

Clay Mineralogical Study of the Tertiary Malubog Formation, Cebu Province, Philippines

著者	ALETA Dennis Gerald A., TOMITA Katsutoshi, KAWANO Motoharu, ALETA Josephine T., LUPO Elena S.
journal or publication title	鹿児島大学理学部紀要=Reports of the Faculty of Science, Kagoshima University
volume	36
page range	43-57
URL	http://hdl.handle.net/10232/00003314

Clay Mineralogical Study of the Tertiary Malubog Formation, Cebu Province, Philippines

Dennis Gerald A. ALETA^{1,3}, Katsutoshi TOMITA¹, Motoharu KAWANO²,
Josephine T. ALETA³ and Elena S. LUPO³
(Received on August 20, 2003)

Abstract

The Early Miocene Malubog Formation (Mbf) is one of the most widespread Tertiary formations in Central Cebu, Philippines. The formation consists of mudstone, shale and occasional beds of conglomerate, limestone and coal. It exhibits poor bedding and shows rapid lithologic changes vertically and horizontally. The formation is subdivided into several members which are all essentially coal measures and limestones.

Mineralogical study of the Malubog Formation focused on the gently dipping strata of the argillaceous-arenaceous sedimentary rocks with generally minimal coal seam interbeds. Analytical testworks, involving x-ray diffraction (XRD), differential thermal analysis-thermogravimetry (DTA-TG), scanning electron microscopy (SEM) and energy dispersive x-ray (EDX), performed on the <2 μ m size fraction indicate that multi-phase phyllosilicates of smectite, kaolinite, illite, mica, chlorite and mixed-layer varieties constitute essentially the argillaceous-arenaceous sedimentary rocks. These clays blend into several mineral assemblages that are almost all smectite-dominated. Most combinations include three or four clay species with varying peculiarities. Accessory non-phyllosilicates minerals are finely crystalline silica polymorphs (quartz, cristobalite, tridymite), feldspar, calcite, zeolite and jarosite (some alunite). Although the mineralogical components in many assemblages may appear the same, they reflect quite differences in characteristics and diversity of the sedimentary horizons.

Most of these clays and mineral assemblages seem to convey diagenetic style of sedimentary petrogenesis, few relate to pedogenesis, and some exhibit effects of hydrothermal alteration. The regime of diagenetic alterations infers to have progressed in alkaline marine environment, stimulated by low to moderate thermodynamic conditions at shallow to moderate burial depth. In the pedogenetic environment, chemical weathering suggests moderate conversion condition without reaching monosiallitization. Clays and mineral assemblages in hydrothermally altered ground reveal acid-sulfate to intermediate types.

Keywords : Clay Mineral, Malubog Formation, Philippines, Argillaceous-arenaceous sedimentary rocks.

INTRODUCTION

Despite the widespread occurrence of the Malubog Formation in Central Cebu, Philippines, nothing is known much about its clay mineral constitution and distribution. This is rather unusual considering that this rock formation hosts a wide variety of shales or mudrocks or other fine sedimentary clastic rocks. Previous studies made were more inclined to stratigraphy and paleontology as gleaned from BMG (1981). Available descriptions about this lithology were based mostly on ocular examinations of the physical properties and qualities. Oftentimes, this sedimentary rock sequence, particularly the shaly sections, is described as that could be easily weathered into clays of various

¹ Department of Earth and Environmental Sciences, Faculty of Science, Kagoshima University, 1-21-35 Korimoto, Kagoshima City, 890-0065 Japan

² Department of Environmental Sciences and Technology, Faculty of Agriculture, Kagoshima University, 1-21-24 Korimoto, Kagoshima City, 890-0065 Japan

³ Mines and Geosciences Bureau, Department of Environment and Natural Resources, Region 7, Greenplains Subdivision, Banilad, 6014 Mandaue City, Cebu, Philippines

colors, but nowhere in the available documents describe what specific kinds of clays and clay mineral assemblages exist. It is evident from the stated previews that important complementary data on laboratory works pertaining to mineralogical aspects that are deemed of value are still regrettably lacking. Intrinsic and more detailed properties beyond the visual field features are therefore felt necessary to obtain in order to have a fuller knowledge and better understanding of the rock formation.

This study sets forth as a first attempt to investigate the minerals contained in the stratified argillaceous-arenaceous sedimentary rocks and some associated soils.

The central objectives of this study were to generate accurate analyses and characterizations, by means of several laboratory methods and techniques, of the minerals and mineral assemblages in the selected sedimentary sequences of the Tertiary Malubog Formation and to render some rational interpretations of the mineralogy in relation to sedimentary genesis.

GEOLOGY

Malubog Formation (MbF)

The following descriptions of the Malubog Formation (MbF) are chiefly taken from Santos-Ynigo (1951) and BMG (1981) with minor modifications.

The Malubog Formation is one of the most widespread Tertiary formations in Central Cebu (Figure 1). The present Malubog areas represent folded and faulted monoclinical components of a once extensive elongate dome. Uplift was centered within the broad area now occupied by the Central Highlands. Faulting and folding at various geologic periods along the margins of this up-arched area and subsequent truncation by erosion may account for the present distribution of the Malubog in Central Cebu.

The Malubog Formation follows upon the Cebu Formation as part of conformable transgressive series. It is made up essentially of shale and sandstone with occasional beds of conglomerate, limestone, carbonaceous shale, and coal.

The Malubog varies in thickness from 500 to over 1000 meters. Thicker sections may reach a maximum of 2000 meters. Malubog areas are generally characterized by smooth, low-rolling topography occasionally broken by sharp sandstone or limestone ridges in folded localities. Fresh exposures of Malubog shale, sandstone and conglomerate are typically gray like those of the older Cebu Coal Measures. In deeply weathered sections these sediments turn to lighter shades of reddish brown or yellowish brown. Shaly sections are easily weathered to clays of various colors.

SAMPLES AND EXPERIMENTAL WORKS

The majority of specimens analyzed in this study were collected from stratified sedimentary outcrops of the Malubog Formation along the segments of the Cebu Transcentral Highway and other minor roads in Central Cebu. The spatial distribution is shown in Figure 1. These samples were obtained from the argillaceous-arenaceous sequences of mostly mudstones and siltstones. Two specimens labeled as MAN-1 and MAN-1A were derived from soil overlying the Malubog Formation along the Toledo-Tabunoc (Manipis) Road.

The fine clay size fraction was segregated following the generally prescribed procedures of dispersion, sedimentation and centrifugation. X-ray diffraction (XRD) analyses of oriented $<2 \mu\text{m}$ size fraction were carried out using a RINT 2000 x-ray diffractometer with a carbon monochromator ($\text{CuK}\alpha$ radiation) and operational setting of 30kV and 14mA. Thermal tests were performed with a Rigaku Thermo Plus TG 8120 DTA-TGA apparatus using about few grams of fine air-dried samples. Thermal graphs were recorded from ambient temperature to 1,000°C with a heating rate of 10°C/min. Scanning electron microscopy (SEM) studies of mineral morphology and aggregations

