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Clay Mineralogical Study of the Pliocene-Pleistocene Carcar Formation and the Quaternary Alluvium in Consolacion-Liloan, Cebu Province, Philippines

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Abstract

The Pliocene-Pleistocene Carcar Formation and the Quaternary Alluvium are two major lithologies that rim the entire island province of Cebu. The Carcar Formation (CaF) is predominantly limestone rock mass characterized by rolling to hilly topography while the Quaternary Alluvium (QAl) is generally unconsolidated sedimentary deposit on coastal plain marked by low relief and undulating landscape. Mineralogical examinations of the vertisolic soil/clay horizons that mantle these rock formations were conducted to identify and characterize the nature of clay minerals using X-ray diffraction (XRD), differential thermal analysis (DTA), thermogravimetry (TG), scanning electron microscopy (SEM), and energy dispersive x-ray (EDX). Analytical qualitative results show that the clays derived from the Carcar Formation are chiefly smectite-rich assemblage with supplemental association of mixed-layer kaolinite/smectite. Clays from the Quaternary Alluvium are the same as in the CaF, however, mixed-layer kaolinite/smectite in the QAl appears relatively richer than in the CaF. Quantitative estimates by computer simulation yield slight to moderate variations in the proportions of kaolinite and smectite in the mixed-layer phase, and correlatively, the degree of ordering is determined to be random in both CaF and QAl clay assemblages. Kaolinite content participating in the interstratified phase is discerned to be diagnostically higher in the alluvium than in the limestone. Calcite impurities occur greater in clays sourced from the Carcar Formation and are found comparatively rarer in the Quaternary Alluvium. Quartz is noted to be frequently present in minor to moderate amounts in both lithologies but is generally more persistent in the QAl.

The mixed-layer kaolinite/smectite phase is observed in both CaF and QAl and revealed that it is not an exotic clay phase exclusively confined in the red-burning clay area. Illite or illitic facies is found only in the QAl and is envisaged as authigenically or neogenically formed. Smectite with high rehydration capacity is recorded only in the CaF and is believed to be a result of its structure and beidellitic composition.

Keywords : Smectite, Mixed-layer kaolinite/smectite, illite, Carcar Formation, Quaternary Alluvium

Introduction

Aleta et al., (1998) and Aleta et al., (1999) conducted mineralogical and characterization studies of the red-burning clay deposit in the Quaternaiy Alluvium (QAl) in Liloan, Cebu, Philippines, and eventually came up with the findings that kaolinite/smectite mixed-layer in random interstratification constitutes the principal phyllosilicate minerals in the clay resource. The study area at that time was limited within the delineated confinement of the red-burning clay site, and therefore, exploration of the lateral abundance and extent of occurrence of the kaolinite/smectite mixed-layer in the adjoining areas was restrained. Since the interstratified kaolinite/smectite is presumably of rarer species compared to other types of interstratified combinations e.g. illite/smectite,

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chlorite/smectite, mica/chlorite, chlorite/vermiculite, etc., curiosity and interest dictate the need to perform further examinations and determinations whether the mixed-layer kaolinite/smectite assemblage is indeed exotic and restricted only within the periphery of the red-burning clay area or whether its kind has also similar juxtaposed occurrences in the alluvial coastal plains and immediate carbonate hilly parts of Consolacion-Liloan towns. This view in mind prompted the present study. And collection of supplementary vertisolic soil/clay samples in surrounding areas both underlain by Quatemary Alluvium and Carcar Formation was undertaken.

The objectives of this study were (1) to identify and characterize the clay minerals and clay assemblages in the vertisolic soil/clay horizons veneering the Plio-Pleistocene Carcar Formation and the Quaternary Alluvium using various analytical techniques (XRD, DTA-TG, SEM and EDX); (2) to correlate the present data with the previous data obtained from the red-burning clay deposit in Liloan, Cebu, Philippines; and (3) to discuss the mineralogical and geological significance and implications of the clays and clay assemblages with respect to their probable mode of origin and evolution.

GEOLOGY

Carcar Formation

The Carcar is a transgressive limestone of Pliocene-Pleistocene age which occupies the lower flanks of the island ridge and covers practically almost all the coastal areas of Cebu. This limestone is characterized by imperfectly developed haycock topography, broken only by occasional cliffs. All around the island it dips seaward at maximum of 20 to 30 degrees. It is unconformably underlain by the Barili Marl (Santos-Ynigo, 1951; BMG, 1981; JICA-MMAJ, 1990).

The Carcar is a typically porous, coralline, poorly bedded or massive limestone. It is locally rubbly, marly, or well bedded. Besides the common coralline forms, other mega-fossils and some micro-fossils are found locally and sparingly. This limestone has an average thickness of about 300 meters and is seldom less than 150 meters thick (Santos-Ynigo, 1951; BMG, 1981).

In the present study area the Carcar Formation is observed to be generally coralline, conglomeratic and rubbly with typically porous and fragmental aggregation. It is slightly bedded. Brown to black vertisol superficially covers this carbonate formation.

Quaternary Alluvium

The Quatemary Alluvium is the youngest of all formations and generally overlies the Carcar Formation and fringes almost entirely the coastline of Cebu Island. It consists of loose, porous, unconsolidated, fine to coarse detrital sediments of mud, clay, silt, sand and gravel derived from older rocks and deposited along river channels, floodplains and shorelines (BMG, 1981).

In the present study site, this Quatemary Alluvium is generally silty to sandy and is veneered by soil of varying thickness. The vertisol has also color ranges from brown to black.

SAMPLES AND EXPERIMENTAL WORKS

The 16 (C-1 to C-6 and L-8 to L-17) samples used in this investigation were collected from vertisolic soil/clay blanketing the Carcar Formation and the Quatemary Alluvium in Consolacion-Liloan area (Figure 1). Vertisolic soil/clay in the study area have varied thickness in different locations, and therefore, sampling depth correspondingly varies but usually in the range from ground surface to about 15 cm or basically equivalent to the A-horizon (top soil) in the study area. The soil colors in both lithologies are generally brown to black and the textures are generally clayey to sandy.

