Clay Mineralogy of the Middle Miocene Paghumayan Formation, Vallehermoso, Negros Oriental, Philippines

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Abstract

Clay minerals of stratified tuff and mudrocks of the Middle Miocene Paghumayan Formation in Vallehermoso, Negros Oriental, Philippines were examined. The results showed homogeneity of clay mineralogy in the sedimentary sequence with single-phase smectite as the dominant phyllosilicate present and with little association of kaolinite. Feldspar, zeolite, cristobalite, quartz and calcite are typical non-sheeted accessories that yield to some mineral assemblages along with smectite. The signature mineral assemblage is smectite-feldspar-zeolite-silica. The smectite is of the dioctahedral montmorillonite type, the feldspar is plagioclase and the zeolite is of the clinoptilolite or heulandite species. Between the silica polymorphs, cristobalite is more prevalent than quartz in most of the assemblages. One sample is detected to contain almost entirely of crystalline calcite with smectite which authenticate the presence of calcareous horizon or several horizons intercalated with the tuff and mud beds. The minerals and mineral assemblages formation is strongly implicit of halmyrolysis in continuum with early diagenesis in a closed system submarine environ and envisaged to have been induced favorably by calcic-silicic-alkalic, moderate pH, and low-temperature-pressure conditions of shallow burial sedimentation.

Keywords : Smectite, feldspar, zeolite, silica, calcite, diagenesis, Paghumayan Formation

Introduction

Negros Island is one of the main islands in the Visayas, Philippines (Figure 1). It is divided into 2 provinces: Negros Oriental and Negros Occidental. The former is the focus in this study. Dumaguete City, the capital, is about one hour flight from Manila.

The Municipality of Vallehermoso is located in the northeastermost section of Negros Oriental. It lies approximately within geographic framework of 10°22'00" to 10°16'30" N latitude and 123°15'00" to 123°20'00" E longitude. It is about 145 km north of Dumaguete City and may be reached by land travel through the all-weather coastal road via commercial buses plying the Dumaguete City to Bacolod City route.

Topography of Vallehermoso is characterized generally by steep slopes and deep valleys with peak elevation reaching 378 m above sea level. However, in the particular study area, landscape is undulating, rolling and hilly, and relief elevation is in the 20 to 100 meters range. The study area is incised and drained by the major Kabulihan River that follows a dendritic drainage pattern and fed by swarms of micro-dendritic tributaries from its upper reaches.

The study area, as shown in Figure 1, is underlain by the Paghumayan Formation in Barangay Kabulihan,

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Vallehermoso. This rock formation, Middle Miocene in age, is composed of the lower Fuentes Green Tuff and the upper Paghumayan Clastics (BMG, 1981). Only the Green Tuff is covered in this clay study. This Fuentes Green Tuff is composed of massive volcanic tuff breccia with thin tuffaceous shale and arenaceous limestone (BMG, 1981).

The Paghumayan Formation was described by Melendres and Barnes (1957), Caguiat (1967) and Yap (1972) in their surveys concerning geology and oil possibilities in Negros island. There were no subsequent major studies ever since. This rock sequence is still vague and in so far as mineralogical information is concerned, there is not any or plenty.

The main objectives of this study were to investigate the mineralogy of tuffs and mudrocks of the Fuentes Green Tuff member and to propose interpretations of its sedimentary petrogenesis based on the minerals and mineral assemblages.

EXPERIMENTAL MATERIALS AND METHODS

The location and geology of the study area and the distribution of sampling stations are shown in Figure 1. The network of samples obtained seems to project geographic orientation rather than stratigraphic one. Samples were collected primarily from gently dipping outcrops of sedimentary rock sequences comprised chiefly of tuffaceous and argillaceous strata. Several tuff beds are green-colored and hence the "Green Tuff" appellation, while others are in tones of brown. A total of 12 samples were analyzed.

Bulk sample analysis for x-ray diffraction simply used few grams of the raw materials of each sample, homogenized by manual dry grinding using agate mortar and pestle and subsequently mounted on 2.7cm x 4.7cm glass slides.