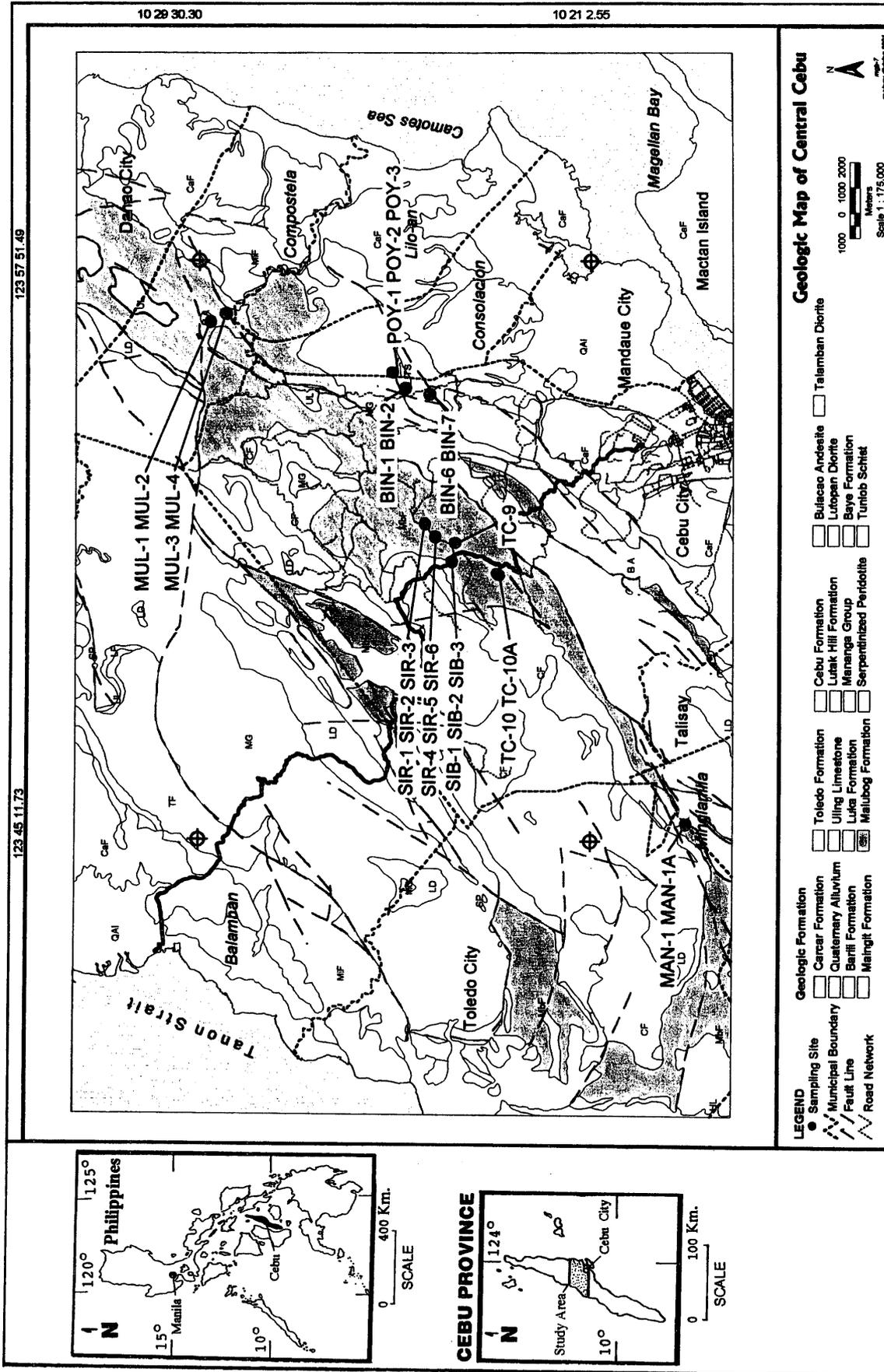


Figure 1. Geological and sampling location map of the study area in central Cebu, Philippines. Geological map is based from the Philippine Bureau of Mines and Geosciences quadrangle maps.

used Hitachi S-4000 FE-SEM. The specimens were coated with gold-palladium using FINE COAT ION SPUTTER JFC-1100. Other powder specimens were sputtered with carbon using JEOL JEC-520 CARBON COATER. 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.

RESULTS

X-ray Diffraction (XRD)

The x-ray diffraction patterns of samples from the Malubog Formation appear varied but they usually convey the composite associations of the principal clay groups of smectite, kaolinite, illite, mica and chlorite together with interstratified varieties. The typical non-phyllsilicate accessories are free-silica, feldspar, calcite, zeolite and jarosite (minor alunite). The differences in peak intensities and breadth may be attributed to the proportional contents of individual clay phases, the degree of crystallinity, order of stratification, particle sizes and impurities. Responses to different means of treatments may also be observed by the changes in diffraction patterns.

Four examples of selected x-ray diagrams are shown in Figures 2, 3, 4 and 5. Sample TC-10A (Figure 2) reveals kaolinite-dominated assemblage (7.15 Å and 3.57 Å) with minimal amounts of smectite (14.5 Å), illite (10 Å) and chlorite (14 Å). Non-sheet minerals are quartz (3.34 Å) and feldspar (3.18 Å). Ethylene glycolation (EG) shows broadening of the smectite basal peak but kaolinite peaks remained steady although reduced slightly in intensity. The 6N HCl acid treatment for 1 hr shows enhancement of kaolinite reflections. Heat treatment shows stable peaks of kaolinite and illite and reversible contraction-expansion of smectite peak at 300°C-500°C series.

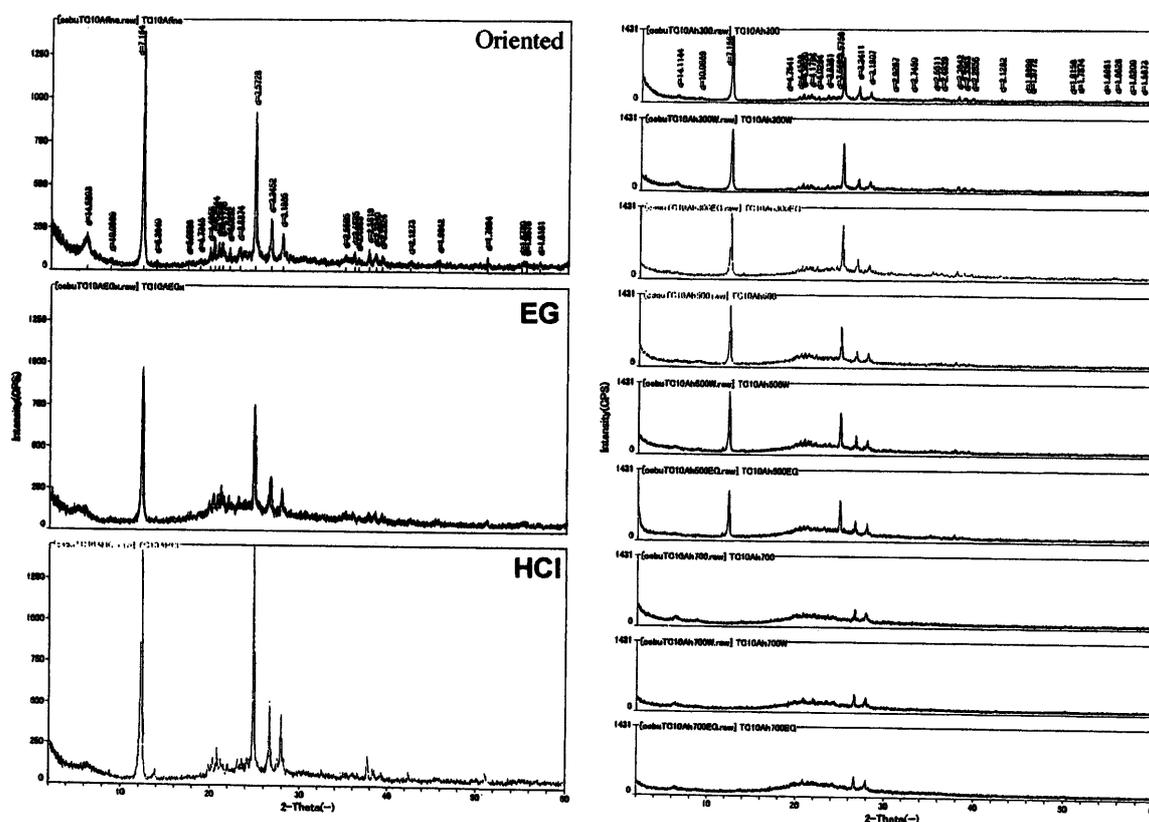


Figure 2. X-ray diffraction patterns of sample TC-10A showing kaolinite-dominated assemblage with subordinate association of smectite, chlorite and illite. Right column-top to bottom shows series of heat treatment at 300°C, 300°C + H₂O, 300°C + EG; 500°C, 500°C + H₂O, 500°C + EG; 700°C, 700°C + H₂O, 700°C + EG.