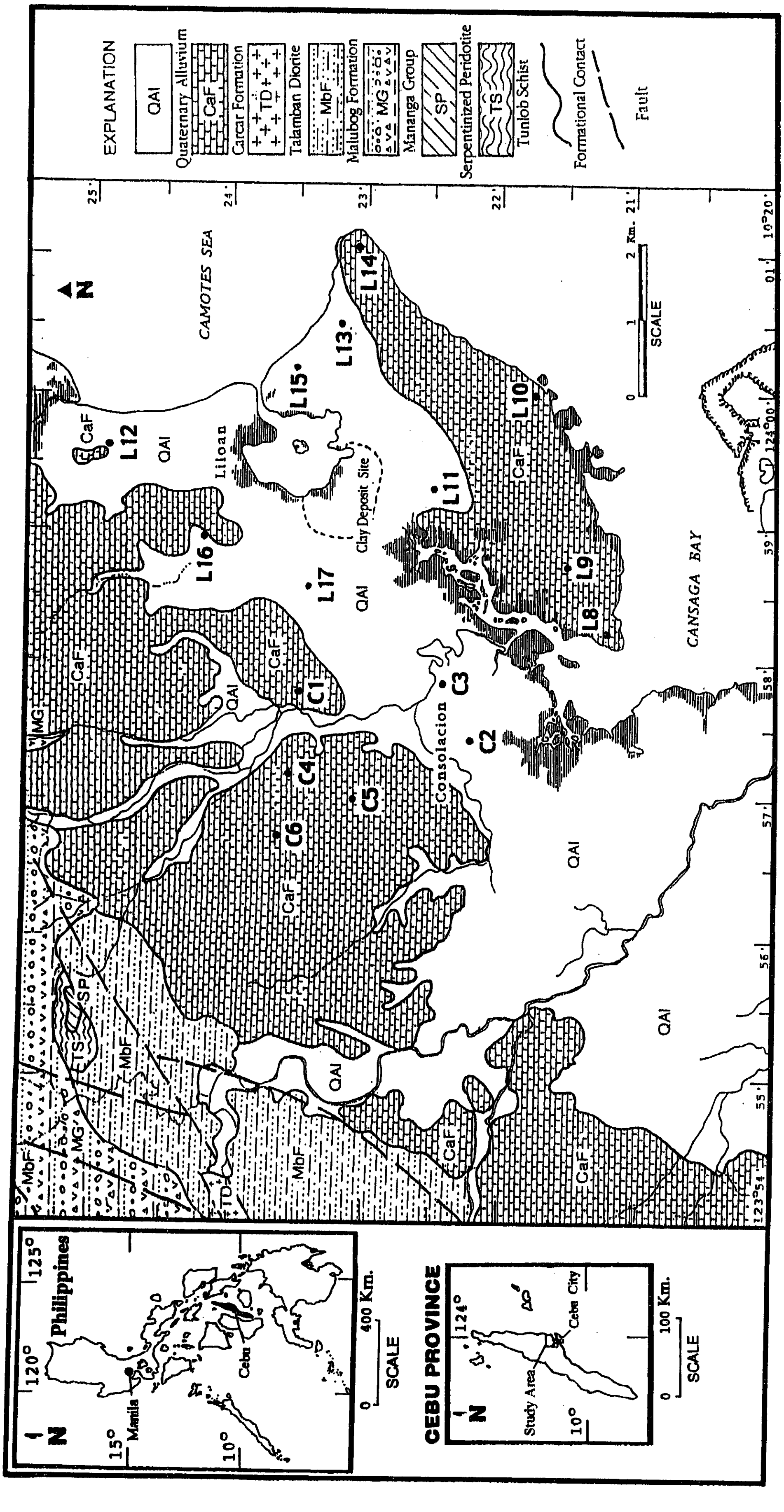


Figure 1. Geological and sampling location map of Consolacion-Liloan study area, Cebu Province Philippines. Based from the Philippine Bureau of Mines and Geosciences map.

The red-burning clay deposit site covered in the previous studies is also indicated in the geological and sampling map (Figure 1).

Segregation of the fine clay size fraction follows the generally prescribed procedures of dispersion, sedimentation and centrifugation. X-ray diffraction (XRD) analyses of oriented <2 μm size fraction were carried out using a RINT 2000 x-ray diffractometer with a carbon monochromator (CuK α radiation) and operational setting of 30kV and 14mA. Thermal tests were performed with a Rigaku Thermo Plus TG 8120 DTA-TG apparatus using about few grams of fine air-dried samples. Thermal graphs were recorded from room temperature to 1,000℃ with a heating rate of 10℃/min. Scanning electron microscopy (SEM) studies of mineral morphology and aggregations used Hitachi S-4000 FE-SEM. The specimens were coated with gold-palladium using FINE COAT ION SPUTTER JFC-1100. Energy dispersive x-ray (EDX) analyses utilized the same Hitachi S-4000 FE-SEM equipped with LINKS ISIS EDX operated at an accelerating voltage of 15 kV. ZAF method was used as quantitative correction, utilizing standard samples albite for Na, MgO for Mg, Al_2O_3 for Al, FeS_2 for S, wollastonite for Ca, GaP for P, Mn for Mn, and Fe metal for Fe. The powder specimens for EDX were spread in carbon tapes attached in brass cylinders and sputtered with carbon using JEOL JEC-520 CARBON COATER. Most of the analytical area is less than 4 μm^2.

RESULTS

X-ray Diffraction (XRD)

Figure 2 shows the x-ray diffractograms of untreated, parallel oriented <2 μm size fraction of samples from the Carcar Formation (CaF) and the Quaternary Alluvium (QAl). Figures 3, 4, 5 and 6 display some details of the x-ray analyses of selected samples C-1, L-9, C-3, and L-12 respectively. The x-ray traces generally show distinct peak at around 15.6Å followed by subtler and weaker peak at around 7.17Å reflections for specimens derived from the CaF soil. For the QAl soil, the x-ray traces display more distinct 7.24Å and 3.56Å reflections aside from the 15.6Å reflection. Subsequent treatments of the samples, alongside with comparison with x-ray identification descriptions of Brown (1961), Reynolds (1980) and Wilson (1987) revealed that these x-ray patterns best fit the profile of smectite-rich assemblage with intimate association of interstratified kaolinite/smectite (K/S) phase. The more prominent reflections observed at around 12° 2 θ or 7.24Å space and at around 25° 2 θ or 3.56Å space may indicate the greater percentage of interstratified K/S and the greater enrichment of kaolinite proportion in the interstratified K/S associated with the QAl. Among the samples, only sample C-3 from the QAl is observed to contain illite as shown by 9.95Å trace (Figure 5). Both moisture (H_20) treatment and ethylene glycol (EG) treatment produced peak migration and increased of basal spacing of the clay assemblages indicating the expandable behavior of the layer components from discrete smectite as well as from the smectite in the interstratified K/S. Heat treatment for 1 hr at 300℃ and 500℃ effected temporary contraction of basal spacing to about 13Å for most samples (about 10Å for sample C-3), but expansion was easily regained after H_20 and EG treatments. The 700℃ heat treatment done for both assemblages of CaF and QAI, dehydrated and dehydroxylated the clays and the basal spacing seemed permanently contracted to around 10.0Å. The clays apparently never showed rehydration even after moisture (H_20) and EG treatments with the exception of sample L-9. This sample L-9 still showed high rehydration capacity even after heat treatment at 700℃ as evidenced by its H_20 and EG adsorptions that produced broad peak traces at 15.6 Å and 16.3Å respectively. The rehydration is observed to cease somewhere at range <750℃ (Figure 4). The 10 Å peak reflection of illite in sample C-3 appears inert in all the heat treatments conducted that seemingly no significant drifting or shifting of the peak was observed. Acid treatment for 1 hr using 6N HCl greatly diminished the (001) peak patterns of smectite component but enhances the (001) peak traces of kaolinite component in the samples. The ~10Å peak of illite under acid treatment remains steadfast.

Calcite is recognized by a series of sharp and slender peak reflections with highest intensity near the 3.03Å peak. These reflections vanished after HCI treatment. Quartz is also identified by a distinct reflections with greatest intensity near the 3.33 Å peak. These reflections are resistant and remained visible after HCI treatment. The calcite peak reflections apparently disappeared upon temperature treatment at 700℃ but quartz peak reflections still persisted.

Calcite and quartz are seemingly the only recognizable non-sheet phyllosilicate impurities in the clay assemblage. Calcite is observed to be more dominant in the CaF while quartz is more conspicuous in the QAl.

Differential Thermal Analysis (DTA)

The representative DTA curves from soils of limestone and alluvium are shown in Figure 7. It is noticeable that

