The Soils on the Krakatau Islands

III. Mineralogy of the Soils

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Introduction

In the deposits of Krakatau islands, their characterization was made in the two main types of ejecta; the pyroclastic flow occasioned by 1883 year's great eruption and the ash and scoria from the Anak crater after 1927.

Among soil formation factors, their mineralogical properties are of great importance because of their affection not only in the releasing plants-nutritional elements during the weathering but also in the formation of colloids (secondary clay minerals) which are most active in soils.

Van Baren[1] described the approximate abundance of minerals in the order of plagioclase > volcanic glass > amphibole > augite > hypersthene > ilmenite > magnetite in the pyroclastic pumiceous materials of 1883. Newsome[3] estimated the contents of the minerals in the volcanic ash of Be subsurface (which is pyroclastic, too) by X-ray fluorescence method: i.e. quartz 27.04, orthoclase 12.58, albite 35.20, anothite 11.76, Mg rich pyroxene 2.14, ilmenite 0.23, hematite 3.53, apatite 0.46%, respectively. Oba et al[4] made the detailed geochemical study on the lava flow, ejecta and pyroclastic flow from the Krakatau group and concluded that rocks of lava flows and volcanic bomb are basaltic andesites both lithologically and geochemically, while the pyroclastic flow is lithologically andesitic and geochemically dacitic, which is to be characterized by the presence of a large amount of volcanic glass.

In this study, the mineralogical compositions of the two type of ejecta were investigated with special attention to the finer fractions, and the obtained results were put on a trial to correlate it with the weathering or soil forming process of volcanic ash in the tropical regions.

Materials and Methods

Soil samples were fractionated into the respectively sized particles as mentioned in Part II of this series.

Sand fractions (2–0.2, 0.2–0.02 mm) were treated with Na-dithionite-citrate-bicarbonate for removal of free Fe and Al hydrous oxides. Thus treated particles were then separated into heavy and light ones using Thoulet heavy liquid (HgI_2 7 : KI 6 : H_2O 2) of Sp. Gr. 2.80. The

separated particles were observed under polarized microscope and identified the mineral species. Their pulverized samples were also examined by X-ray diffraction analysis, using RAD-RB (12 kW) system of Rigaku-Denki. Obtained data were referred to JCPDS file with computer.

Clay fractions $(-2 \mu m)$ were examined by X-ray diffractometer, differential thermal analysis (DTA), thermo-gravimetry (TG), infra-red spectroscopy (IR), electron microscopy (EM) and P-absorption test.

X-ray diffraction patterns were obtained with the parallely oriented Mg- and K-saturated specimens. The changes of $d(001)$ spacings after ethylene glycol solvation for Mg-clay and heatings at 350°C and 550°C for K-clay were also measured. The powder samples were used for random orientation method.

DTA and TG curves were obtained at the elevation temperature of 20°C per minute with Themoflex TG–DTA of Rigaku-Denki.

IR spectra were obtained in the range of 5000 to 330 cm^{-1} with KBr tablet (0.8 mg sample/200 mg KBr), using spectrophotometer A302 (Jasco).

For the EM observation, usual transparent and scanning methods were employed using Hitachi H–700(H) apparatus.

The P-retention was measured as follows: 10 ml of 0.032 M KH_2PO_4 adjusted at pH 4.6 was added to 1.0 g sample and shaken for 24 hours at 30°C. The difference between the P content of original solution and that of treated one determined spectroscopically was taken as the amount of P-sorption.

Mineralogy of sand fractions

The result of separation of sand fraction (2–0.02 mm) by heavy liquid for St–3 samples is shown in Table 1. In this profile, just the lowest 3–9 layer is the one from the pyroclastic flow of 1883 and others are various ejecta from An crater different in the falling age. Light mineral predominates over heavy mineral in all the samples. The quantum ratios are mutually varied, especially the 3–9 layer is characterized by the quite low contents of heavy mineral, counting less than about 5%.

Table 1. Content of heavy (Sp. Gr. >2.80) and light (Sp. Gr. <2.80) mineral in St–3 sample

Sample No.	Particle Size (mm)	Heavy Min. (%)	Light Min. (%)
ST 3–1	2 –0.2	19.6	80.4
	0.2–0.02	22.3	77.7
–2	2 –0.2	22.0	78.0
	0.2–0.02	29.3	70.7
–3	2 –0.2	11.6	88.4
	0.2–0.02	15.5	84.5
–4	2 –0.2	14.2	85.8
	0.2–0.02	11.6	88.4
–5	2 –0.2	11.3	88.7
	0.2–0.02	14.3	85.7
–6	2 –0.2	16.8	83.2
	0.2–0.02	16.5	83.5
–9	2 –0.2	5.6	94.4
	0.2–0.02	4.6	95.4

This indicates the difference in mineralogy between the pyroclastic materials and other ejecta.