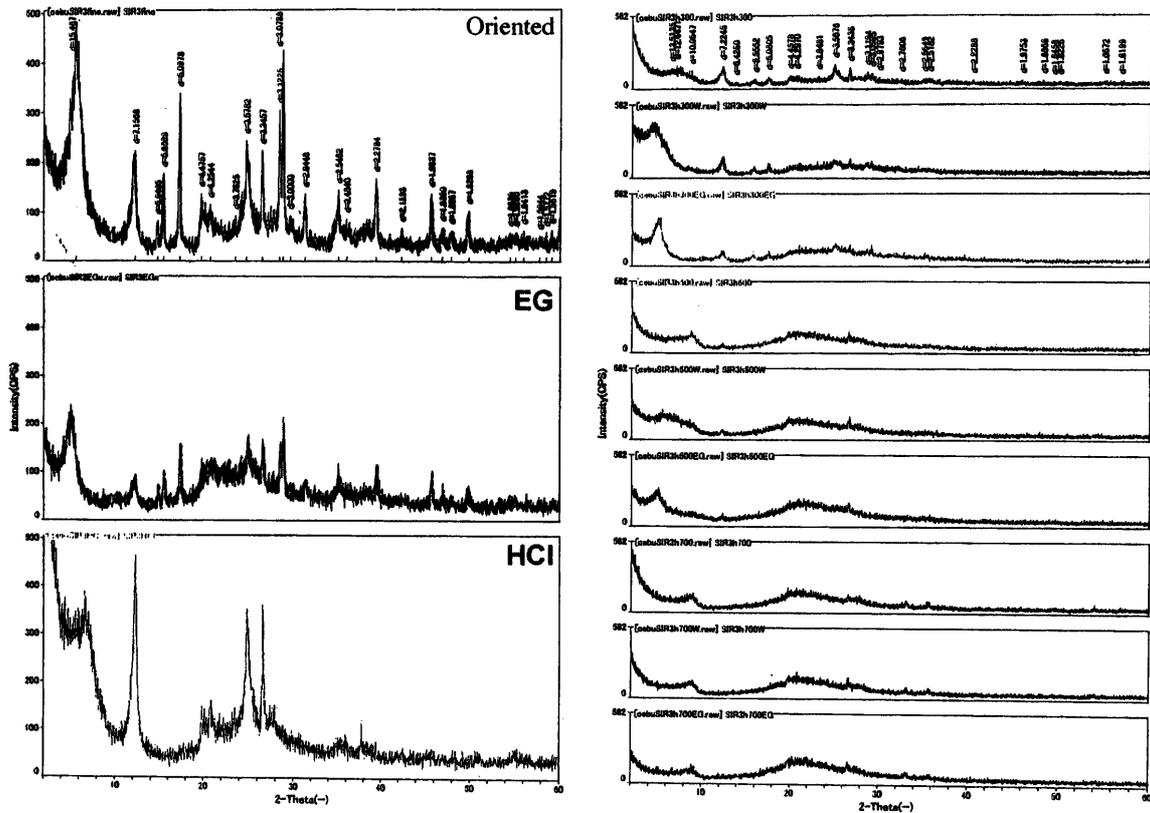


Figure 3. X-ray diffraction patterns of sample SIR-3 showing smectite-kaolinite-dominated assemblage with ample association of jarosite. Right column-top to bottom shows series of heat treatment at 300°C, 300°C + H₂O, 300°C + EG; 500°C, 500°C + H₂O, 500°C + EG; 700°C, 700°C + H₂O, 700°C + EG.

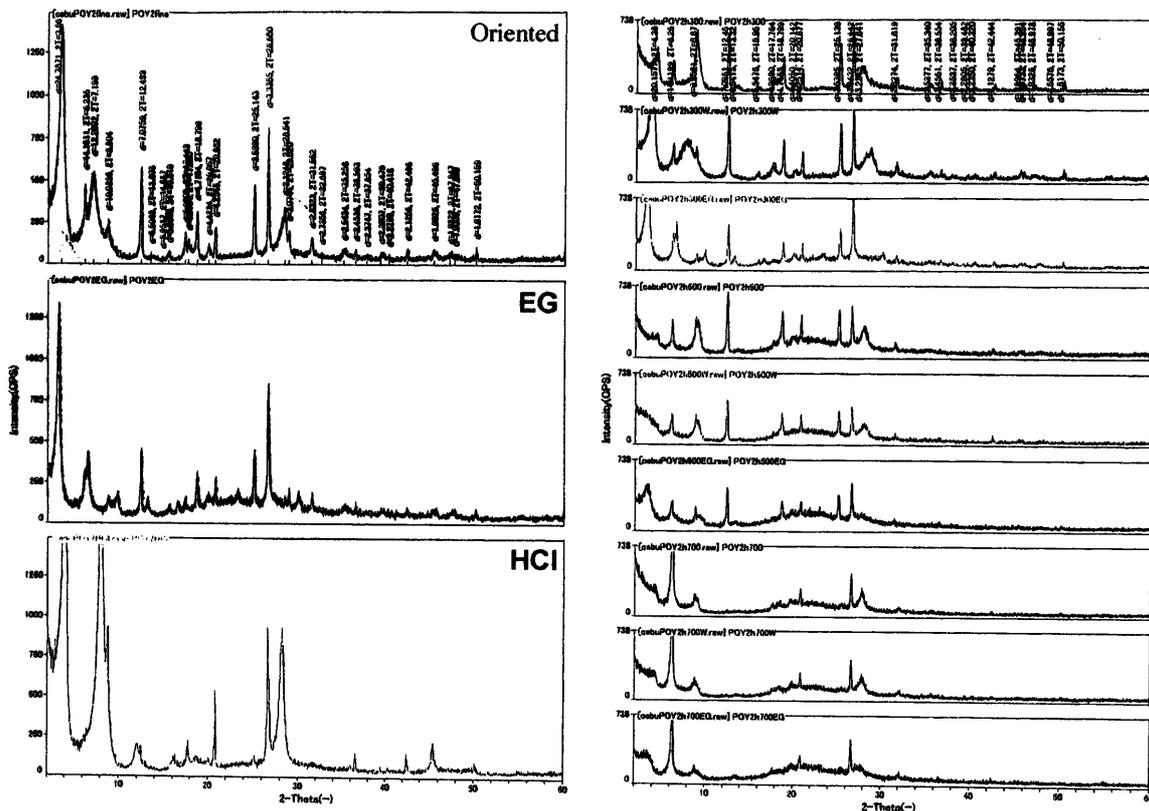


Figure 4. X-ray diffraction patterns of sample POY-2 showing interstratified mica/smectite-dominated assemblage with moderate association of kaolinite and chlorite. Right column-top to bottom shows series of heat treatment at 300 °C, 300°C + H₂O, 300°C + EG; 500°C, 500°C + H₂O, 500°C + EG; 700°C, 700°C + H₂O, 700°C + EG.