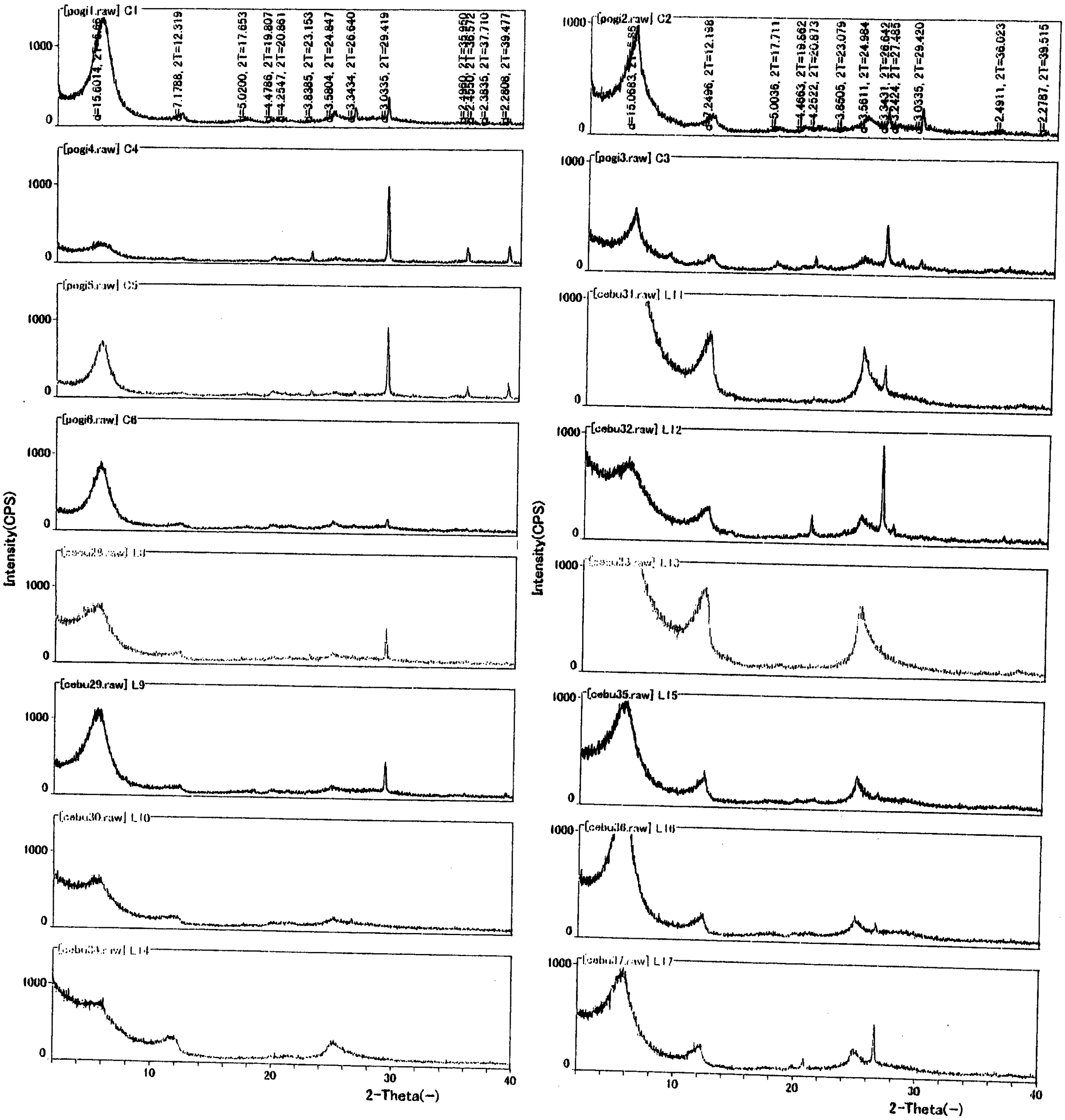


Figure 2. X-ray diffraction (XRD) patterns of untreated, oriented <2~.tm size fraction samples from the Carcar Formation (CaF) and the Quaternary Alluvium (QAl). Left column = samples C-1, C-4, C-5, C-6, L-8, L-9, L-1O, L-14 from the CaF; right column = samples C-2, C-3, L-11, L-12, L-13, L-15, L-16, L-17 from the QAl.

there are 2 distinct endotherms for all the samples - one in the <200℃ range with peaks below 100℃ and another one between the 500℃ and 600℃ range with peaks hovering at 506℃ to 520℃. These basically correspond to dehydration and dehydroxylation processes respectively which match smectite and kaolinite curves that are superimposed. Mild endo/exothermic reaction is seen at around 720℃ to 780℃ which may be equivalent to calcination. This is apparently absent in alluvium soil sample L-12. The subtle low temperature exotherinic reactions in 320℃ to 342℃ may be related to iron oxy-hydroxides (plus combustion of organic impurities?). High temperature exothermic reaction is apparently not distinct.

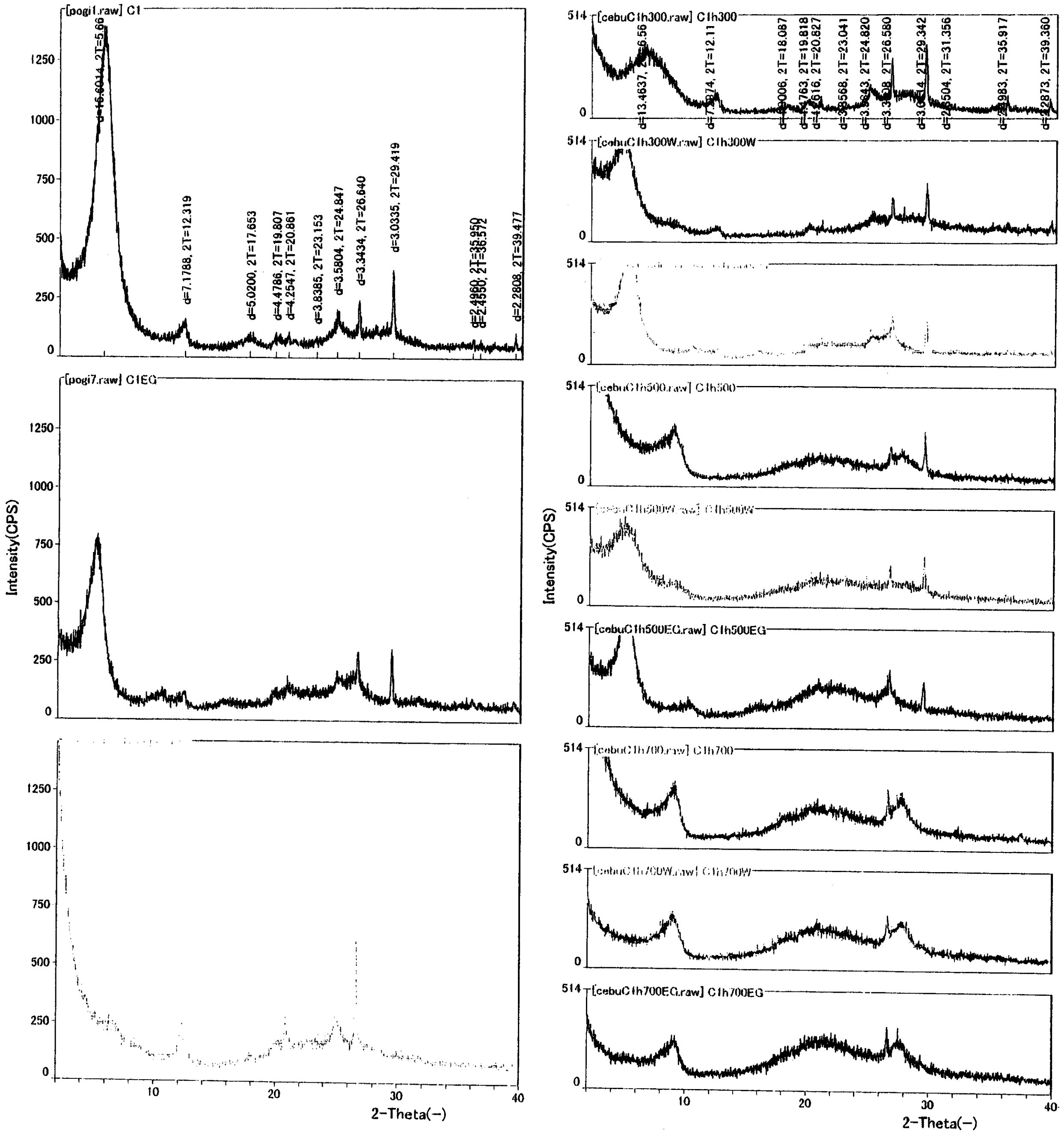


Figure 3. X-ray diffraction (XRD) patterns (left column) of untreated (top), EG treated (middle), HCl treated (bottom) and (right column-top to bottom) heat treated at 300℃, 300℃+H_2O, 300℃+EG, 500℃, 500℃+H_2O, 500℃+EG; 700℃, 700℃+H_2O, 700℃+EG; oriented <2 μm size fraction sample C-1 from the Carcar Formation.