These samples were X-ray analyzed to identify the mineral species (Table 2). The mineral composition of St 3–9 (pyroclastic flow) is clearly different from those of other layers in the following items: the amount of heavy mineral is quite small, containing ilmenite and not olivine at all, and as to light minerals, the main constituent, volcanic glass, belongs to colorless ones (under optical microscope) and plagioclase is mainly albite but not anorthite. The pyroclastic flow are also fixed to be pumiceous, not containing scoria as in the case of the volcanic bombs.

Table 2. Mineralogial composition of sand fractions (St-3 profile)

No.	Particle size (mm)	Ft	St	Hy	Au	Mg	It	Plagioclase		Glass		Unknown Opaque min.
								An	Al	Dark	-Less	
1	2 –0.2			+ +				+ + +	+	+ + +		+ + +
	0.2–0.02	+ +		+ +				+ +	+	+ + +		+ + +
2	2 –0.2	+ + +	+			+		+ + +	+	+ + +		+ + +
	0.2–0.02	+ +			+			+ +		+ + +		+ +
3	2 –0.2		+ +	+	+ +	+		+ + + +	+	+ + +		+ + + +
	0.2–0.02		+ +		+ +			+ +	+	+ + +		+ + +
4	2 –0.2	+ +	+ +	+ +		+		+ + + +	+	+ + + +		+ +
	0.2–0.02			+ +	+ +			+ + +	+	+ + +		+ +
5	2 –0.2		+ +	+ +	+	+		+ +	+	+ + + +		+ +
	0.2–0.02			+ +	+ +	+		+ + +	+	+ + + +		+ +
6	2 –0.2			+ +	+	+		+ + +	+	+ + + +		+ +
	0.2–0.02	+ +		+ +	+			+ + +	+	+ + +		+ +
9	2 –0.2				+	+	+	+	+ + +	+ + + +		+ +
	0.2–0.02				+	+	+		+ + +	+ + + +		+ +

Abbreviations: Ft, Forsterite ferroan; St, Orthoferrosilite magnesian; Hy, Hypersthene; Au, Augite; Mg, Magnetite; It, Ilmenite; An, Anorthite; Al, Albite; Dark, Dark-colored; –Less. Colorless

Unknown opaque min.; Andesitic. Sample 1 to 6, mainly scoria and Sample 9, mainly pumice

Symbols representing the relative abundance of the constituent minerals: + + + + > + + + > + + > +

The other St–3 layers show relatively high contents of heavy minerals, especially in the newly deposited ashes (upper two layers). In the heavy minerals are included forsterite (Mg-olivine) and larger amounts of orthoferrosilite magnesian (pyroxene) together with common occurrence of hypersthene and augite. Among light minerals, plagioclase belongs to anorthite and volcanic glass mainly to colored ones.

Mineralogical compositions of clay (−2 μm) fractions

As mentioned in part II of this series, the samples from pyroclastic flow of 1883 and those from younger ejecta of Anak crater after 1929 were different from each other in their textures; i.e. the formers were finer while the latters more sandy.

In terms of mineralogical constituents, X-ray diffraction analysis also revealed a distinct difference between the clay fractions ($-2\,\mu m$) of both the samples.

In the freshest and unweathered An samples, it is not possible to detect any reflection peak of crystalline clay (secondary) minerals other than small peaks of feldspar (primary mineral) around 3.2 Å etc. in the $-2\,\mu m$ fractions, as shown in Fig. 1.

The X-ray figures indicate that these fractions mainly consist of amorphous materials.