The $<2\,\mu$m size fraction of the clastic samples were used for the various experiments. The generally prescribed methods of dispersion, sedimentation and centrifugation were adopted in the segregation of the fine clay size fraction from the whole rock. X-ray diffraction (XRD) analyses of oriented $<2\,\mu$m size fraction samples mounted on glass slides by "natural setting method" were carried out using RINT 2000 x-ray diffractometer with a graphite monochrometer (CuKα radiation) and operational setting of 30 kV and 14 mA. Differential thermal-thermogravimetric (DTA-TGA) analyses were made using Rigaku Thermo Plus TG 8120 DTA-TGA equipment. Scanning electron microscopy (SEM) studies used Hitachi S-4000 FESEM. The specimens were coated with carbon using JEOL JEC-520 Carbon Coater. The same Hitachi S-4000 FESEM equipped with LINKS ISIS EDX operated at an accelerating voltage of 15 kV was utilized in conducting the energy dispersive x-ray (EDX).
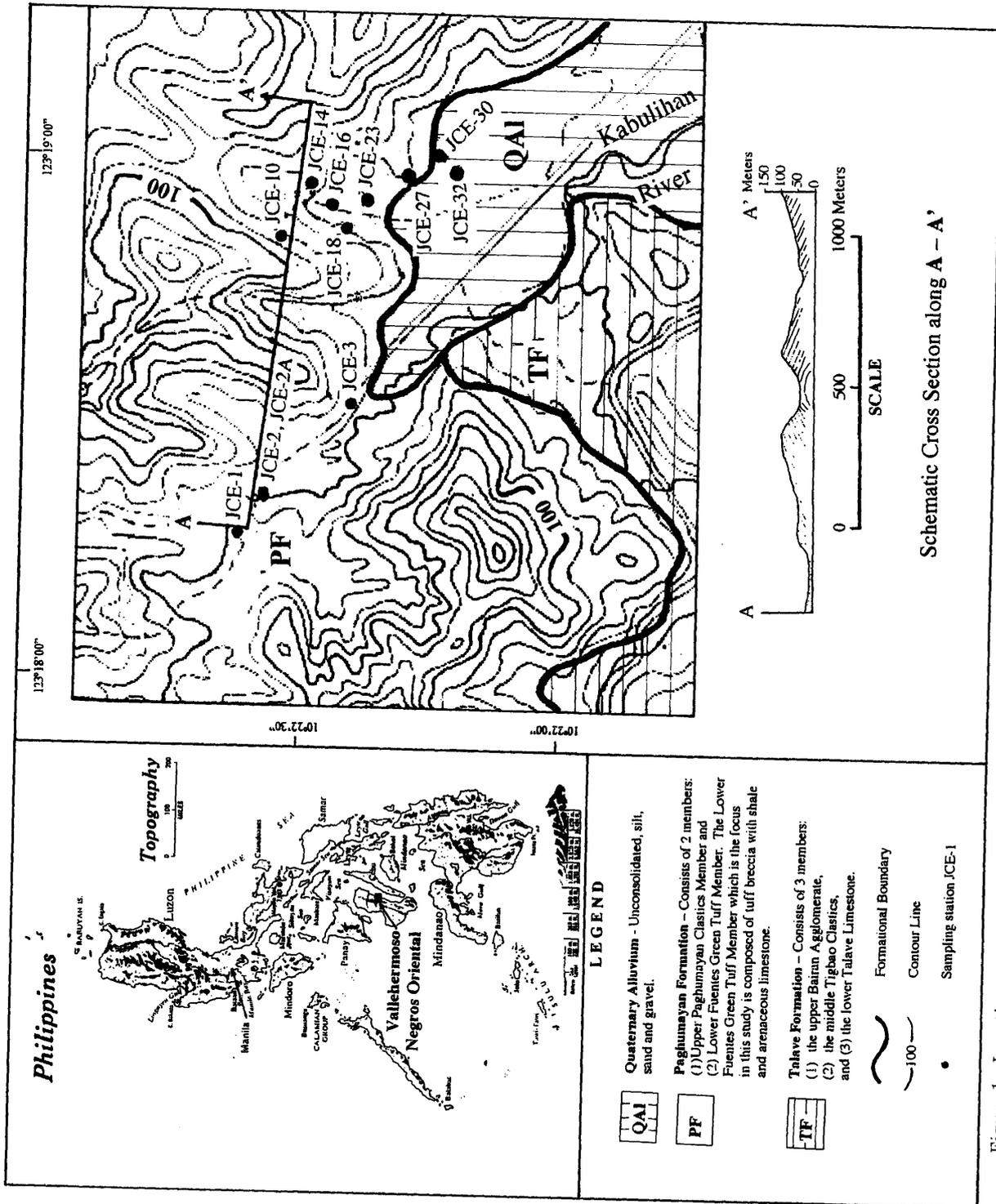
Figure 1. Location and geological maps of the study area showing the sampling network and cross-section along A-A'. Vallehermoso, Negros Oriental, Philippines.