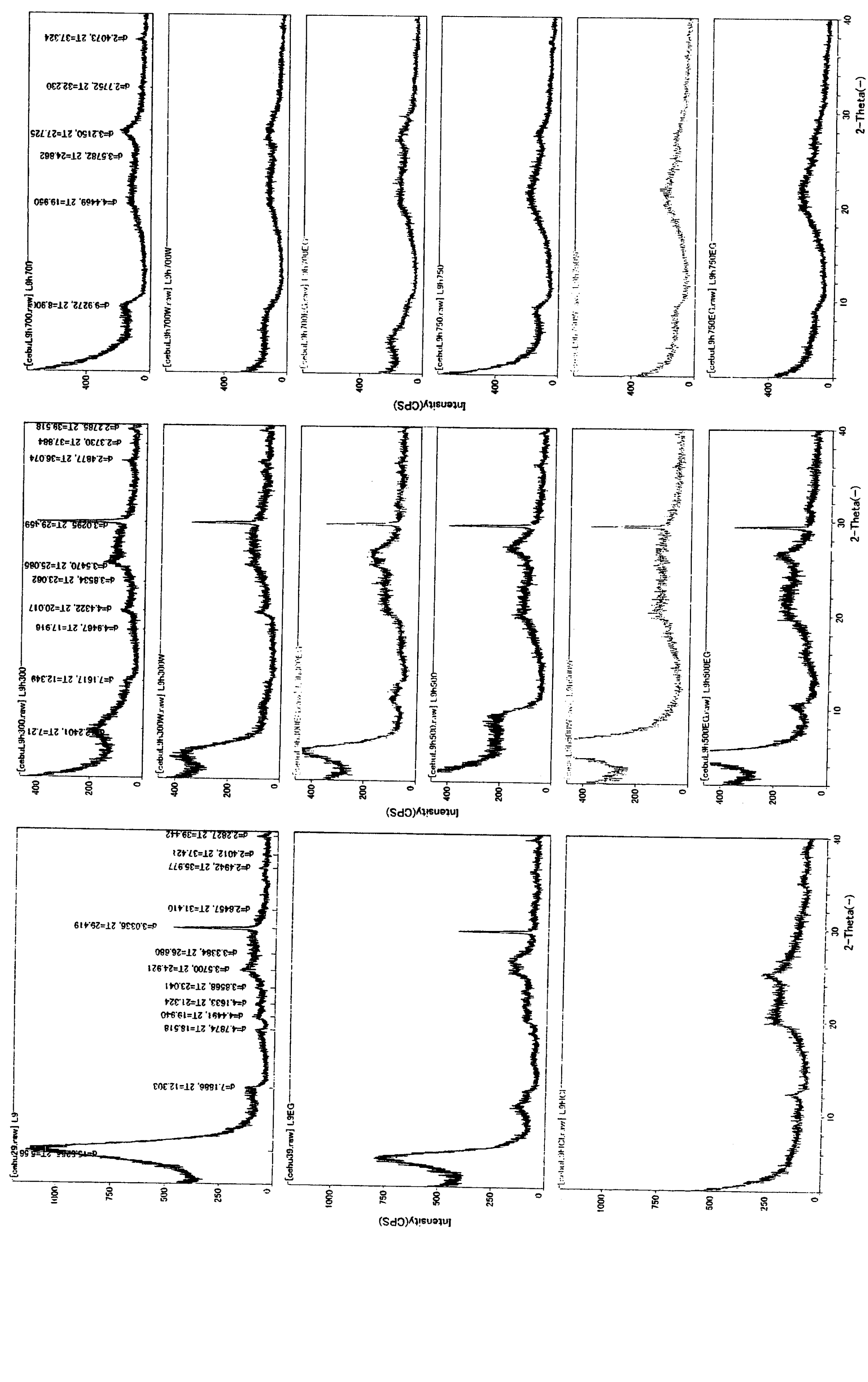


Figure 4. X-ray diffraction (XRD) patterns of untreated (top-left), EG treated (middle-left), HCl treated (bottom-left) and heat treated series (center column-top to bottom) at 300℃, 300℃+H_2O, 300℃+EG, 500℃, 500℃+H_2O, 500℃+EG; (right column-top to bottom) 700℃, 700℃+H_2O, 700℃+EG; 750℃, 750℃+H_2O, 750℃+EG; oriented $<2\,\mu m$ size fraction sample L-9 from the Carcar Formation.

Thermogravimetric Analysis (TGA)

Weight decrease of 7% to over 14% may be observed to be abrupt in the <2OO℃ range arising from the release of sorbed water in the clay mineral particles in all the samples (Figure 7). This is followed by minimal weight loss of about 1% to 4% before another sudden weight drop of about 4% to 6% related to OH release is reached. Except for sample L-12, another weight loss in the range 1% to 7% which is ascribed to CO_2 liberation, apparently from calcite, is noticeable. Total weight loss is observed to be generally higher in the soil limestone

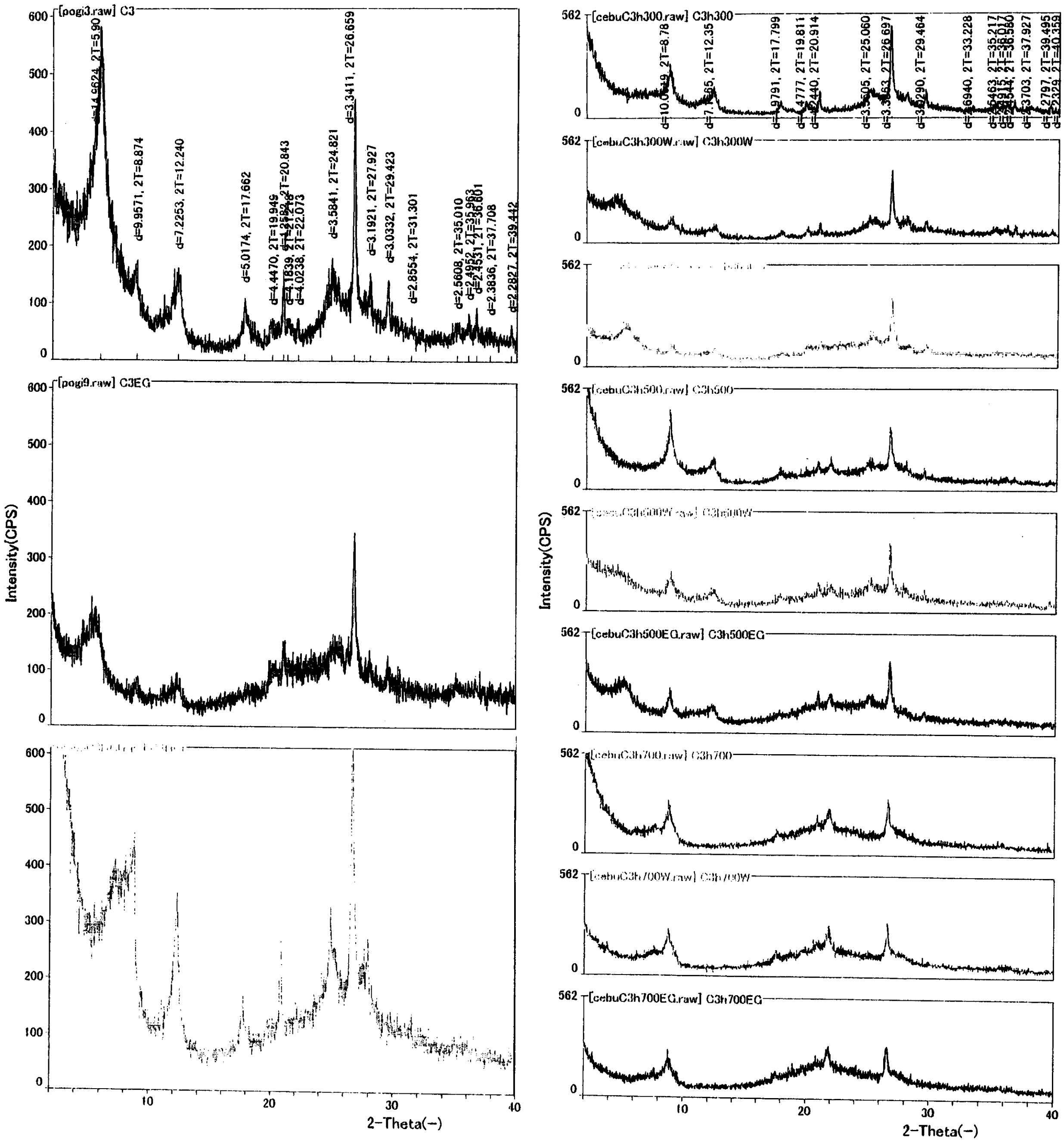


Figure 5. X-ray diffraction (XRD) patterns (left column) of untreated (top), EG treated (middle), HCl treated (bottom) and (right column-top to bottom) heat treated at 300℃, 300℃+H_2O, 300℃+EG; 500℃, 500℃+H_2O, 500℃+EG; 700℃, 700℃+H_2O, 700℃+EG; oriented <2 μm size fraction sample C-3 from the Quaternary Alluvium.

samples (24% to 28%) than in the soil alluvium samples (17% to 18%) which is possibly due to greater proportion of discrete smectite that lost H_2O and OH and also greater decarbonatization of subsidiary calcite.