IR spectrum of an An clay (Fig. 2) also showed the characteristic absorption of glassy material in the range of 1000 to 1100 cm^{-1} together with slight but sharp absorptions at 630, 585, 545, 470 cm^{-1} etc. due to anorthite, but any formation of allophane, a secondary amorphous aluminosilicate clay, was not detected in this pattern.
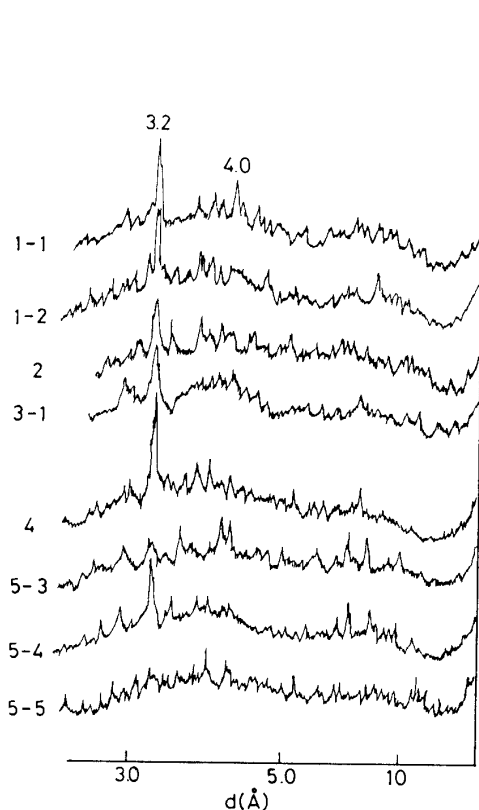

Fig. 1. X-ray diffraction patterns for An clays.
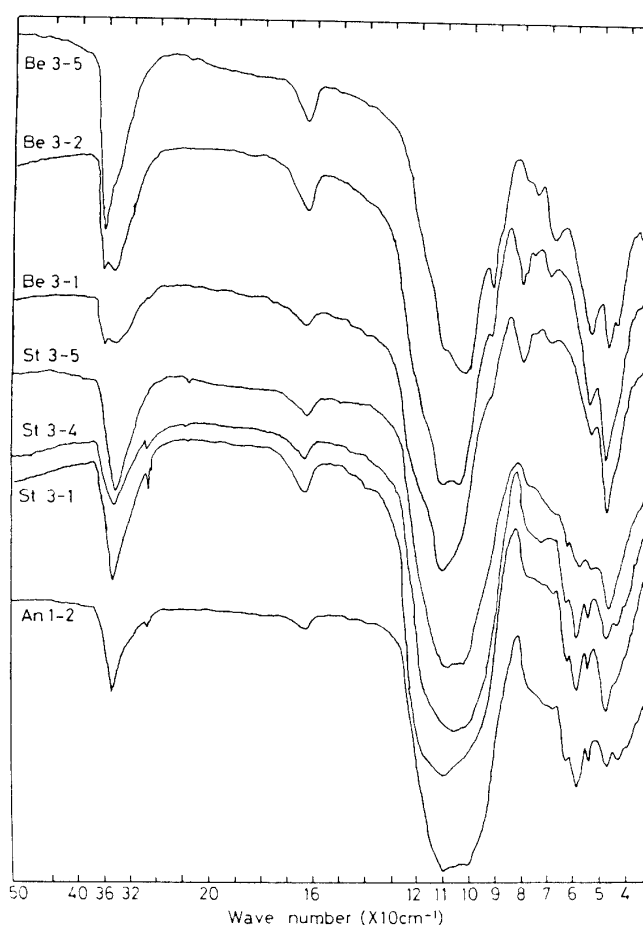(Mg-saturated, parallely oriented)

Fig. 2. Infra-red absorption spcetra for each clay fraction.

DTA curves of those showing no significant exo- or endo-thermic peak (Fig. 3) indicate also that the amorphous materials are not of allophanic clay, due to the fact that allophane has a broad endothermic peak around 100°C and a sharp exothermic peak between 900–1000°C.

Thus the amorphous materials forming the main constituents of An clay fractions are concluded not to be allophanic clays but some fragments of the primary volcanic glass.