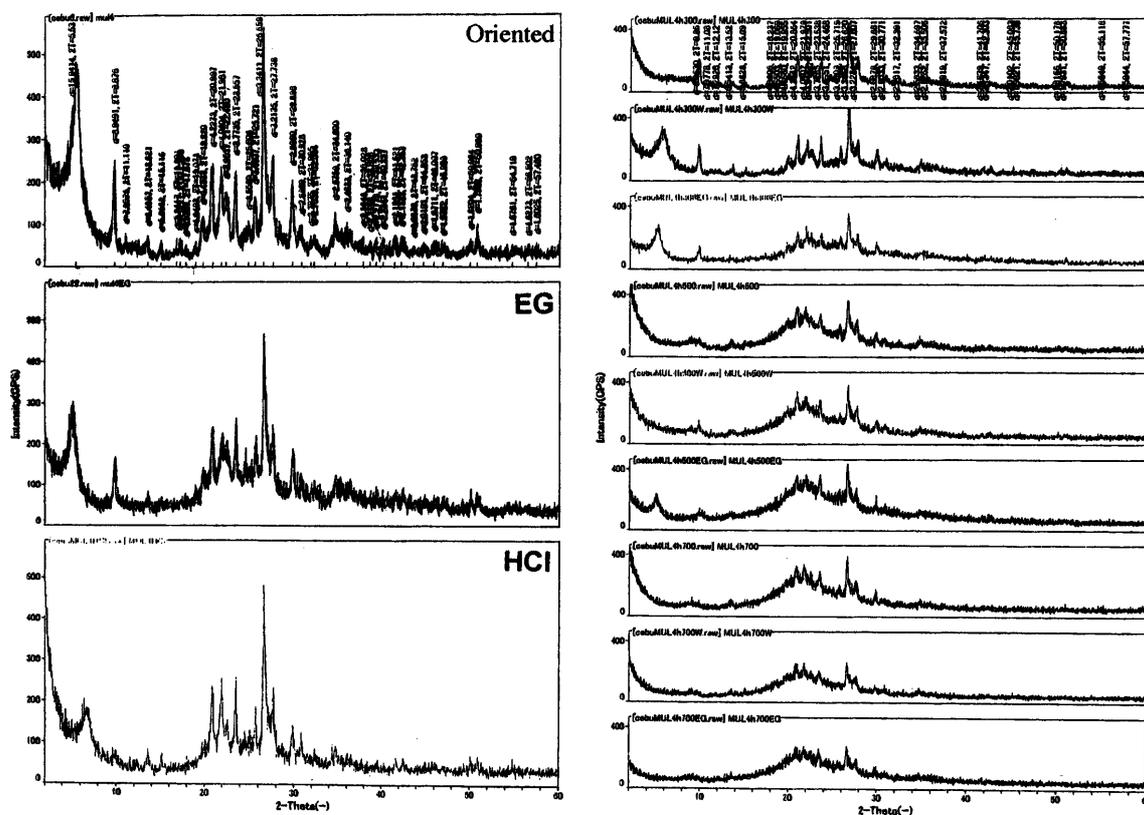


Figure 5. X-ray diffraction patterns of sample MUL-4 showing smectite-dominated assemblage with ample association of quartz-cristobalite and some zeolite.

Right column-top to bottom shows series of heat treatment at 300°C, 300°C + H₂O, 300°C + EG; 500°C, 500°C + H₂O, 500°C + EG; 700°C, 700°C + H₂O, 700°C + EG.

Kaolinite peaks disappear at <700°C. Extremely subtle peak with about 14 Å space at 700°C heat treatment may be due to extremely low amount of chlorite.

Sample SIR-3 (Figure 3) gives chiefly smectite-kaolinite-dominated assemblage with association of appreciable jarosite (peak doublet 3.07-3.12 Å), and some quartz and feldspar. EG treatment shows a general intensity decrease of all reflections. Smectite layers swelled to around 17 Å. Acid treatment shows intensity enhancement of kaolinite peaks (7.15 Å and 3.57 Å) and disappearance of jarosite peaks. Heat treatment shows contraction-expansion of smectite peak in the 300°C to 500°C series, and irreversible contraction to ~10 Å at 700°C. Gradual decrease of peak intensity of kaolinite may be noted at 300°C to 500°C series and complete loss at 700°C.

Sample POY-2 (Figure 4) indicates interstratified mica/smectite (M/S)-dominated assemblage with moderate kaolinite, chlorite and non-sheet accessories jarosite and quartz. EG treatment shows the general sharpening of the XRD reflections. HCl treatment illustrates great enhancement of interstratified M/S peaks and disappearance of chlorite and jarosite peaks. Heat treatment effects broadening-sharpening of interstratified M/S peaks at 300°C-500°C series, and irreversible contraction to ~10 Å at 700°C series. Gradual amplification of 14 Å peak intensity discloses the attributes of chlorite at 300°C-700°C series. Kaolinite peaks resist the 300°C-500°C thermal series but decompose at <700°C.

Sample MUL-4 (Figure 5) displays smectite-kaolinite-illite-dominated assemblage with ample association of silica polymorphs (quartz [3.34 Å] and cristobalite [4.04 Å], minimal tridymite?), some feldspar (3.21 Å) and zeolite (8.94 Å). EG treatment yields slight decrease in intensity of reflections with apparent shift in the basal peak of

smectite. Other peaks remain steady. HCl treatment produces diminution of smectite and zeolite peaks and sharpening of silica polytypes peaks. Heat treatment shows contraction-expansion of smectite peak at 300°C-500 °C thermal series, and irreversible contraction to $\sim 10 \text{ \AA}$ at 700°C. Silica polytypes peaks remain steady and persistent throughout 300°C-700°C series.

Differential Thermal Analysis -Thermogravimetry (DTA-TG)

The differential thermal analysis-thermogravimetry (DTA-TG) curves display the composite thermochemical reactions of the different clay species in the different assemblages.

The endothermic and exothermic reactions of the samples depicted in the DTA curves show various behaviors that suggest superposition of reaction patterns of the clay mineral constituents. The endotherms are usually dual, one in the low temperature (80°C-100°C) with either mild or moderate shoulder (<200°C) and another one in the high temperature (500°C-527°C). The exotherms are also usually dual, one in the low temperature (300°C-416°C) and another one in the high temperature (>900°C). The reactions below <200°C are generally related to dehydration and the reactions within 500°C are generally related to dehydroxylation. The low-temperature exothermic regimes may be correlated with elimination of amorphous impurities and the high-temperature regimes may be ascribed to crystallization of anhydrous phases. Some mild endotherms in about 770°C may be due to CO₂ expulsion from the accessory detrital calcite crystallites.

The various configurations of weight loss and rate of loss are shown in the TG curves. The weight decrement is generally correspondent to dehydration and dehydroxylation of the predominantly phyllosilicates assemblages and are coincidental with the DTA curves. Weight loss is notably observed large and abrupt below <200°C. Moderate and gradual weight loss follows until about 500°C is reached. Within 500°C-600°C range weight loss is relatively precipitous. Above the given temperature range weight loss is minimal and gradual. Variable total weight loss is