Scanning Electron Microscopy (SEM)

Morphology of clays from the Carcar Formation is characterized by flakes with irregular and slightly curled edges resembling "jigsaw puzzle" which likely typifies smectite (Figure 8). Clays from the Quaternary Alluvium

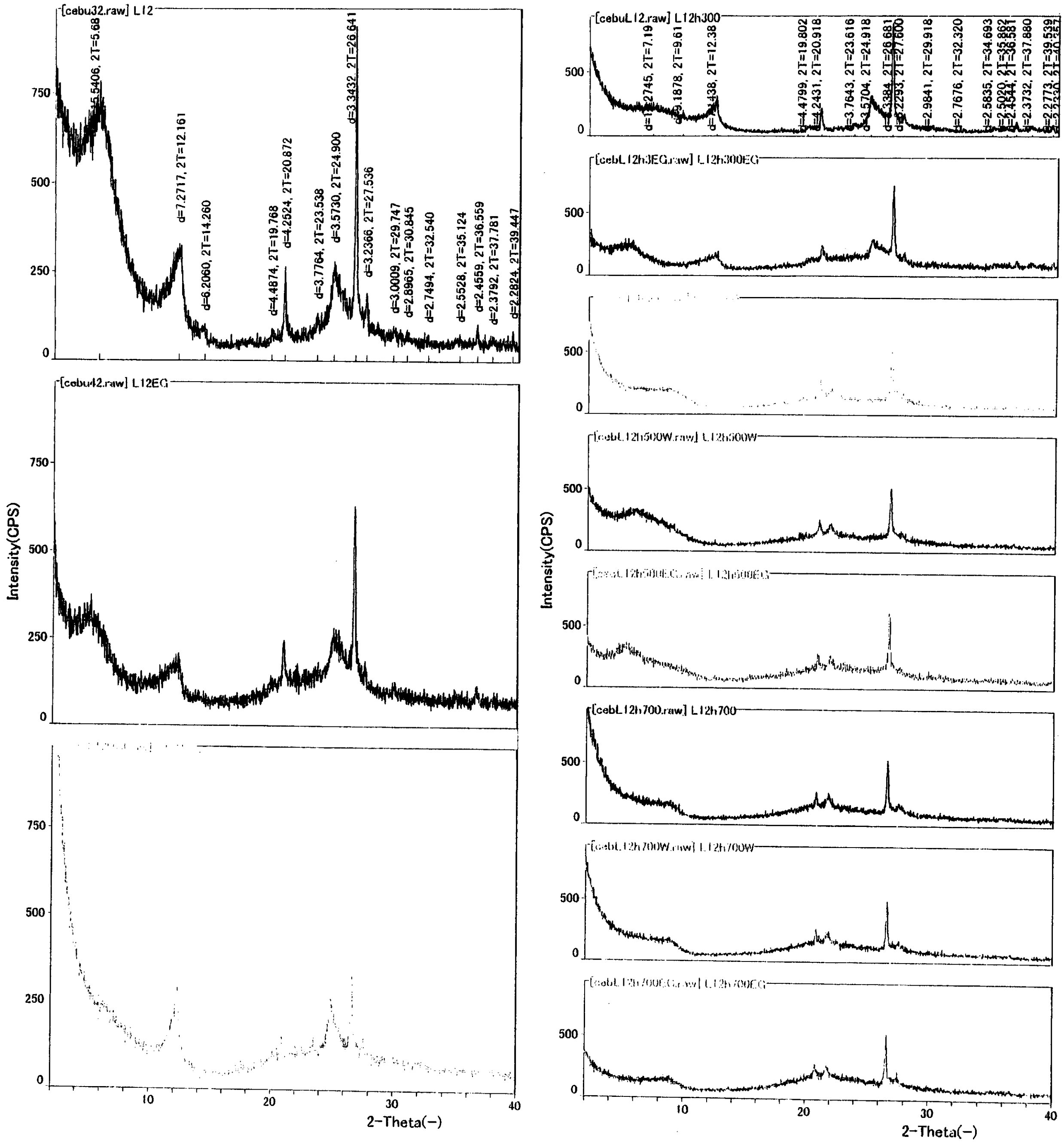


Figure 6. X-ray diffraction (XRD) patterns (left column) of untreated (top), EG treated (middle), HCI treated (bottom) and (right column-top to bottom) heat treated at 300℃, 300℃+H_2O, 300℃+EG, 500℃, 500℃+H_2O, 500℃+EG; 700℃, 700℃+H_2O, 700℃+EG; oriented <2 μm size fraction sample L-12 from the Quaternary Alluvium.

exhibit disaggregated to somewhat subhedral flaky particles (Figure 9). Illite is displayed by wavy and foliated morphology with better orientation and stacking arrangement of thin flakes than smectite as shown by sample C-3 (Figure 9, bottom). Kaolinite crystallites associated in the mixed-layer K/S phase are hardly discernible. The aggregation appears to be more porous and incoherent in the Alluvium in contrast to the denser and more compact aggregation in the Carcar. The curviplanar surfaces of the clays in both limestone and alluvium do not contain numerous blobs and are generally smoother compared to the clays observed in the red-burning clay deposit.

Energy Dispersive X-ray (EDX)

Figure 10 gives the semi-quantitative chemical composition of representative samples from the soils of limestone (C-1 and L-9) and alluvium (C-3 and L-12). It is observed that soils from alluvium are more siliceous than soils from limestone and this may be attributed to the comparatively higher content of discrete quartz and amorphous silica. The soils from limestone however may be noticed to be more aluminous than soils from alluvium which suggest that smectite may be beidellitic, indicating possible aluminum ion substitution for silicon ion in the tetrahedral sheets. Little amount of TiO_2 is shown in all the samples. FeO is contained in appreciable amount in all the samples. The CaO appears highest in limestone (C-1), however L-9 also from limestone appears CaO-poor. MgO is somewhat erratic. A small amount is contained in limestone (C-1) and alluvium (C-3) while it is not detected (N.D.) in L-9 and L-12 which are also limestone and alluvium respectively. Na_2O goes undetected in all the samples. K_20 occurs in small amounts but appears relatively higher in the alluvium soils particularly in sample C-3 which has illite component.