The $-2\,\mu m$ fractions of upper deposits of St and Ke deriving from An crater after 1927 and remaining in more advanced weathering stage than An, showed similar aspects in their X-ray diffraction patterns: i.e. their relativley small amounts of clay fractions do not have any crystalline clay mineral reflection, either (X-ray diagrams for St–1 to –6, in Fig. 4).
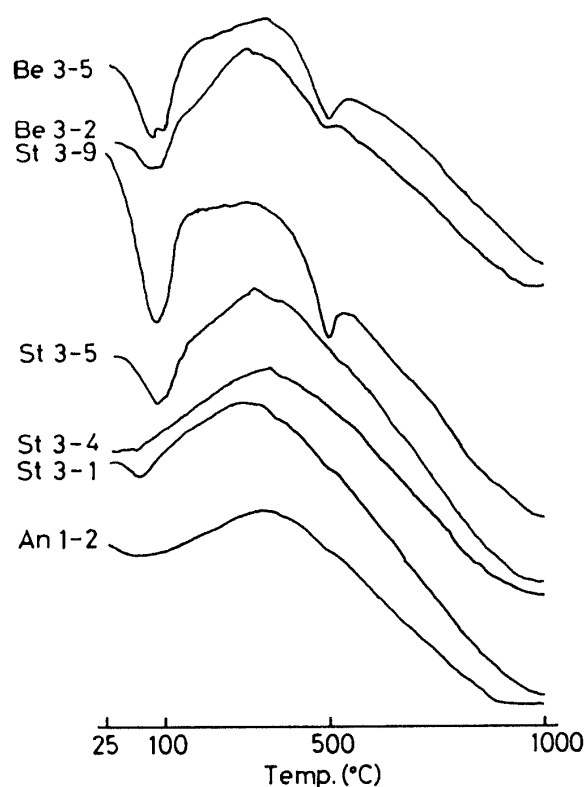
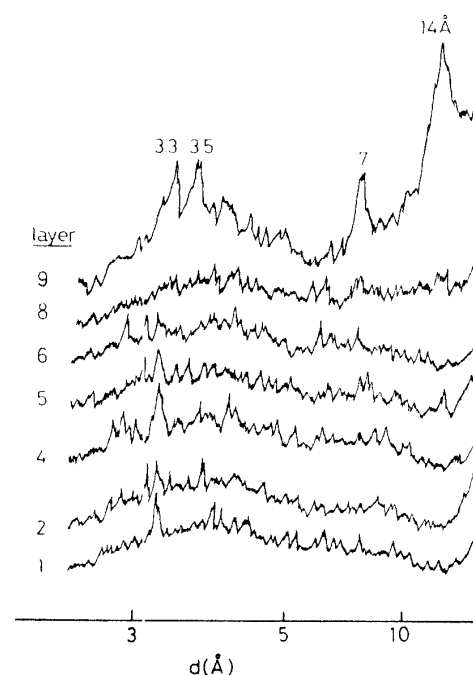Fig. 3. Differential thermal analysis curves for each clay fraction.

Fig. 4. X-ray diffraction patterns for St–3 clays. (Mg-saturated, parallely oriented)

Although their DTA curves of them (Fig. 3) are also absent from exothermic peak in high temperature region, somewhat different figures were obtained on IR and TG patterns. In IR patterns (Fig. 2), broad Si–O band with absorption maximum at 1100–1000 cm^{-1} shows some
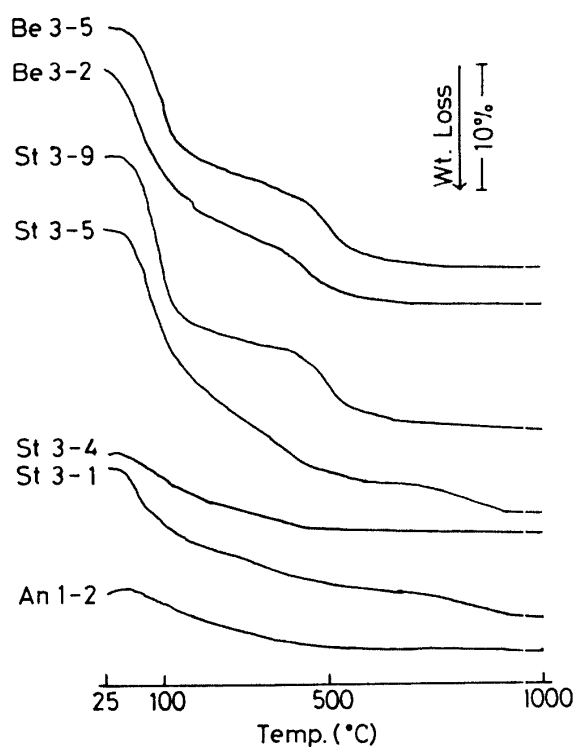

Fig. 5. Thermo-gravimetric analysis curves for each clay fraction.

shoulder or swelling toward lower wave number (1000–900 cm^{-1}), suggesting a formation of secondary Si–O–Al as allophanic clay though its content is quite small. This was confirmed by the continuous losing of weight on heating up to 500–600°C (Fig. 5). Such weight-loss is attributed to the surface-edged OH of the gel-like substances having above-mentioned Si–O–Al bonding together with the gel-like Al or Fe hydroxides. Much weight-loss occasioned by heating on the "brown layes" (VB, 3–5 in the case of St) whose clay contents are relatively higher compared with other An ejecta migtht be due to the latter Al or Fe gels, corresponding to their relatively high P-absorption coefficiency (see Part II).

From these data, the clay fractions of the upper deposits of St and Ke are assumed to contain small amounts of gel-like substances having surface-edged OH groups, in addition to the bulk of volcanic glass, accompanied by feldspar as in the case of the An clays.

