily recognizable because of its tubular structure consisting of nanotubes and have a few hundred microns length. Table 4 shows that clay samples from Mt. Merapi and Mt. Slamet were observed the length of imogolite at range of 536-1100 and 50-150 nm, respectively, except for sample from Kalitengah Lor was unmeasured.

CONCLUSION

The content of allophane, imogolite, ferrihydrite and Al/Si ratio from Mt. Merapi were obtained at range of 15.2-27.3, 2.4-6.8, 0.04-0.06 and 1.14-1.39%, respectively. While soil samples from Mt. Slamet were obtained at range of 15.8-40.5, 0.6-25.6, 0.1-0.6 and 0.1-1.71%, respectively. Infrared spectral characteristics of clay from Mt. Merapi and Mt. Slamet were observed the peaks derived from OH functional groups, HOH deformation vibration of adsorbed water and Si-O-Al bonding. The unit particle of allophane is a hollow spherule with an external diameter at range of 2.9-5.0 nm for samples from Mt. Merapi and 3.5-5.4 nm for samples from Mt. Slamet. While imogolite shaped like a long tubes (nanotubes) with length of 536-1100 nm for samples from Mt. Merapi and 50-150 nm for Mt. Slamet, except for sample from Kalitengah Lor was unmeasured.

SIGNIFICANCE STATEMENTS

This study discovers some important chemical properties and morphology of amorphous material from specific volcanic areas such as Mt. Merapi and Mt. Slamet situated in Central Java Indonesia that can be beneficial for selecting a strategy in land management. This study will help the researcher to uncover the critical area of amorphous minerals which has an important role in controling nutrient availabilty in andic soils that many researchers were not able to explore. Thus, a new theory on genesis of allophane and imgolite should take into consideration the age and activity of the volcano.

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