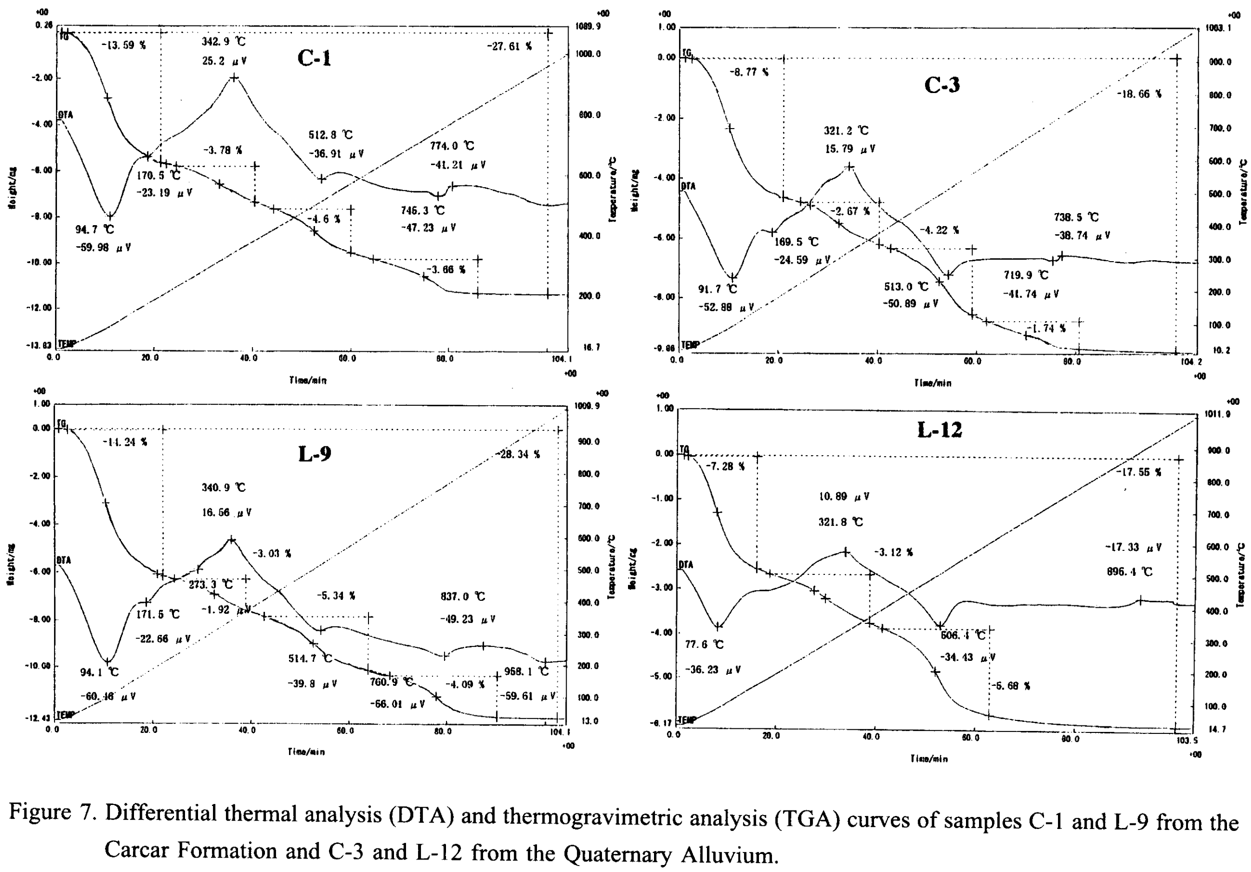


Figure 7. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) curves of samples C-1 and L-9 from the Carcar Formation and C-3 and L-12 from the Quaternary Alluvium.

DISCUSSIONS

Laboratory tests reveal that similar mineralogy occurs in both rock formations.

Predominantly smectite with intimate association of mixed-layer kaolinite/smectite are the main components of clays in the vertisolic soil horizons of the Carcar Formation and the Quaternary Alluvium. The clay assemblages occur in various proportions and layer sequences. The proportion of the interstratified K/S clay phase appears generally higher in the alluvium soil than in the limestone soil as seen from the XRD graphs. Computer simulations using the equation of Kakinoki and Komura (1952) indicate that the kaolinite proportion in the interstratified K/S is relatively higher in the Quatemary Alluvium soil than in the Carcar Formation soil. The interstratified K/S in

Figure 8. Scanning electron micrographs (SEM) of samples C-1 (top) and L-8 (bottom) from the Carcar Formation showing flaky morphology and dense aggregation. Bar scale=2microns.

Quaternary Alluvium soil shows a ratio of about ≦30% kaolinite and ≧70% smectite while in the Carcar Formation soil the ratio is about ≦10% kaolinite and ≧90% smectite. The order of structural interlayering of the K/S is determined to be random in both lithologies.

The above findings indicate that the mixed-layer K/S phase is widespread and not that too rare at first thought. Its occurrence, therefore, is evidently not only limited in the red-burning clay area in Liloan where it was first reported (cf. Aleta et al., 1998; Aleta et al., 1999). Further, it is shown that it not only occurs as an exotic major clay constituent of the red-burning clay or important component of soil of the Quaternary Alluvium but that it is also shown that it is an essential ingredient of soil of the Carcar Formation as well. There may be some recognizable differences though. The proportion of kaolinite layers in the interstratified K/S associated with the red-burning clay,

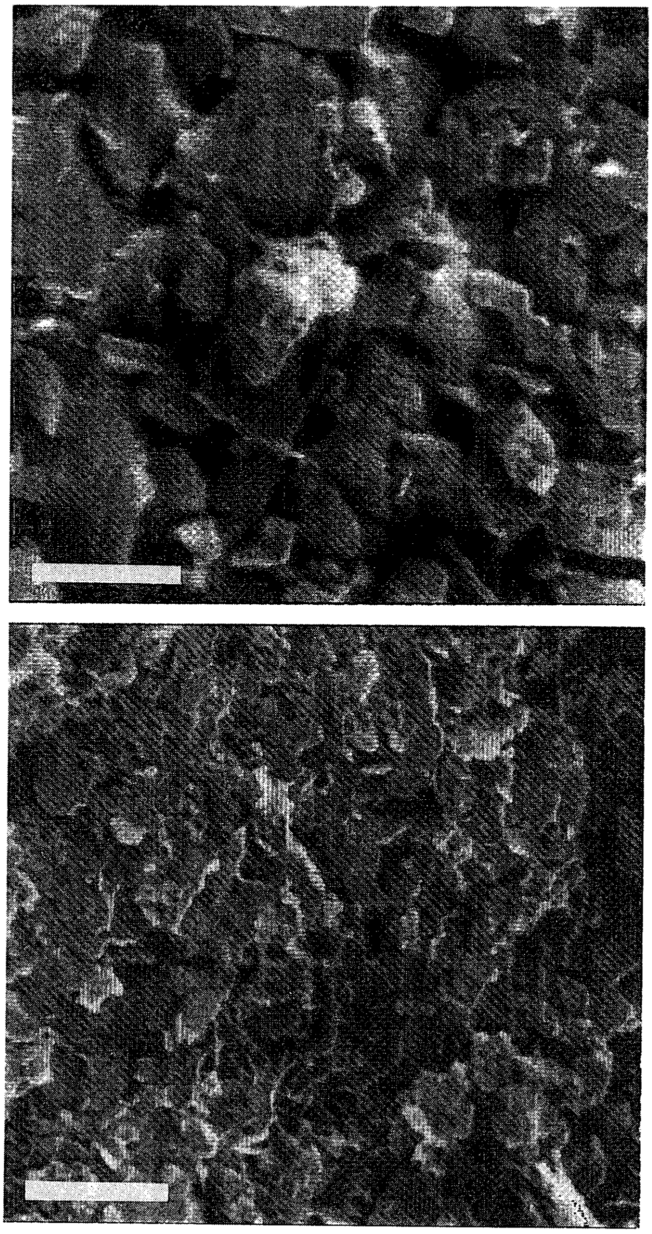


Figure 9. Scanning electron micrographs (SEM) of samples L-12 (top) and C-3 (bottom) from the Quaternary Alluvium. Sample L-12 shows platy and irregular morphology with porous aggregation. Sample C-3 exhibits foliated and wavy morphology with closer-packing arrangement. Bar scale=2microns.