On the other hand, in these analyses, the clays of Be and lower deposits of St and Ke from the pyroclastic flow of 1883 demonstrated distinct differences from the An ejecta.

First of all, the contents of their clay fractions are apparently higher than that of An ejecta, and their X-ray diagrams showed some sharp reflection peaks at 14, 7, 3.5, 3.3 Å etc. with Mg-saturated and parallely oriented specimens (St 3–9 in Fig. 4 and Be-clays in Fig. 6). The 14 Å peak swelled to 17.0 Å with ethylene-glycol solvation, contracted to 12–13 Å with K-saturation and to 10 Å by heating over 350°C (Fig. 7). The behaviors observable on the respective treatments are in good accordance with those of smectite. The 7 Å peak remained as it was, with the treatments by
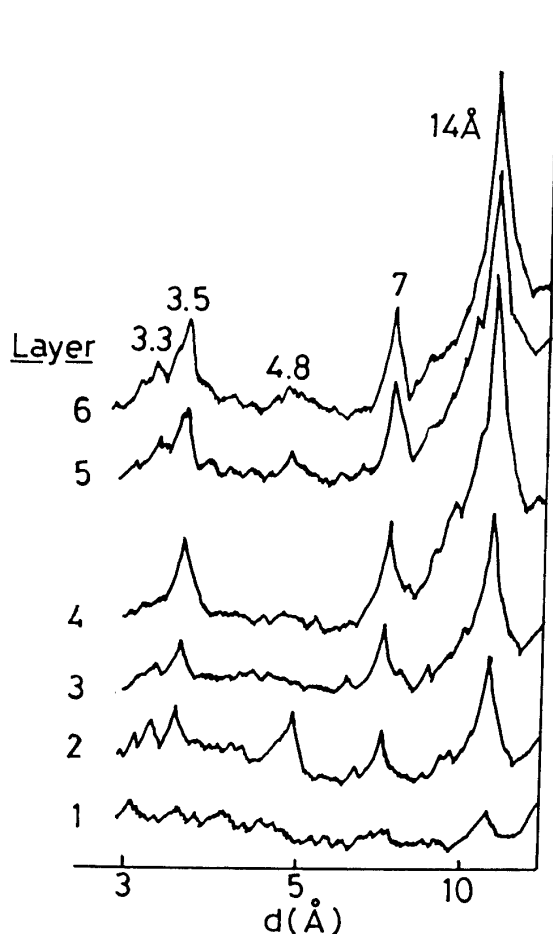

Fig. 6.   X-ray diffraction patterns for Be–3 clays.
(Mg-saturated, parallely oriented)
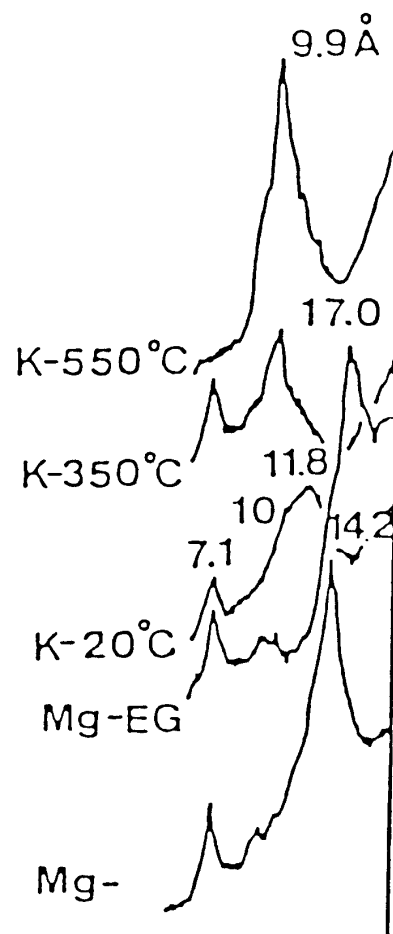
Fig. 7.   X-ray diffraction patterns after each treatment. (Be 3–5, parallely oriented)