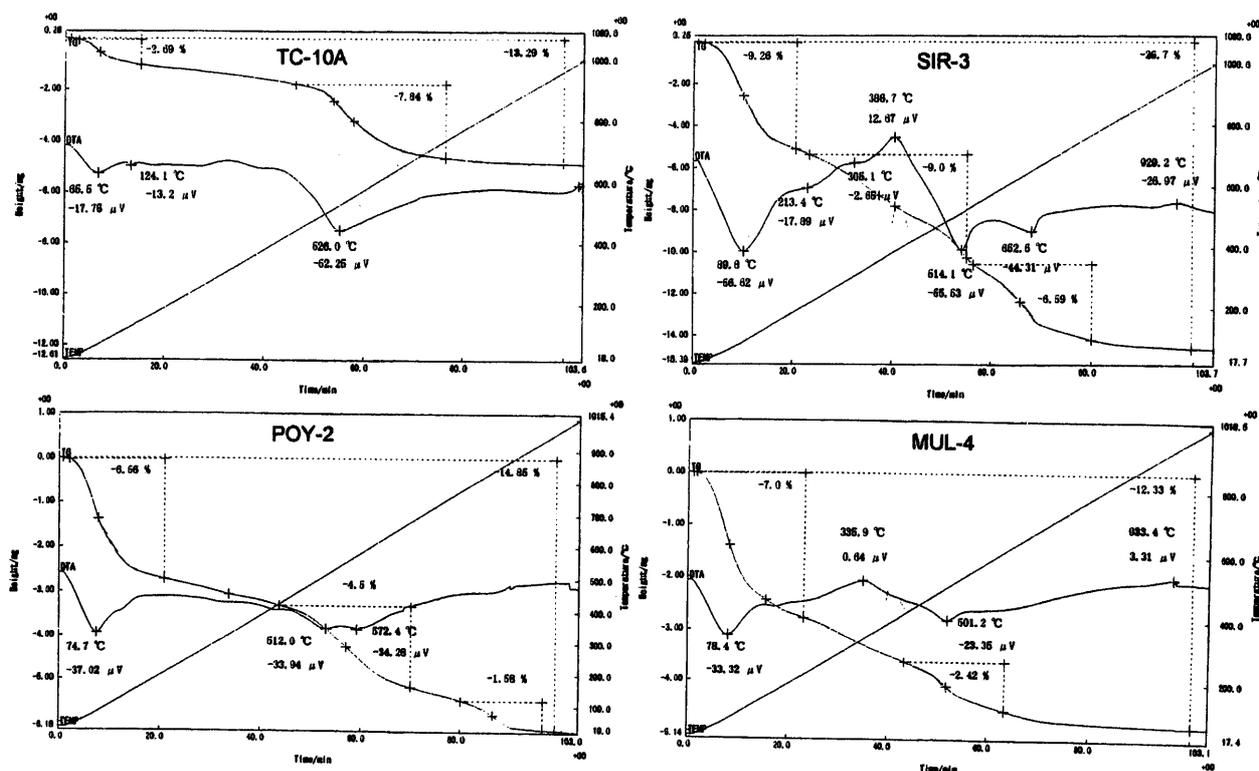


Figure 6. Differential thermal analysis-thermogravimetry (DTA-TG) curves displaying the thermoanalytical behaviors and characteristics of samples TC-10A, SIR-3, POY-2 and MUL-4.

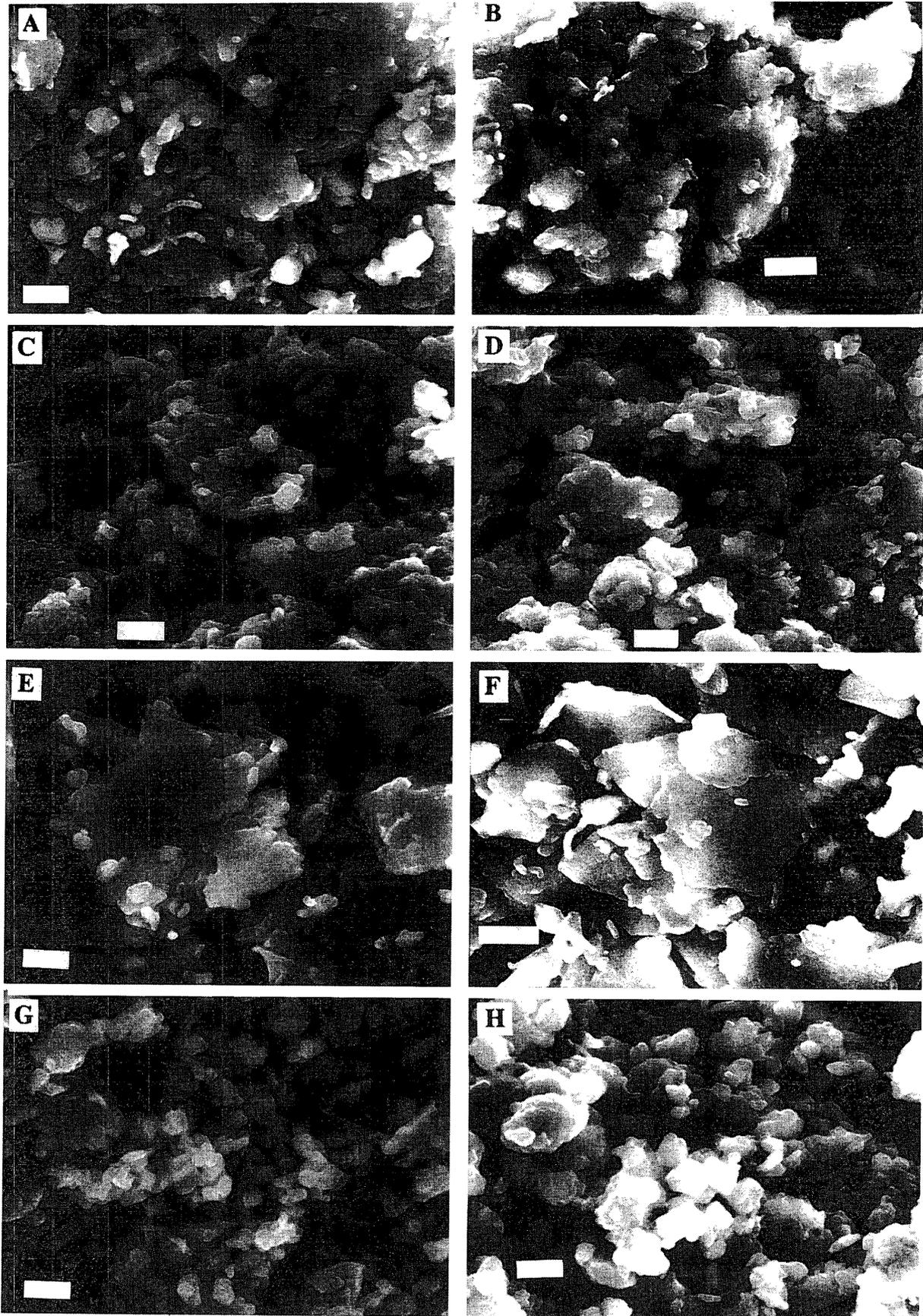


Figure 7. Scanning electron microscopy (SEM) photos showing the various mineral morphologies of samples TC-10A, SIR-3, POY-2 and MUL-4.

seen but usually fall in the range of 17%-26%.

Figure 6 gives 4 examples of the DTA-TG curves of samples TC-10A, SIR-3, POY-2 and MUL-4.

DTA of sample TC-10A (kaolinite-smectite-illite-quartz-feldspar) exhibits shallow endotherm at 65°C correspondent to dehydration and broad endotherm at 526°C correspondent to dehydroxylation. TG shows little weight loss of 2% during dehydration and moderate weight loss of 7% during dehydroxylation with total loss of 13%.

DTA of sample SIR-3 (smectite-kaolinite-jarosite-quartz-feldspar) reveals deep, broad, shouldered endothermic reaction with peak at 89°C and dual endotherms 514°C and 652°C. Very feeble "pseudo" exotherm is seen at 929°C. TG curve shows weight loss appears continuous reaching a total of 26%.

DTA of sample POY-2 (smectite-kaolinite-chlorite-interstratified M/S-jarosite-quartz) illustrates moderate endotherm at 74°C and trifling endotherms at 512°C and 572°C. TG curve displays abrupt weight drop of 6% during dehydration and moderate weight decrement 4% during dehydroxylation with final loss of 14%.

DTA of sample MUL-4 (smectite-kaolinite-illite-quartz-feldspar-cristobalite-tridymite-zeolite) exemplifies