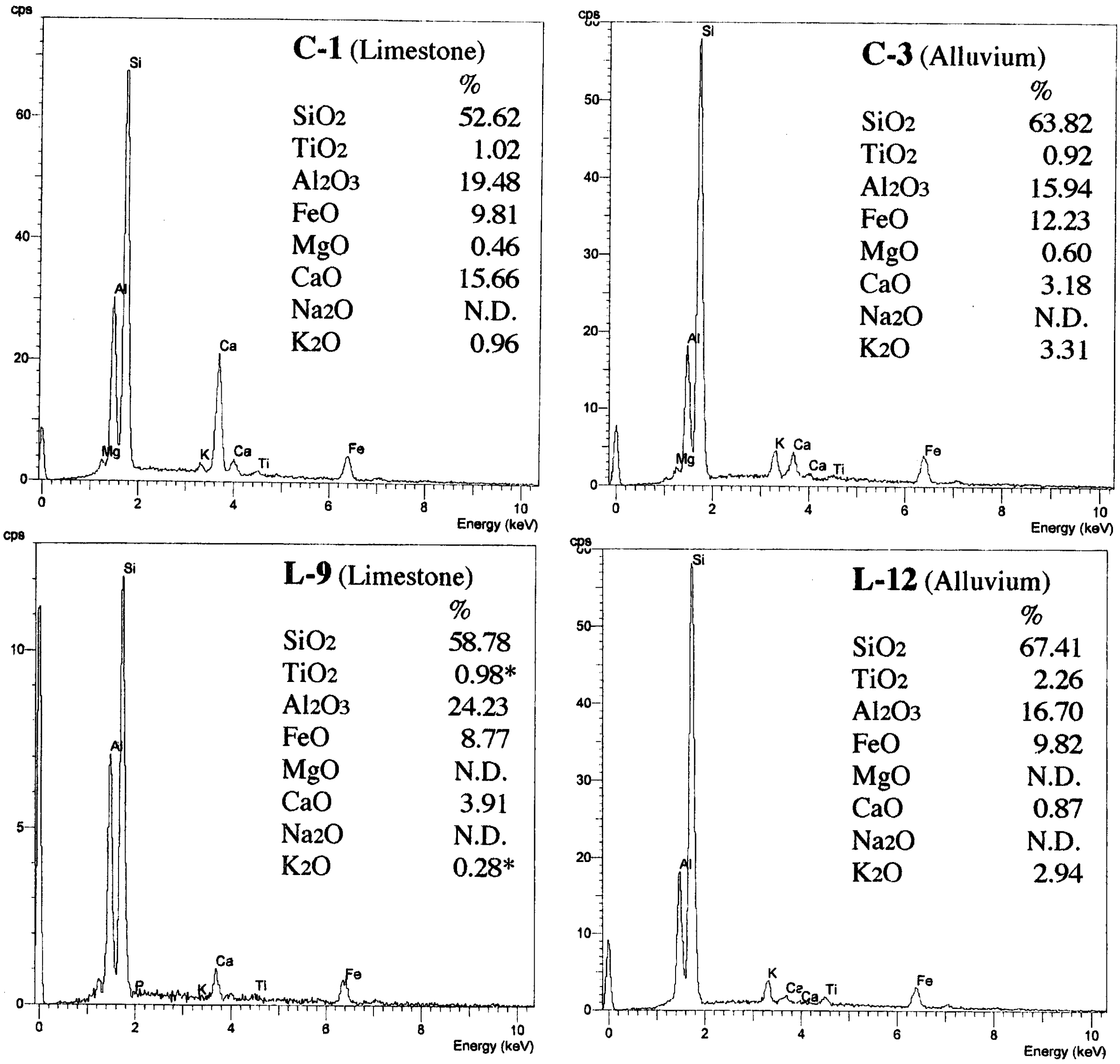
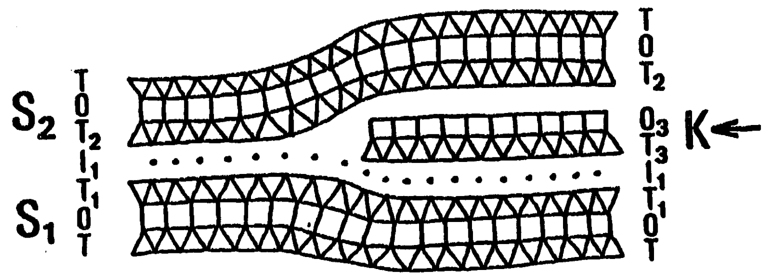


Figure 10. Energy dispersive x-ray (EDX) analysis of samples C-1 and L-9 from the Carcar Formation and C-3 and L-12 from the Quaternary Alluvium.

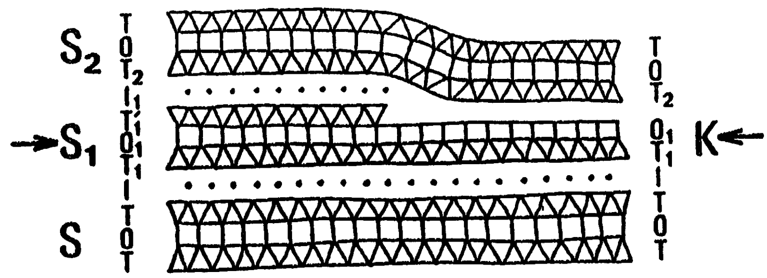
which is about 67%, seems relatively higher than the proportions found in both the limestone soil and the alluvium soil.

Another thing is the remarkable difference in morphology shown by SEM photos (cf Aleta et al., 1998; Aleta et al., 1999). The clay surfaces of the red-burning clay are characteristically blobby compared to the smoother clay surfaces of both the limestone soil and the alluvium soil. In addition, the aggregation of the clay particles of the red-burning clay appears more compact and dense than that of the alluvium soil which appears porous and incoherent. However, the compact and dense aggregation seems similar for both the red-burning clay and the limestone soil except for the numerous pustules in the aggregation observed in the red-burning clay. The variations in constituent proportion and morphology seem to be primary effect of differential chemical weathering. It appears that weathering in the milieu of the red-burning clay deposit seems more aggressive.

Illite component or illitic fades is observed only in the alluvium as shown by sample C-3 and its occurrence



A. Intercalation of a kaolinite layer K between 2 smectite layers S_1 and S_2. View parallel to the layers. T, O and I respectively denote the tetrahedral, octahedral and interlayer levels. A double structure is probably present: $T_1I_1T_3$ structure of smectite type, and $T_3O_3T_2$ of kaolinite type (Amouric and Olives, 1998).



B. Transformation of 1 smectite layer (S_1) into 1 kaolinite layer (K). View parallel to the layers. Same notations as in **A**. The $T_1O_1T_2$ structure is probably of kaolinite type (Amouric and Olives, 1998).

Figure 11. Mechanisms of the interstratified kaolinite/smectite (K/S) formation based on Amouric and Olives (1998).

seems to be very limited in that particular site. It may be speculated that the illite is possibly authigenically formed or neoformed. Generally, there is little evidence for the large-scale neoformation of illitic material in modem soils, though it is quite possible that a significant amount forms in aridic soil (Weaver, 1989). Hence, the illite occurrence may only be observed in parochial area around sampling point C-3. The presence of illite indicates that there was possibly a local and abnormal enrichment of potassium (K) ions in the specific area, and K must be strongly enriched (Harder, 1974) or the Al/Si ratio modified (Weaver, 1989). The source, whether anthropogenic or natural, however is unknown. If anthropogenic, it is truly difficult to surmise. If natural, the most likely source mineral for the formation of pedogenic illite or mica is K-feldspar or plagioclase plus mica. Si and Al are available in most environments; K is the essential ingredient for the formation of illite (Weaver, 1989). As recorded in the EDX, K_2O appears highest in this sample. Repeated wetting and drying cycle of the alluvial soil through time possibly caused the K ion fixation in some of the interlayer regions of expandable smectite and subsequent contraction of the layer spacing to about 10.0Å which eventually corresponds to illite. This reasoning is in good agreement with the explanations of Weaver (1958), Eberl and Hower (1977), Eberl (1978a), Eberl (1978b), Eberl et al. (1986) and Weaver (1989) that alternate wetting and drying increases the amount of fixed K and the proportion of illitic layers in expandable phyllosilicates. The possibility that the illite component may be detrital or that it was translocated from other sources, such as from limestone soil, may also be entertained. However, should this be the case, illite clay must also be found in the adjacent areas particularly the hills and hillslopes of the Carcar Formation as these would likely be the immediate sources of translocated materials. Muscovite and illite are relatively resistant to weathering, and relatively intense weathering is required before they are appreciably altered (Weaver, 1989). Hence, if illite exists in the limestone soil and subsequently transported in the alluvial lowlands, there must be strong possibility that it would survive and could be found distributed in some areas within the basin. However, all analyses suggest negative occurrence of illite in the alluvial soil. And it is also absent in the limestone soil. It seems in these findings that the illite component or illitic facies in the clay assemblage is relatively rarer and more exotic in occurrence than the interstratified K/S phase.