ethylene-glycol solvation, K-saturation and 350°C heating but it collapsed after 550°C heating. These indicate that the 7 Å reflection is to be attributed to the basal spacing of kaolin mineral but not to the (002) spacing of 14 Å mineral. Newsome[3] misunderstood the 7 Å reflection as the d (002) of chlorite because of nondisappearance of the reflection after heating at 300°C (7 Å due to 1:1 type mineral doesn't disappear until heating over 500–550°C). The 3.5 Å spacing was assigned to (002) spacing of the kaolin mineral and the 3.3 Å to the primary mineral quartz and/or (003) spacing of 10 Å detected as a shoulder of the 14 Å reflection. The X-ray patterns for their randomly oriented (powder) specimens are shown in Fig. 8. As a matter of course, the (hkl) reflection peaks or bands such as those around 4.46, 2.56 Å etc. appears strongly together with the weakened (001) reflections. These (hkl) spacings are mostly common to both kaolin and smectite.
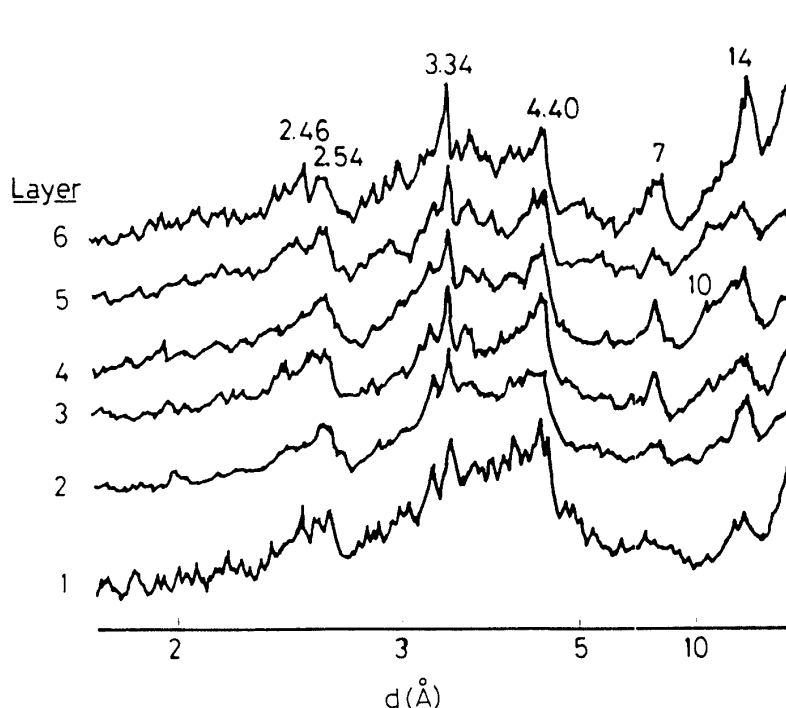

Fig. 8.   X-ray diffraction patterns for Be–3 clays.   (Na-saturated, randomly oriented)

The stepwise weight-loss during heating was shown by TG analysis of them (Fig. 5). The first distinct weight-loss occurred near 100°C due to evaporation of absorbed H_2O and then 500–550°C due to the removal of OH groups bonded to Al in octahedron-layer. These thermal behaviors are fixed to be those of halloysite. IR absorption spectra of them (Fig. 2) are also quite similar to that of kaolin (meta-halloysite). DTA curves (Fig. 3) showed two endo-thermic peaks around 100 and 500°C, which corresponded to the results of TG analysis attributable to kaolin. However the DTA curves showed no exothermic peak in high temperature region which is due to the formation of new crystalline phase appearing always in both smectite and kaolin minerals. The endo-thermic peak at 700–800°C occurring with smectite was also absent. The reason of the absence of these exo-or endo-thermic reactions was not clear and further studies are needed.

From these results, it was found out that the clays of pyroclastic flow of 1883 are constituted of smectite and kaolin (meta-halloysite) with small amounts of primary mineral quartz mixed.

The amount-ratio of both minerals in the fraction remains undetermined here. The NaOH dissolution method resulted in no selectivity for each mineral. However, from the results from DTA, TG and IR together with X-ray powder analysis, a predominace of kaolin mineral (perhaps

meta-halloysite) over smectite was suspected.   The phenomenon that the 14 Å peak of smectite is apparently higher than 7 Å of kaolin in the oriented X-ray pattern is considered not to be reflecting real amount ratio as may be noted in the common case of co-existing system of 2 : 1 and 1 : 1 type clay minerals.

In the pyroclastic flow deposits, the clay fractions of the uppermost layer (1-st sometimes 1 to 2-nd layer) seemed to be nearly amorphous or to be containing only such small amounts of crystalline clay minerals as appeared in the oriented X-ray diffraction patterns.   The uppermost layers are affected more or less by the fresh ash-fall from An crater, but $-2\,\mu$ content of ash is so small that the minerals of the clay fractions are originated chiefly from the pyroclastic materials.

The powder X-ray patterns have nearly the same heights of (hkl) peaks of the surface clays as those in the other pyroclastic clays.   The DTA and TG curves as well as the IR spectra of them are all similar to those obtained from the clays of lower pyroclastic flow deposits.