RESULTS

X-ray Diffraction (XRD)

Bulk fraction generally shows profusion of sharp slender peaks that correspond to feldspar (3.18 Å), zeolite (8.96 Å), cristobalite (4.04 Å) and quartz (3.34 Å), and moderately broad unimodal peak that corresponds to smectite (15.5 Å) clay (Figures 2 & 3). Only sample JCE-30 shows high intensity peaks that relate almost entirely to calcite (3.03 Å). The strongest peak reflection indicated in each mineral has semblance to the ones given by

Wilson (1987), which hints on the chemical composition of the mineral.

The oriented <2 μm size fraction exhibits lower intensity and weaker sharpness of peaks of the non-sheeted minerals but better resolution and greater enhancement of peak of the layered expandable mineral smectite (Figures 2 & 3). The feldspar, however, still shows good reflections. The ~15Å peak of smectite in sample JCE-30 becomes clearer in the fine fraction.

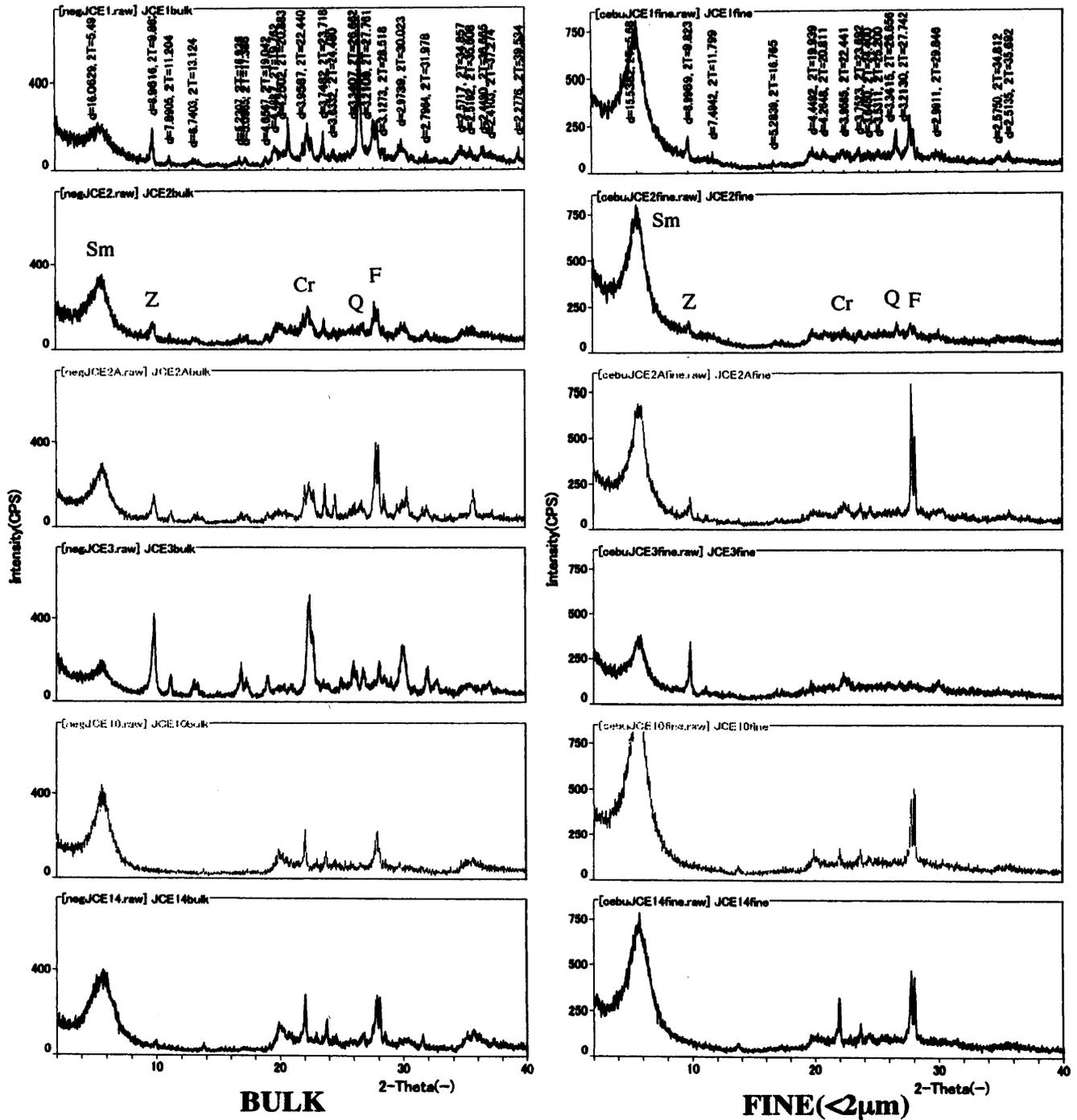

Figure 2.   X-ray diffractograms of bulk and fine (<2μm) samples marked JCE-1,-2, -2A, -3, -10 and -14. Sm=smectite, F=feldspar, Z=zeolite, Cr=cristobalite, Q=quartz.
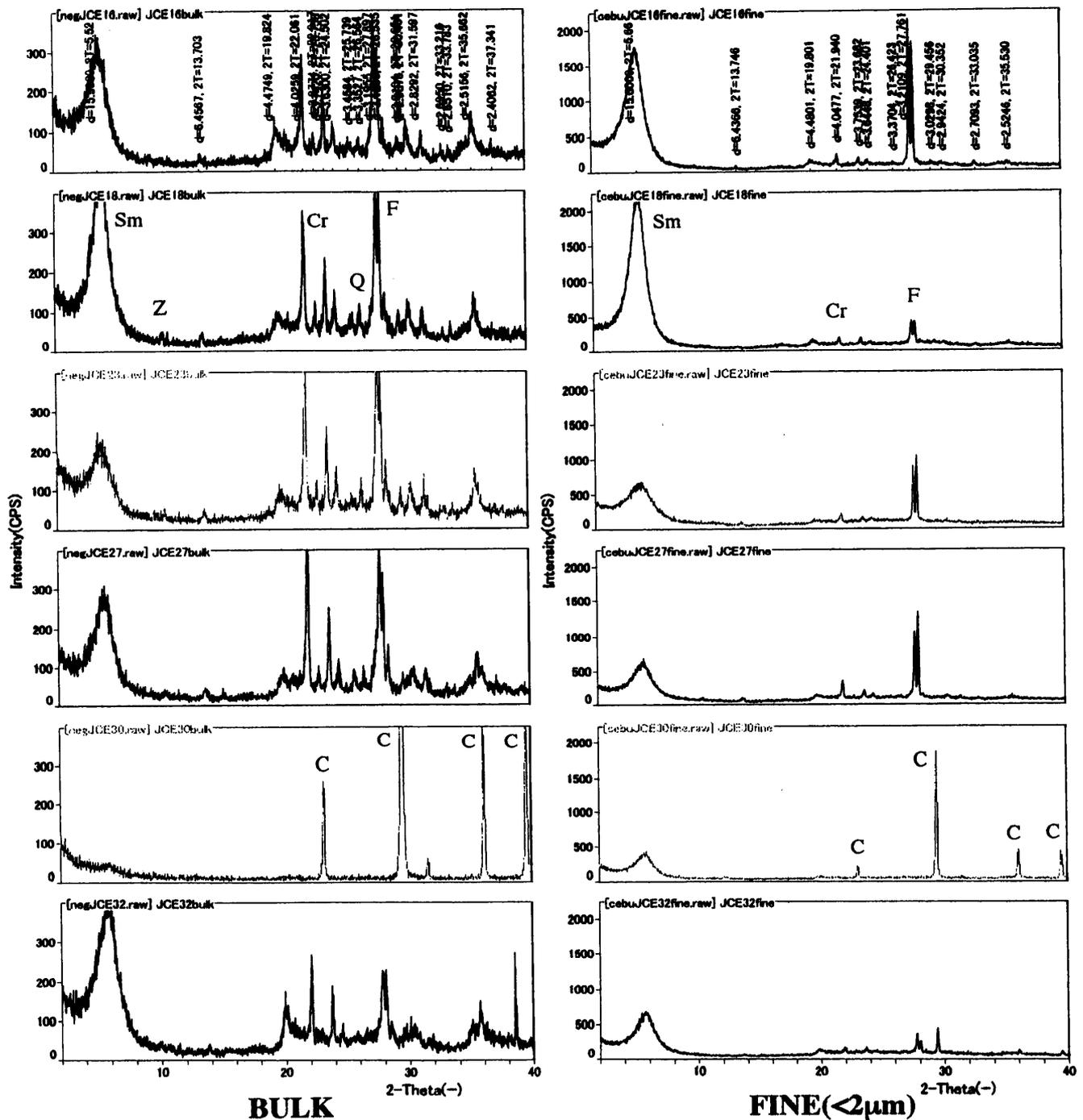
Figure 3.   X-ray diffractograms of bulk and fine (<2 μm) samples marked JCE-16, -18, -23, -27, -30 and -32.
Sm=smectite, F=feldspar, Z=zeolite, Cr=cristobalite, Q=quartz, C=calcite.

The smectite displays normal behavior of peak shift to ~17.2 Å on ethylene glycolation. Peaks of other non-clay minerals remain unchanged (Figures 4, 5, 6 & 7).