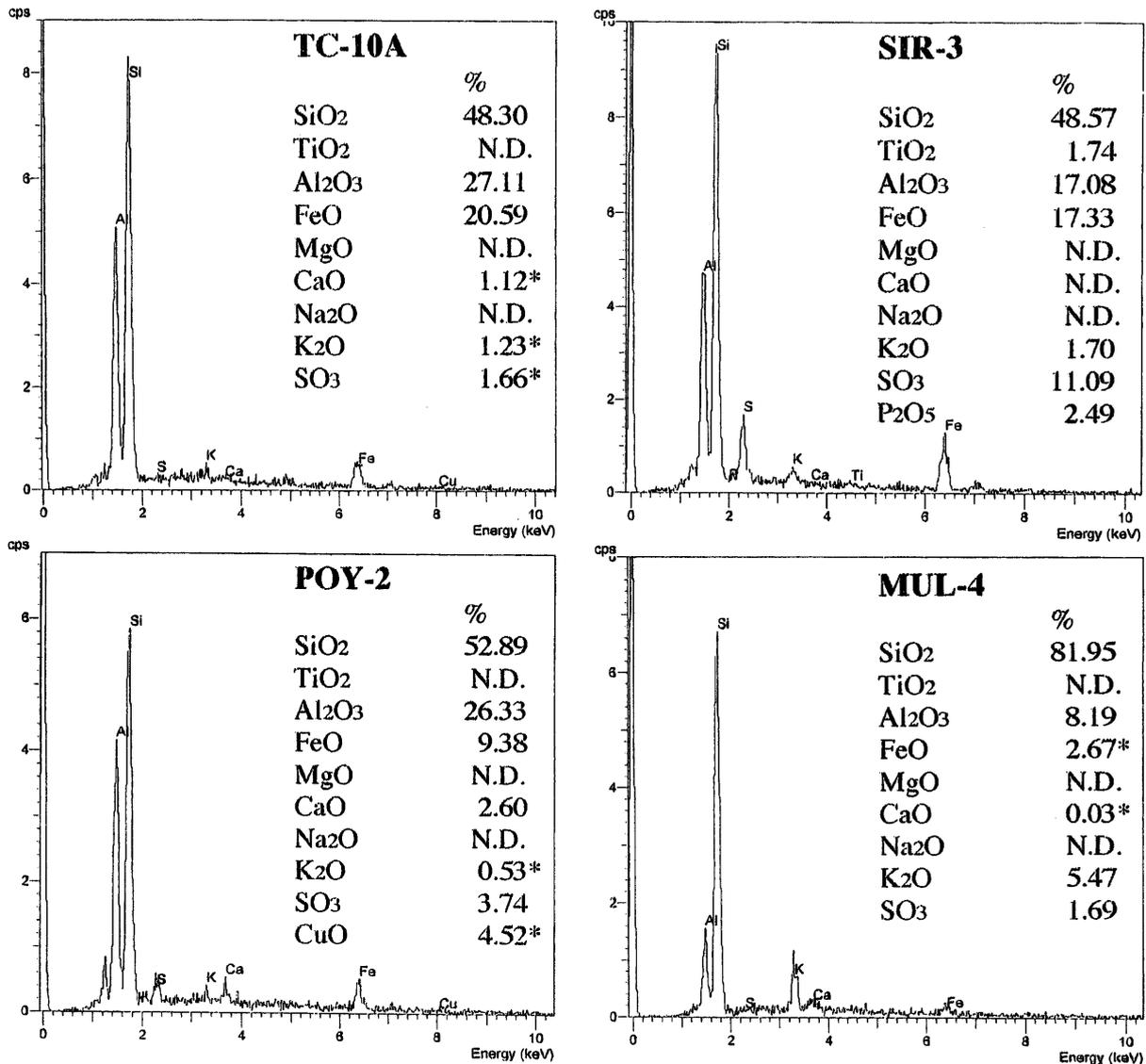


Figure 8. Energy dispersive x-ray (EDX) analysis denoting approximate semi-quantitative chemical compositions of samples TC-10A, SIR-3, POY-2 and MUL-4.

moderate endothermic peak at 78°C and another mild peak at 501°C. TG curve indicates weight decline of 7% is abrupt in the low-temperature endotherm than the high-temperature endotherm with about 2% weight drop. Total weight loss is about 12%.

Scanning Electron Microscopy (SEM)

The morphologies of selected samples are exhibited in Figure 7. TC-IOA shows agged to circular clay flakes with porous aggregation (Figure 7 A and B). SIR-3 exhibits abundant, tiny, pseudo-cubic crystals of jarosite in intimate association with the clusters of fine clay flakes (Figure 7 C and D). POY-2 reveals rather thick and wide irregular plates and flakes of clays with slight curled edges (Figure 7 E and F). MUL-4 shows plentiful, tiny, globular and subhedral quartz and cristobalite (with tridymite) crystals scattered in the platy matrix of the clays (Figure 7 G and H).

Energy Dispersive X-ray (EDX)

Figure 8 shows the semi-quantitative analyses of samples TC-IOA, SIR-3, POY-2 and MUL-4. The variations in chemical compositions reflect the relative abundance of significant mineral species. TC-IOA is exceptionally rich in FeO with 20.59% suggesting the participation of iron mineral complexes. SIR-3 is recognized with high content of FeO and SO₃ which may be attributed to the association of jarosite. POY-2 has typical amounts of SiO₂ and Al₂O₃ with appreciable FeO and SO₃ which may be correlated with regular order interstratified mica/smectite with impurities of jarosite. MUL-4 is high in SiO₂ (81.95%) due to quartz, cristobalite accessories and some tridymite.

DISCUSSIONS

The clays and clay mineral assemblages of the Malubog Formation are observed polymineralic and varied. The polyminerals include the phyllosilicates consisting (2:1 type) smectite, illite, mica, (1:1 type) kaolinite and (2:1:1) chlorite, and the non-phyllosilicates accessories consisting silica polymorphs (quartz, cristobalite, tridymite), feldspar, calcite, zeolite and jarosite (some alunite). The phyllosilicates and accessories occur in different combinations producing varieties of mineral assemblages. Within the assemblages, different proportions of phases of both phyllosilicates and non-phyllosilicates are observed. The proportional contents of the component phases as well as the absence or presence of some component phases in the assemblages seemingly yielded the diversity in behaviors and attributes in the analytical/experimental results.

The various minerals identified and various mineral assemblages distinguished (with corresponding samples) are as follow:

- 1) smectite-kaolinite-illite-quartz-feldspar = MUL-1 and MUL-2
- 2) smectite-kaolinite-illite-quartz-feldspar-cristobalite-tridymite-zeolite = MUL-3 and MUL-4
- 3) smectite-illite-chlorite-kaolinite-quartz-cristobalite-feldspar = BIN-1, BIN-2, BIN-6 and BIN-7
- 4) smectite-kaolinite-illite-quartz-calcite-feldspar = SIB-1, SIB-2 and SIB-3
- 5) smectite-kaolinite-quartz-feldspar = SIR-1, SIR-2, SIR-3, SIR-4, SIR-S and SIR-6
- 6) smectite-interstratified illite/smectite (I/S) -kaolinite-quartz-feldspar = TC-9
- 7) kaolinite-smectite-illite-quartz-feldspar = TC-10 and TC-10A
- 8) intersratified mica/smectite (MIS) -kaolinite-chlorite-jarosite-quartz = POY-1, POY-2 and POY-3
- 9) smectite-kaolintue-illite-interstratified I/S-quartz = MAN-1 and MAN-1A

The minerals and mineral assemblages listed above show the heterogeneity of strata comprising the sedimentary rocks of the Malubog Fortmation. They also indicat the lateral distribution of the clay minerals in particular stratum in different localities.

The variations and heterogeneities apparently offer a reflection of the differences in the process of mineral formation and the environment. Diagenesis is perceived to be the prevailing process in the clay formation and evolution. Hydrothermal alteration is inferred to have spawned some variations in the originally diagenetic mineral assemblages in some localities clustering within POY sampling stations. Pedogenesis with attendant weathering could have also played key role in the formation of some mineral and assemblage as in MAN-1 and MAN-1A.

Except the assemblage of MAN-1 and MAN-1A all the other assemblages may be asserted as diagenetic considering that sedimentary rocks are involved. In other words, diagenesis is substantially the major process considered consonant with sedimentary petrogenesis as emphasized by many investigators (Larsen and Chilingar, 1983; Velde, 1985; Weaver, 1989; Chamley, 1989). Although it may not seem possible to ascertain patterns for diagenetic reactions demonstrating progressive clay mineral conversions stratigraphically, it may still seem possible to establish diagenetic affinity based on the characteristic minerals in the assemblages.

Smectite is distinguished to be the most dominant and persistent in all the assemblages. The other phyllosilicates are accounted for in subordinate amounts. Despite the varieties of assemblages and ignoring the non-phyllosilicates accessories, it appears that smectite-kaolinite-illite assembly is prevalent. This tri-phase association is typical in other sedimentary successions associated with diagenesis as reckoned from the many investigations by Sudo and Shimoda (1978), Nemezc (1981), Larsen and Chilingar (1983), Velde (1985), Weaver (1989), Chamley (1989).