These indicate that the degradation or the disorder in C-axis stacking occurs in the kaolin and/or smectite structure in the uppermost layers.

Electron micrographs revealed the existence of opaline silica, characteritic laminar disk particle of 2–5 μm diameter, in the surfaces of St, Ke and Be as shown in Fig. 9.

Fig. 9.   Scanning electron micrograph for Be 3–1 clay, showing the presence of opaline silica.

Discussion

As mentioned in Part I and II of this series, the stratifications of volcanic deposits in Krakatau islands are to be principally classified into two types of ejecta, i.e. pyroclastic flow of 1883's great eruption and ash and scoria tephra from Anak crater after 1927.   In Be, pedons have been

developing mostly from the pyroclastic flow.   While in St and Ke, the pyroclastic flows are overlain by the ash and scoria deposits from An crater and in An fresher tephra are depositing.

Both deposits are mutually quite different in their physical and chemical properties.   Generally speaking, the pedons from the pyroclastic materials are in more advanced weathering stage, having more amounts not only of finer particles such as clay fractions ($-2\,\mu$m) but of organic matter (humus) in surface layer.   They also show higher CEC, titration acidity, ΔpH etc..   On the other hand, the pedons from An ejecta, especially those in An, remain in a very young weathering stage or in immature soils.

Time factor (100 years for the pyroclastic flow and less than 50 years or so for the ejecta from An crater after depositing, respectively) probably affects such physico-chemical differences between the both deposits.   The minor presence of anorthite in pyroclastic flow as shown in Table 2 might be an evidence for advanced weathering, i.e. the mineral might have been decomposed in the course of weathering, releasing Ca ion abundant in the deposits.   However, the contents of clay fractions in the pyroclastic flow deposits are much larger than those in the ash and/or scoria layers: the contents reaching approximately 10%.   Furthermore, the fractions are composed of crystalline clay minerals kaolin and smectite.   Such larger occurrences of clays were hardly considered to have been formed from pyroclastic materials by weathering actions in a scant period of 100 years.   Thus it was suggested that the kaolin and smectite minerals had been existed even at the starting of depositing, though their formation mechansim is not clear.   The occurrences of crystalline clays in fresh ash have been observed occasionally as in the cases of recent eruptions of Usu (Kondo et al[2]) and of Gallungung, Indonesia (Unpublished data by the authors).

The containing of clays in the original volcanic materials is a distinct difference between the pyroclastic flow and the other ejecta in Krakatau islands and the occurrence of clays might have accelerated the subsequent soil formation greatly in the pedons from pyroclastic flow deposits.

The more advanced soil formation in Be and the lower layers in St and Ke, therefore, might be attributed not only to time factor but also to the presence of larger amounts of clay minerals.

The main weathering sequenc of volcanic ash in temperate regions have been established as follows: volcanic ash (mainly glass) → allophane, imogolite → halloysite → .

General weathering course of volcanic materials in tropical regions was not confirmed here with the used samples whose ages were 100 and less than 50 years, but a certain weathering way substantially similar to the one in temperate regions was suspected from several experimental data. Firstly, it was illustrated that laminar opaline silica was observed in the surface layer soils aged even less than 50 years.   The formation of opaline silica was usually found out in volcanic ash soils of temperate regions at younger weathering stage (Shoji et al[5]).   Secondary, illustration was made by the continuous weight-loss on heating up to about 500°C in the TG curves of samples from An ejecta, which corresponded nearly to the swelling or having shoulder of Si–O band around 1100 to 1000 cm^{-1} toward lower wave number (1000 to 900 cm^{-1}) in IR spectra of them.   Such natures are indicative of the presence of the edged OH groups in poor crystallinity or of the formation of some Si–O–Al bond, and are all common to allophanic clays.