The smectite is fragile as shown by structure collapse upon 6N HCl acid treatment. Calcite readily dissolved too (Figures 6 & 7). The other non-phyllosilicates show stability and their peaks even improved.

Heat treatment shown in Figures 4, 5, 6 & 7 shows the usual contraction-expansion related to dehydration-rehydration of the smectite up to 500℃ and the permanent collapse of the structure due to dehydration and

Figure 4.   X-ray diffractograms of JCE-3. Left column, top to bottom: parallel oriented untreated <2 μm size fraction; EG treated; and HCl acid treated. Right column, top to bottom: X-ray behavior of heat treated sample at 300℃, 300℃ + H₂O, 300℃ + EG; 500℃, 500℃ + H₂O, 500℃ + EG; 700℃, 700℃ + H₂O, 700℃ + EG.
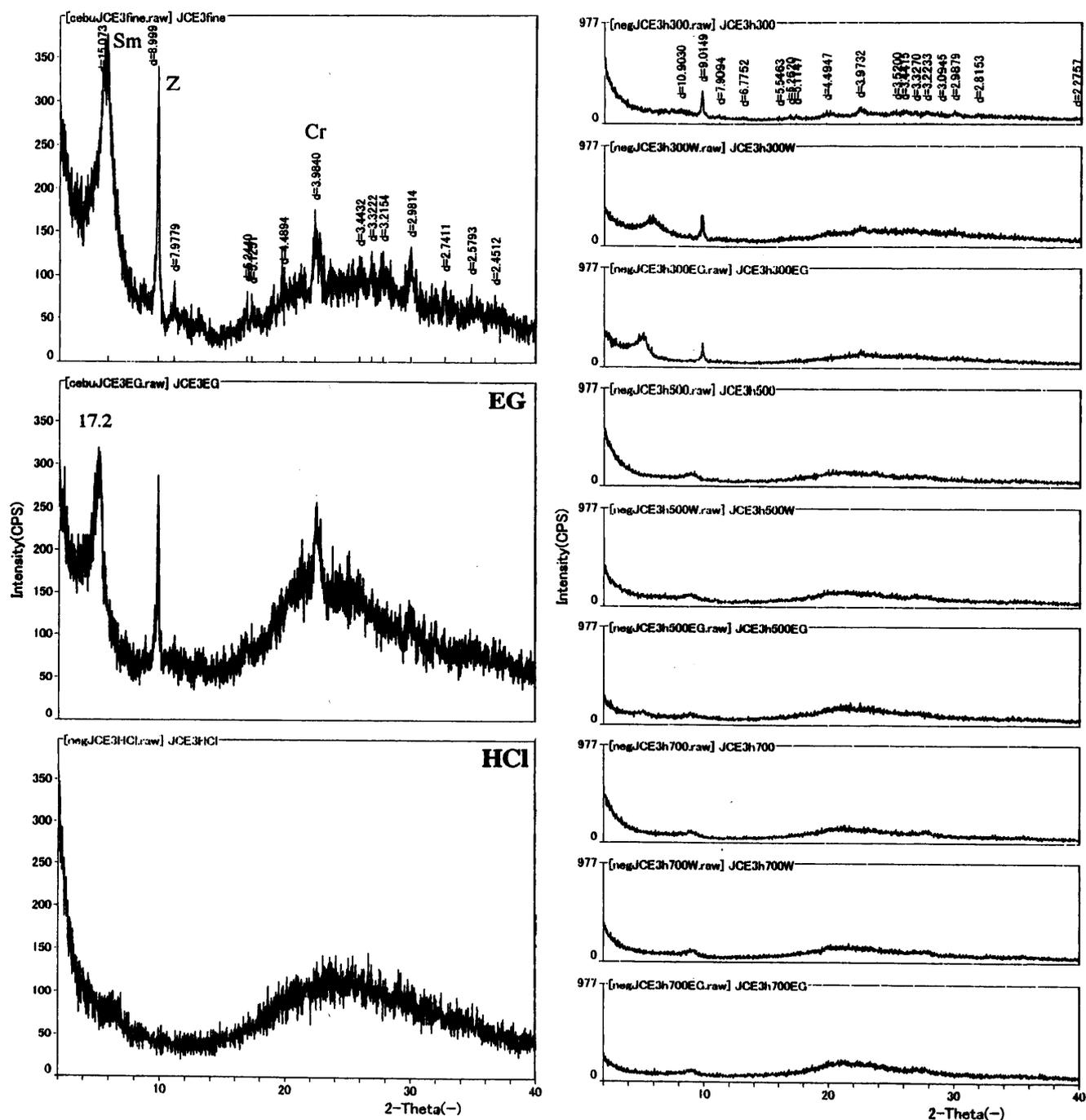
Figure 5.   X-ray diffractograms of JCE-14. Left column, top to bottom: parallel oriented untreated <2 μm size fraction; EG treated; and HCl acid treated. Right column, top to bottom: X-ray behavior of heat treated sample at 300℃, 300℃ + H₂O, 300℃ + EG; 500℃, 500℃ + H₂O, 500℃ + EG; 700℃, 700℃ + H₂O, 700℃ + EG.