MUL-3 and MUL-4 have somewhat the same mineralogy as MUL-1 and MUL-2 except that the former 2 have relatively elevated amount of quartz, cristobalite and some tridymite. MUL-3 and MUL-4 may be approximated to be analogous to the cristobalite-rich facies of the bentonite in Balamban (Aleta et al., 2000) and the clay assemblages in the Paghumayan Formation, Negros Oriental (Aleta et al., 2002). The enrichment of quartz, cristobalite (and tridymite) may represent authigenesis and may have been responsible for the effective silicification of the argillaceous-arenaceous beds.

BIN-1, BIN-2, BIN-6 and BIN-7 contain the smectite-kaolinite-illite assembly and differ only due to inclusion of chlorite.

SIB-1, SIB-2 and SIB-3 also bear the smectite-kaolinite-illite assembly and deviate only due to presence of non-sheet calcite accessory.

SIR-1, SIR-2, SIR-3, SIR-4, SIR-5 and SIR-6 lack the illite component. These samples are generally smectite-kaolinite-dominated. SIR-3 possesses almost the same mineral signatures as the other SIR samples except that it contains appreciable amount of jarosite (minimal alunite). It may be seen from the SEM that the jarosite are disseminated as fine, pseudo-cubic crystals in clay matrix. There are no clear indications of hydrothermal alteration activity within the vicinity of this sample, and therefore, the jarosite may not be hydrothermally related. In this case, the jarosite may have formed from pyrite or other sulfide-rich minerals in contact with sulfate-rich solution as a result of evaporation of water (Faure, 1991). It could be inferred that the strata where sample SIR-3 was collected may have localized pyrite or other sulfide-rich mineral enrichment.

TC-9 has illite component but it occurs as an interstratified mineral together with smectite. Interstratification of illite and smectite is determined to be ordered R=1. This sample shows high order spacing of about 25 Å.

TC-10 and TC-10A carry the tri-phase combination but kaolinite is observed to be more dominant here than smectite. This assemblage shows semblance with the kaolinite-dominated assemblage of the Cebu Formation.

POY-1, POY-2 and POY-3 may have been highly influenced by hydrothermal alteration as shown by the rich imprints of interstratified mica/smectite phase and jarosite in the mineral assemblage. Hydrothermal fluids could have possibly promoted the "hybrid" formation of the interstratified mica/smectite by rejuvenating the supply of K ions in the system and subsequently fixed it in the interlayer regions of the smectite. The potassiation and K-fixation mechanisms are generally held by many (Eberl, 1978; Eberl and Hower, 1977; Sudo and Shimoda, 1978; Inoue, 1983; Weaver, 1989). The thermal energy generated by the hydrothermal activity probably provided more

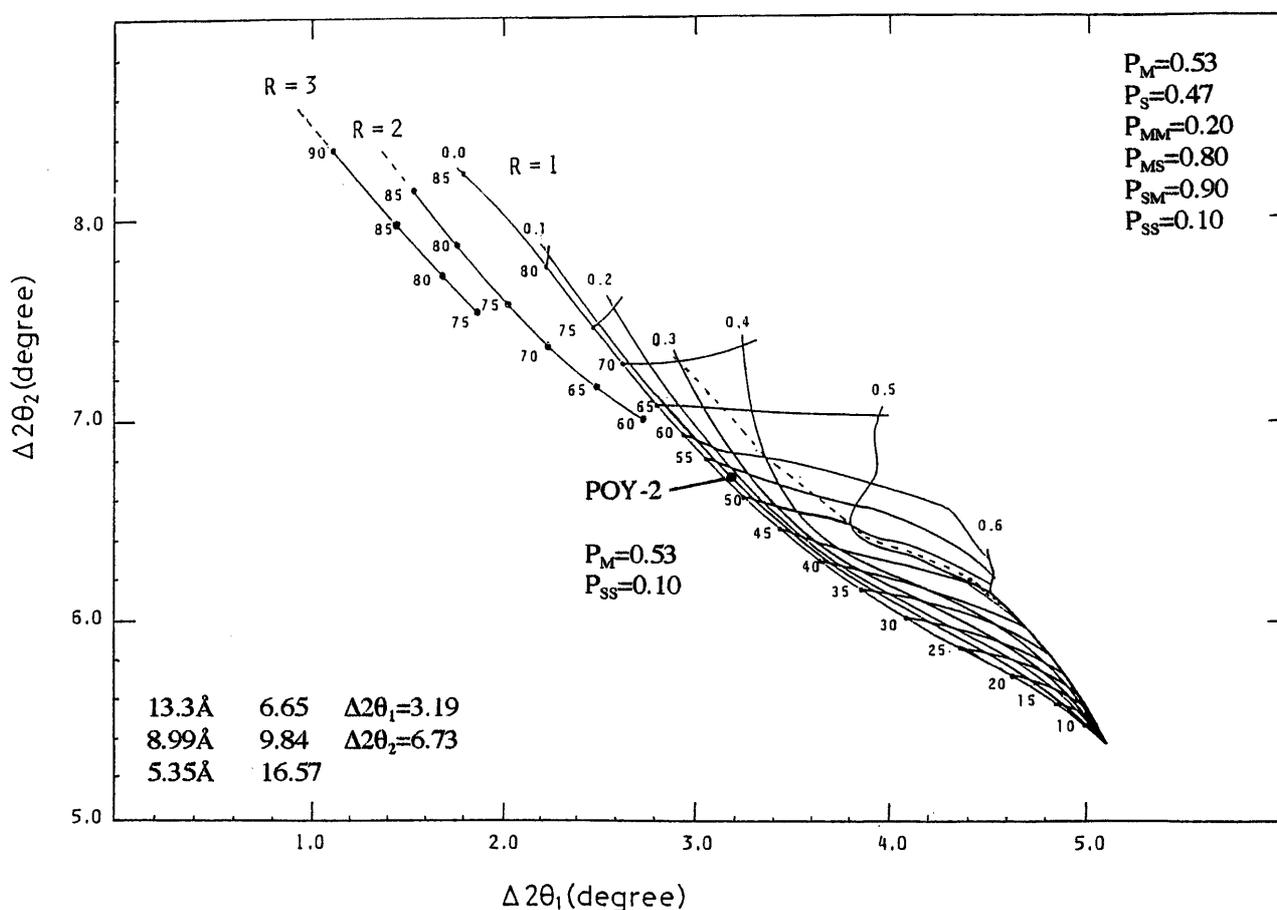


Figure 9. Plot of sample POY-2 in the quantification curves diagram for interstratified mica/smectite of Tomita and Takahashi (1985) and Tomita et al. (1988).

energy required to force the silica tetrahedrons to rotate enough to lock in the K ions (Weaver and Pollard, 1973). Hydrothermal alteration may be intermediate to acid-sulfate type gauged from the ensemble of the mineral phases containing chlorite and kaolinite plus the crystallization of jarosite accessory. In the case of jarosite here, it may be considered that it had formed by reaction of H_2SO_4 derived from the oxidation of pyrite with the gangue and wall rock (Gaines et al., 1997).

Figure 9 shows the plot of sample POY-2 in the quantification curves diagram of Tomita and Takahashi (1985) and Tomita et al. (1988) based on the calculations of Tomita (1988). P_M represents the percentage existence of mica layer equalling to 0.53. P_S represents the percentage existence of smectite layer equalling to 0.47. P_{MM} is the probability that mica succeeds mica assuming that the first layer is mica which in this case equals 0.20. P_{MS} is the probability that smectite succeeds mica assuming that the first layer is mica which in this case equals 0.80. P_{SM} gives 0.90 which is the probability that mica succeeds smectite assuming that the first layer is smectite. P_{SS} pegs 0.10 which is the probability that smectite succeeds smectite assuming that the first layer is smectite.

Interlayering is determined "ordered" based on Reichweite (R) = 1.

Considering keenly the characteristics of the clay minerals and mineral assemblages, it appears that they suitably fit in the early stage of burial diagenesis. Velde (1985) categorized these kinds of clay assemblages to be in the low-temperature and low-pressure range and apparently in "closed" system.

It may be envisaged that the clays were detritally derived from terrigenous paleosources and subsequently

submitted to conditions of diagenesis. Variability in the clay minerals and mineral assemblages may be an ascription to the changing type and amount of sediments during paleodeposition due to shifts in paleoclimatic conditions (Kisch, 1983; Chamley, 1989).