Together with these mineralogical aspects, some chemical properties are also indicative of some similarities to those of volcanic ash soils ("Andosols" in FAO/UNESCO and "Andepts" or "Andisols" in Soil Taxonomy).   For example, the amounts of the P-sorption by clay fractions of Be–3 profile before and after the removal of "free" Al and Fe hydrous oxides are shown in Fig. 10. It is clear that relatively high level of P-sorption by the clay fractions of upper layers, where soil formation proceeds in higher degree, is due to the active "free" hydrous sesquioxides.   The
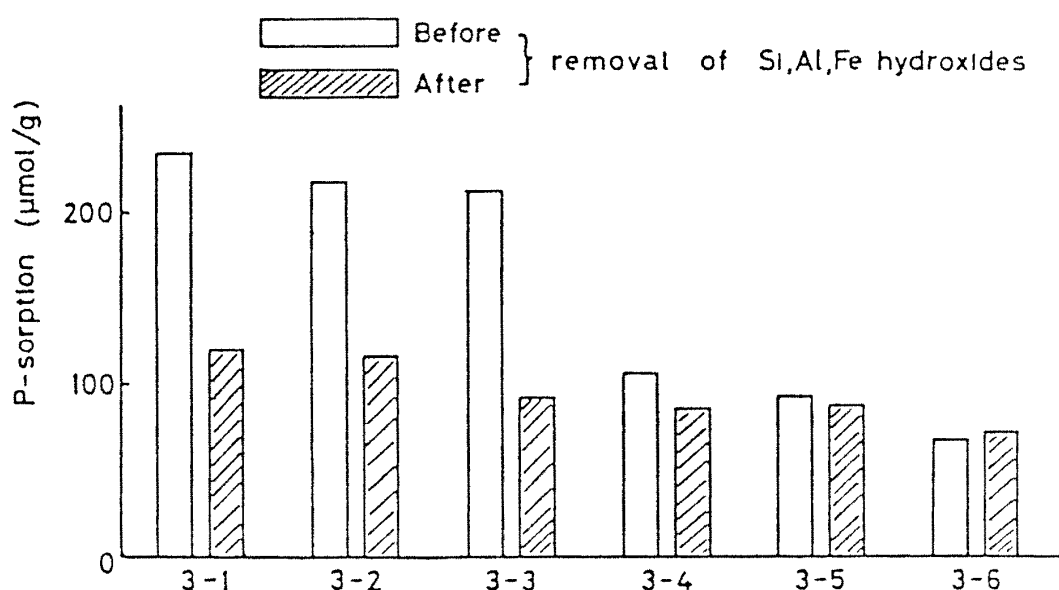
Fig. 10. Amounts of P-sorption by Be clays before and after the removal of "free" Al, Fe and Si hydroxides.

formation of such oxides having high capacity of P-sorption accoompanied by formation of allophanic clays is one of the characteristics of volcanic ash soils.

Thus the weathering and the soil forming process of volcanic ash in the tropics were deduced to be essentially similar to those in temperate regions, though definite evidences for the allophanic clays formation were left unascertained in these young deposits examined here.

Summary

Mineralogy of two main types of deposits, one from pyroclastic flow of 1883's great eruption and the other from various ejecta from An crater after 1927, was studied.

The former is substantially different from the latter in containing large amounts of clay fractions ($-2\,\mu$m) consisted of crystalline clay mineral smectite and kaolin (perhaps meta-halloysite), both of which were considered to have been present at the starting of depositing.

Lithologically, the former is andesitic to dacitic charcterized both by the large amount of light minerals (mainly volcanic glass and albite) and by the quite small amounts of heavy minerals (olivine was not detected), and the latter is basaltic andesite characterized by relatively larger amounts of heavy minerals (Mg-rich olivine forsterite, pyroxene orthoferrosilite, hypersthene, augite and ilmenite) and by the presence of anorthite.

These mineralogical differences were ascertained to have affected the weathering or the soil forming process.

As the pedons in Krakatau, even those from pyroclastic flow, remain in an immatured stage, the course of weathring of volcanic bombs could'nt follow in this study. However, the data obtained in this study indicate a weathering way or a soil formation process similar to the one which proceed usually in the temperate regions; i.e. volcanic ash (mainly volcanic glass)→allophane, imogolite→ halloysite→.

References

1) Van Baren: Properties and constitution of a volcanic soil, built in 50 years in the East-Indian Archipelago. *Mededeelingen van de Landbouwhooge-school*, **35**, 1–28 (1931)

2) Kondo, Y., Kondo, R., Katsui, Y.: Clay minerals of the volcanic ash erupted from the Volcano Usu in August, 1977. *J. Sci. Soil Manure*, **49**, 167–169 (1978)

3) Newsome, D.: The Krakatau centenary expedition, final report. *Hull Univ.* 83–102 (1982)

4) Oba, N., Tomita, K., Yamamoto, M., Istidjab, M., Badruddin, M., Parlin, M., Sadjiman, Djuwandi, A., Sudradjat, A. and Suhanda, T.: Geochemical study of lava flows, ejecta and pyroclastic flow from the Krakatau group, Indonesia. *Rep. Fac. Sci., Kagoshima Univ. (Earth Sci. Biol.)*, **15**, 41–76 (1982)

5) Shoji, S. and Masui, J.: Opaline silica of recent volcanic ash soils in Japan. *J. Soil Sci.*, **22**, 101–108 (1971)