dehydroxylation at 700°C. The calcite resists up to 500°C and eventually destabilized at 700°C with accompanying peak migration due to calcination (Figures 6 & 7) and another peak shift upon H_2O treatment due to conversion into hydrated lime phase. It reverts to original calcite structure upon EG treatment. Other minerals in the assemblage still persist until 700°C with seemingly the same steadiness.
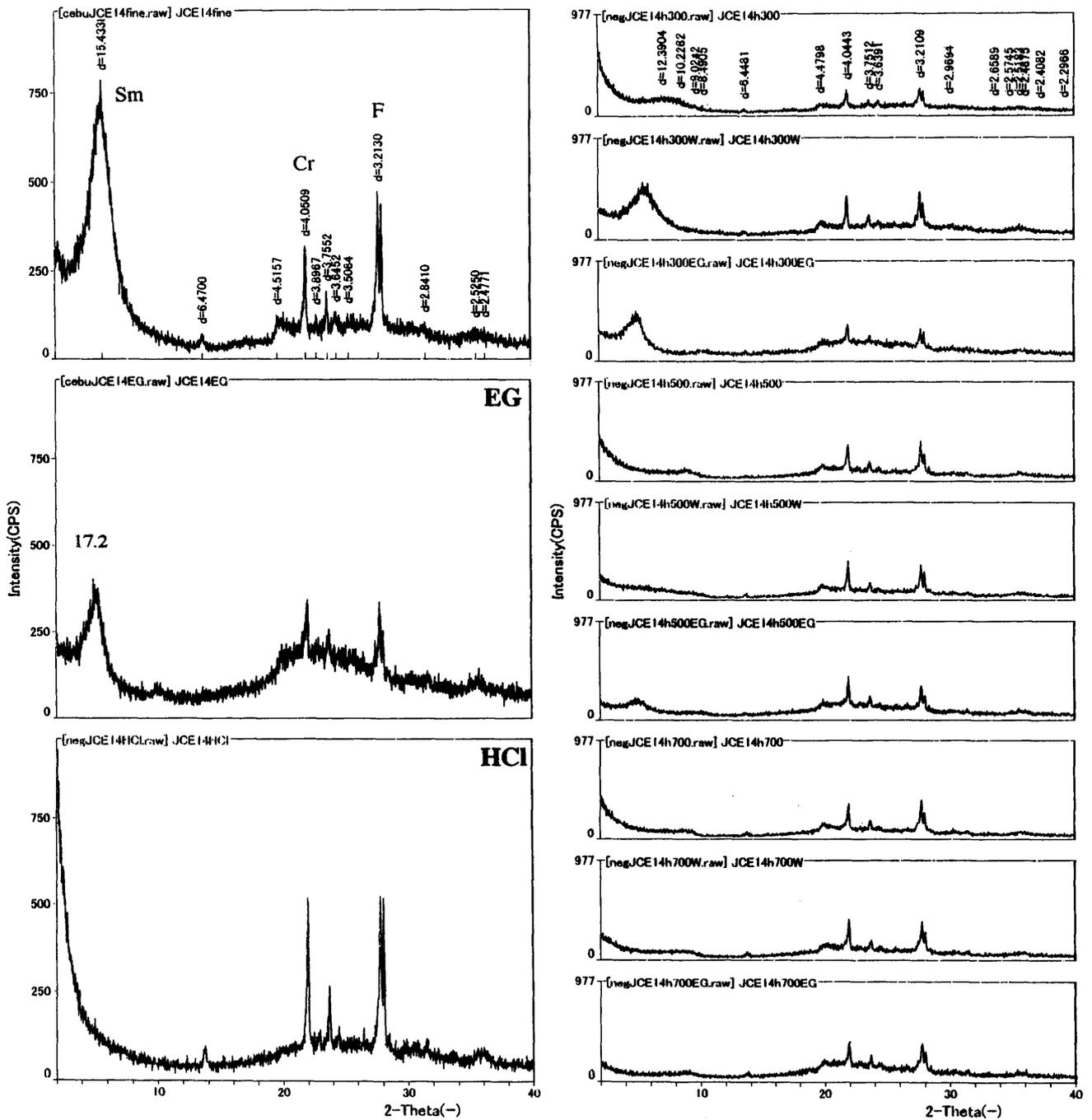