In correlation to the many depth-temperature range studies of Aoyagi and Kazama (1980), Kisch (1983), Velde (1985), Chamley (1989). Weaver (1989), the paleo-depth of deposition of the Malubog Formation sediments may be estimated at around 1200 m to 1800 m or may be even lesser than this range. The burial temperature may be approximated to nestle the 50°C-75°C ranges.

Samples MAN-1 and MAN-1A were collected from soils veneering Malubog Formation. It is only proper to assume that pedogenesis most likely govern their evolution despite some striking similarities of this clay assemblage with those observed from the others produced by diagenesis. The kind of assemblage shown by MAN-1 and MAN-1A is also typical in tropical soils generally associated with vertisols. In this assemblage there may be a genetic link between the diagenetic sedimentary rock and the pedogenetic soil. It may be averred that the soils MAN-1 and MAN-1A were derived chiefly from the geochemical weathering of the underlying sedimentary rock having almost the same mineral assemblage. The mineral assemblage found in the soils is probably a vestige of the original mineral assemblage of the sedimentary rock.

A glimpse of the minerals in the assemblage gives the notion that hydrolysis is not extremely aggressive based on the amount of smectite, illite and interstratified illite/smectite. These minerals indicate that silica and alkalies are still somewhat preserved in the clay lattices and certainly not yet totally exported from the system. This somehow suggests that the condition in the weathering zone may be basic to slightly acidic. Pedro (1997) explained that should hydrolysis be greater, and leads to partial loss of silica and complete loss of alkalies, kaolin-type phyllosilicates will form, which is recognized as monosiallitization process. Evidently, the mineral assemblage of MAN-1 and MAN-1A did not reach the said process.

CONCLUSIONS

Smectite, kaolinite, illite, mica, chlorite and interstratified varieties (M/S, I/S) are evidently identified and characterized as the important phyllosilicate clay minerals in the argillaceous-arenaceous sedimentary rock sequences of the Malubog Formation based on the multiple analytical techniques of mineral investigations conducted. Accessory non-phyllosilicate minerals are finely crystalline quartz, and feldspars as ubiquitous, and calcite, cristobalite (tridymite), zeolite and jarosite (alunite) as sporadic. The various combinations of these phyllosilicates and non-phyllosilicates produced about 9 recognizable assemblages. These clay mineral assemblages are almost all smectite dominated. Tri-phase combination of smectite-kaolinite-illite is observed common.

Majority of the clay facies are considered related to diagenetic style of formation under shallow to moderate marine burial. Paleo-depth range of deposition is estimated at about 1200m to 1800m. The temperature of sedimentary burial is presumed to hover around 50°C - 75°C. Two samples (MAN-1 and MAN- 1A) are considered to have formed under recent pedogenesis and reflect moderate chemical weathering condition not attaining monosiallitization stage. Overprinting of hydrothermal alteration in the diagenetic clays may be observed in some localities (POY-1, POY-2 and POY-3) and the resultant mineral assemblage evinces low-temperature acid to intermediate types of alteration.

ACKNOWLEDGEMENT

This study is realized under the Japanese Government Ministry of Education, Culture, Sports, Science and Technology (Monbukagakusho) Scholarship Program and is sincerely and highly acknowledged. Thanks to the Faculty of Science of the Kagoshima University for the use of laboratory equipment and facilities. The support of

Mines and Geosciences Bureau, Department of Environment and Natural Resources, Region 7, Cebu, Philippines is greatly appreciated.

REFERENCES

- Aleta, D. G. A., Tomita, K. and Kawano, M. (2000) Mineralogical descriptions of the bentonite in Balamban, Cebu Province, Philippines. *Clay Science*, Vol.11, No. 3, 299-316.
- Aleta, D. G. A., Tomita, K., Miel, J. Z., Lupo, E. S., Kawano, M. and Kitamura, R. (2002) Clay Mineralogy of the Middle Miocene Paghumayan Formation, Vallehermoso, Negros Oriental, Philippines. *Reports of the Faculty of Science Kagoshima University*, No.35, 31-48.
- Aoyagi, K. and Kazama, T. (1980) Transformational changes of clay minerals, zeolites and silica minerals during diagenesis. *Sedimentology*, 27, 179-188.
- Bureau of Mines and Geosciences (BMG), (1981) *Geology and mineral resources of the Philippines*. Volume 1, Manila, Philippines. 406 pp.
- Chamley, H. (1989) *Clay sedimentology*. Springer-Verlag, Berlin. Heidelberg, Germany. 623 pp.
- Eberl, D. D. (1978a) The reaction of montmorillonite to mixed-layer clay: the effect of interlayer alkali and alkaline earth cations. *Geochim. Cosmochim. Acta*, 42, 1-7.
- Eberl, D. D. (1978b) Reaction series for dioctahedral smectites. *Clays and Clay Minerals*, 26, 327-340.
- Eberl, D. D. and Hower, J. (1977) The kinetics of illite formation. *Geol. Soc. Am. Bull.*, 87, 1326- 1330.
- Faure, G. (1991) *Principles and applications of inorganic geochemistry: a comprehensive textbook for geology students*. Macmillan Publishing Company, New York, U. S. A. 626 pp.
- Gaines, R. V., Skinner, H. C. W., Foord, E. E., Mason, B. and Rosenzweig, A. (1997) *Dana's new mineralogy: the System of mineralogy of James Dwight Dana and Edward Salisbury Dana*. 8th ed. John Wiley & Sons, Inc., New York, U. S. A. 1819 pp.
- Inoue, A. (1983) Potassium fixation by clay minerals during hydrothermal treatment. *Clays and Clay Minerals*, 31, 81-91.
- Kisch, H. J. (1983) Mineralogy and petrology of burial diagenesis (burial metamorphism) and incipient metamorphism in clastic rocks. In: Larsen G., Chilingar G. V., Eds., *Diagenesis in sediments and sedimentary rocks, 2. Developments in sedimentology*, Elsevier 25B: 289-493 pp.
- Larsen, G. and Chilingar, G. V. (1983) *Diagenesis in sediments and sedimentary rocks 2: Developments in Sedimentology 25B*. Elsevier Scientific Publishing Company, Amsterdam, The Netherlands. 572 pp.
- Nemecz, E. (1981) *Clay Minerals*. Akademiai Kiado, Budapest, Hungary, 547 pp.
- Pedro, G. (1997) Clay minerals in weathered rock materials and in soils; Chapter 1: In Pacquet, H. and Clauer, N., eds., "Soils and Sediments: Mineralogy and Geochemistry". Springer-Verlag Berlin Heidelberg, Germany. 369 pp.
- Santos-Ynigo, L. (1951) *Geology and ore deposits of Central Cebu*. Philippine Bureau of Mines, Cebu, Philippines
- Sudo, T. and Shimoda, S. (1978) *Clays and clay minerals of Japan*. *Developments in sedimentology* 26. Elsevier Scientific Publishing Company, Amsterdam, The Netherlands. 326 pp.
- Tomita, K. and Takahashi, H. (1985) Curves for the quantification of mica/smectite and chlorite/smectite interstratifications by X-ray powder diffraction, *Clays and Clay Minerals*, 33, 379-390.
- Tomita, K., Takahashi, H. and Watanabe, T. (1988) Quantification curves for mica/smectite interstratifications by X-ray powder diffraction, *Clays and Clay Minerals*, 36, 258-262.
- Velde, B. (1985) *Clay minerals: a physico-chemical explanation of their occurrence*. *Developments in sedimentology* 40. Elsevier, Amsterdam, The Netherlands. 427pp.
- Weaver, C. E. (1989) *Clays, muds, and shales, developments in sedimentology* 44. Elsevier Science Publishers B.

V., Amsterdam, The Netherlands.

Weaver, C. E. and Pollard, L. D. (1973) The chemistry of clay minerals: Development in sedimentology 15. Elsevier Scientific Publishing Company, Amsterdam, The Netherlands. 213 pp.