The high rehydration capacity of smectite-kaolinite/smectite mixed-layer assemblage exhibited by sample L-9 from limestone soil may be assumed related to crystal structure and to chemical composition. It could be surmised that there could be possibly higher degree of order in atomic arrangement in the unit cells of crystals and better layer stacking within the aggregates in the sample L-9. This hypothesis parallels to that of Tomita and Dozono (1973) and Tomita (1974) who also observed an expansible mineral having high rehydration capacity not typical in smectite. Tomita et al., (1969), Tomita and Dozono (1973), Tomita and Dozono (1974), Kawano (1993) and Kawano and Tomita (1989a, 1989b, 1991a, 1991b, 1992) also pointed out that composition of clays also exerts influence on the rehydration capacity particularly if there is fairly high substitution of Al for Si tetrahedrally. They indicated that beidellitic smectite has greater rehydration capacity and faster rehydration rate. It may be observed from the EDX results that sample L-9 has relatively higher Al_2O_3 than the other samples. Assumptions could therefore be made that Al may not only be coordinated in the octahedral sheets but also there may be strong possibility that some Al also substitute some of the Si in the tetrahedral sheets which consequently produced the beidellitic character of the smectite. In this regard, the octahedral sheets are almost electrically neutral while tetrahedral sheets have negative layer charge. This crystallochemical feature indicates that no attractive electrostatic force exists between the octahedral sheets and the migrated interlayer cations, and therefore, the migrated cations can be easily extracted from the hexagonal holes, hence, rehydration occurs rapidly (Kawano, 1993, Kawano and Tomita, 1989a, 1989b, 1991a, 1991b, 1992). Sample C-1 from CaF may be noticed to also have high Al content but does not possess the high rehydration ability of sample L-9. This may be attributed to the relatively higher amounts of Ca and perhaps Mg associated in sample C-1 compared to sample L-9. The presence of these ions sometimes blocks, inhibits, or slows reaction kinetics (Weaver, 1989; Larsen and Chilingar, 1983; Eberl et al., 1978; Weaver and Pollard, 1973).

The observable diminution or loss of smectite peak in the X-ray trace after HCl acid treatment may be attributed to the relatively high iron content in the clay structure which made it more susceptible and weaker to acid attack.

Detrital crystalline calcite and quartz are the associated non-clay impuritites. Preponderance of calcite in the clay assemblage of the Carcar Formation reflects the intrinsic calcareous characteristic of the limestone parent rock, and its apparent diminution (or absence) in the alluvium virtually indicates its possible partial dissolution and evacuation due possibly to greater acid leaching and greater weathering in the alluvium. This also implies the greater presence of non-pedogenic calcium carbonate (NPC) compared to pedogenic calcium carbonate (PC). The NPCs are part of the parent material of vertisols (Srivastava et al., 2002). Dissolution of NPCs and recrystallization of dissolved Ca ions are responsible for the formation of PCs (Srivastava et al., 2002). Dominance of quartz in the clay assemblage of the alluvium portrays its higher resistance to acid leaching and weathering and suggests its higher stability in the alluvial environment. This is in good agreement with Velde (1985) that quartz grains in soils and sediments show very little reactivity with their environment and that they are largely inert in many weathering and sedimentary environments.

The smectite and mixed-layer kaolinite/smectite clays detected in the soil formation profiles blanketing the Carcar Formation and the Quatemary Alluvium are strongly suggestive of hydrochemical weathering derivation under essentially warm and humid tropical climatic regime with distinct alternation of wet and dry seasons. Hydrolysis for this clay assemblage seems to be reasonably moderate based on explanation by Pedro (1997), Righi and Meunier (1995), Dixon and Weed (1977). The clay minerals of CaF and QAl are highly indicative of earth-surface condition of formation and significantly devoid of thermodynamic influence exhibited by clays of diagenetic origin or clays affected by hydrothermal alteration. Pedogenesis is considered the substantial and prevalent process. The interstratified K/S constitutes the intermediate phase in the solid-state transformation between smectite and kaolinite poles. These observations are within the contexts discussed in the works of FitzPatrick (1980), Nemecz (1981), Velde (1995) and Pacquet and Clauer (1997).

Mechanisms of Interstratified Kaolinite/Smectite Formation

Several hypotheses on the mechanisms of kaolinite/smectite mixed-layer formation have been advanced by numerous authors such as Sudo and Hayashi (1956), Altschuler et al. (1963), Herbillon et al. (1981), Buhmann and Grubb (1991) and Nurcholis and Tokashiki (1998) among others. Most of these assumptions are generalizations congruent to solid-state transformation by kaolinitization of smectite.

As shown in Figure 11, Amouric and Olives (1998) proposed 2 possible solid-state mechanisms that are responsible for kaolinite formation: 1) lateral transformation of 1 smectite layer into 1 kaolinite layer; 2) the lateral intercalation of 1 kaolinite layer in smectite. The lst mechanism suggests that the main structural modification probably involved the removal (or stripping) of a tetrahedral sheet and the adjacent interlayer region (B). The 2nd mechanism infers that the kaolinite layer K is intercalated between 2 smectite layers S1 and S2, that is, between the interlayer atoms and the tetrahedral level of a smectite layer (A). The 2 mechanisms A and B seem structurally equivalent, as both may produce an additional basal shift. These 2 mechanisms compensate each other, A producing an increase in volume and B a decrease in volume. Nevertheless, the easier one is probably B, since very few atoms have to be supplied in this case (Amouric and Olives, 1998).

In this study however, it may be difficult to forthrightly conclude which of the 2 mechanisms is more applicable or more prevailing. Dr. H. Nakasawa (2001) of National Institute for Research in Inorganic Materials, (personal communication), during the annual clay symposium held in Toyo University, Saitaina Prefecture, had explained that in this study, mechanism A seems to be more favorable in some respects. He emphasized that the soil media covering the CaF and the QAl, and the sampling sites along the hills and coasts are situated in low energy environments and not in high energy ones depicted by diagenesis and hydrothermal alteration environments. Mechanism B allegedly requires higher energy field which is practically absent in the coastal belt covered by this study. In this case, he explained that weathering process and condition in the area could not promote effective stripping of the silica sheets of the smectite. His explanations seem sound and plausible.

CONCLUSIONS

1. Various analytical tests of the soil/clay samples obtained from the Carcar Formation and the Quaternary Alluvium indicated similar mineralogy and assemblage, with the predominance of smectite and subordinate association of mixed-layer kaolinite/smectite (K/S). The proportion of the mixed-layer K/S is noticeably higher in the QAl than in the CaF.
2. In the Carcar Formation vertisol, the interstratification is derived to be random with approximate proportion of $\geqq$90% smectite and $\leqq$10% kaolinite in the mixed-layering. Non-sheet impurities are usually calcite and frequently quartz.
3. In the Quaternary Alluvium vertisol, the approximate proportion of smectite is $\geqq$70% and kaolinite is $\leqq$30% in the random interlayering. Non-sheet impurities are usually quartz and very rarely calcite.
4. The present study confirms the widespread lateral occurrence of mixed-layer kaolinite/smectite in the Quaternary Alluvium. It is also observed to be widespread in the Carcar Formation although in relatively minor amounts.
5. The mixed-layer kaolinite/smectite in this study seems to be correlative with the mixed-layer kaolinite/smectite found in the red-burning clay deposit in the previous studies and indicates that it is evidently not only confined

as exotic mineral within the red-burning clay site.

6. The kaolinite proportion in the K/S interstratification is noted to be considerably higher in the red-burning clay deposit compared to the vertisols of CaF and QAl covered in this present study, and this possibly suggests the greater maturity and more intense weathering of clays in the red-burning clay deposit site than outside its margin.
7. Illite or illitic fades is found to occur solely in vertisol of QAl and is envisaged to have formed by authigenesis or neogenesis where potassication and K-fixation is triggered by repeated wetting and drying cycle in the alluvial plain.
8. Smectite having high rehydration capacity is found to occur solely in vertisol of CaF and its unique capacity for rehydration is ascribed to its structure and beidellitic composition.
9. Pedogenesis and differential chemical weathering under tropical environment are believed to be the important processes in catalyzing the formation and evolution of the clays and clay assemblages in the study area.

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