Figure 6.   X-ray diffractograms of JCE-30. Left column, top to bottom: parallel oriented untreated <2 μm size fraction; EG treated; and HCl acid treated. Right column, top to bottom: X-ray behavior of heat treated sample at 300°C, 300°C + H_2O, 300°C + EG; 500°C, 500°C + H_2O, 500°C + EG; 700°C, 700°C + H_2O, 700°C + EG.
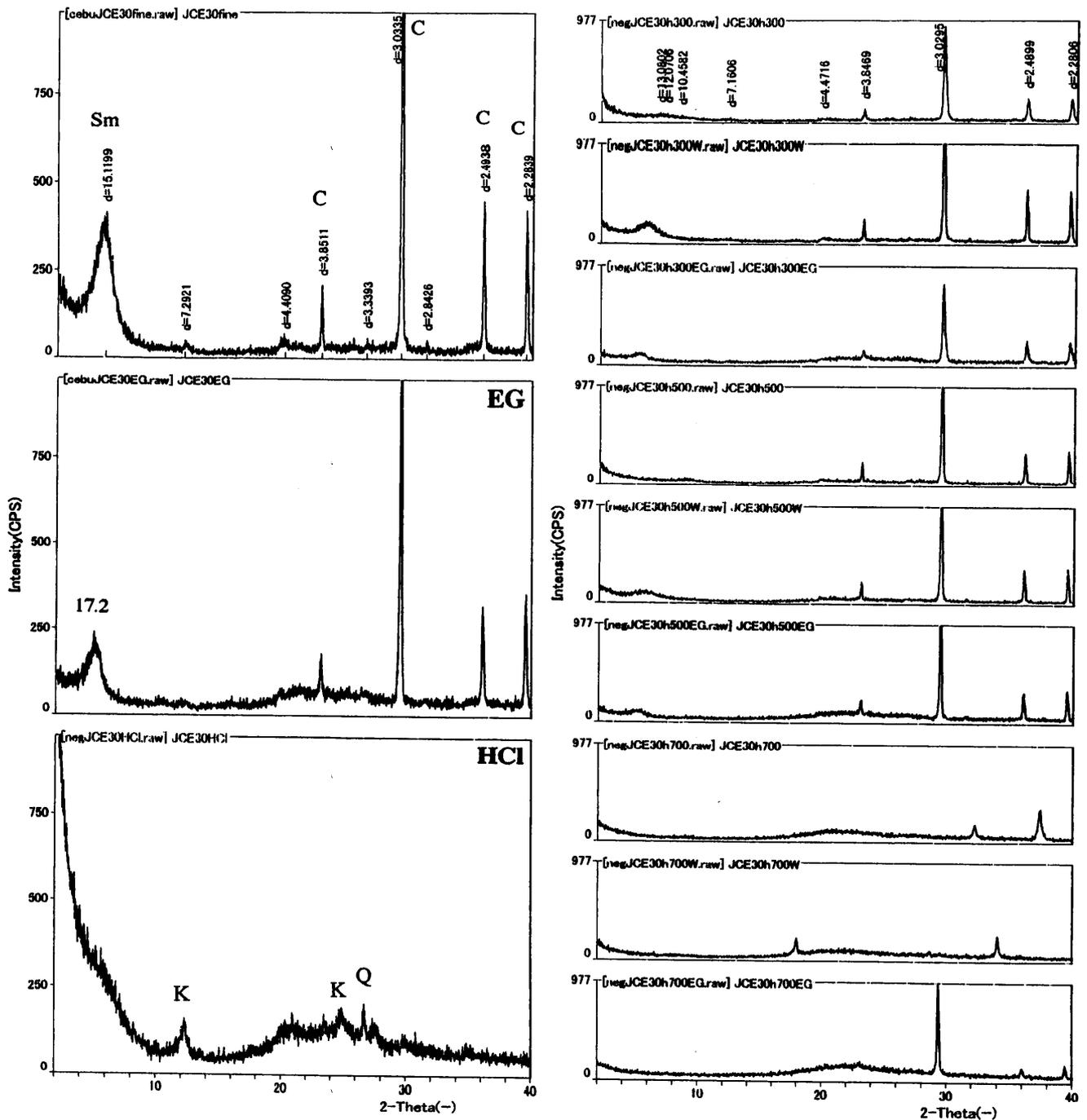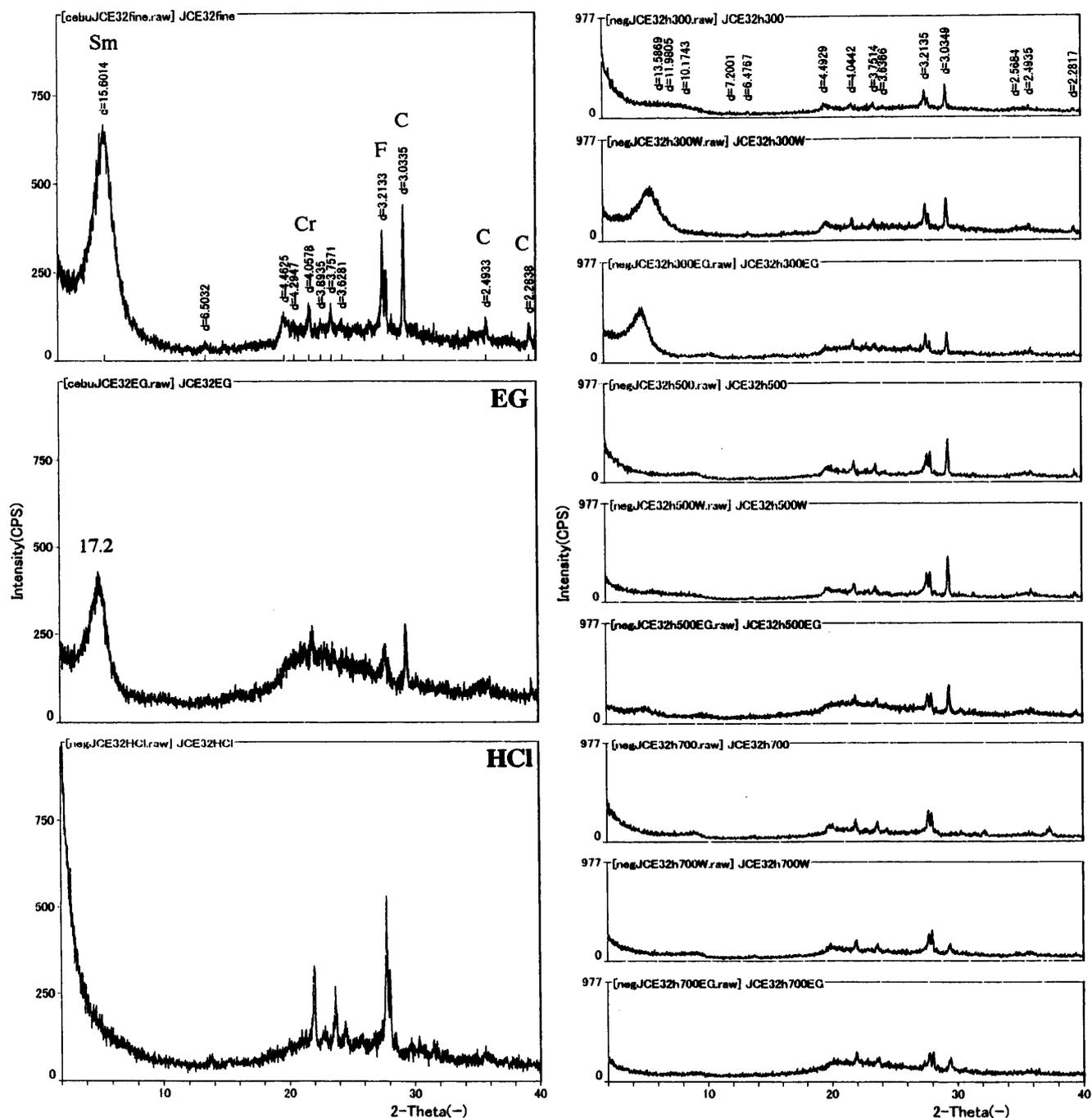
Figure 7.   X-ray diffractograms of JCE-32. Left column, top to bottom: parallel oriented untreated <2μm size fraction; EG treated; and HCl acid treated. Right column, top to bottom: X-ray behavior of heat treated sample at 300℃, 300℃＋H₂O, 300℃＋EG; 500℃, 500℃＋H₂O, 500℃＋EG; 700℃, 700℃＋H₂O, 700℃＋EG.

Differential Thermal Analysis (DTA)

The DTA graphs are shown in Figure 8.   Generally, the thermal behavior exhibits broad and deep endotherms below 200℃ and another shallow endotherms near 500℃.   The lower temperature endotherms, usually accompanied with mild shoulder at 150℃-160℃, correspond to dehydration or loss of sorbed water molecules from the minerals especially from smectite.   The higher endotherms correspond to dehydroxylation or loss of OH radical particularly from smectite.   The endotherm/exotherm reactions near 850C℃-900℃ are not distinct.   Most of the endothermic
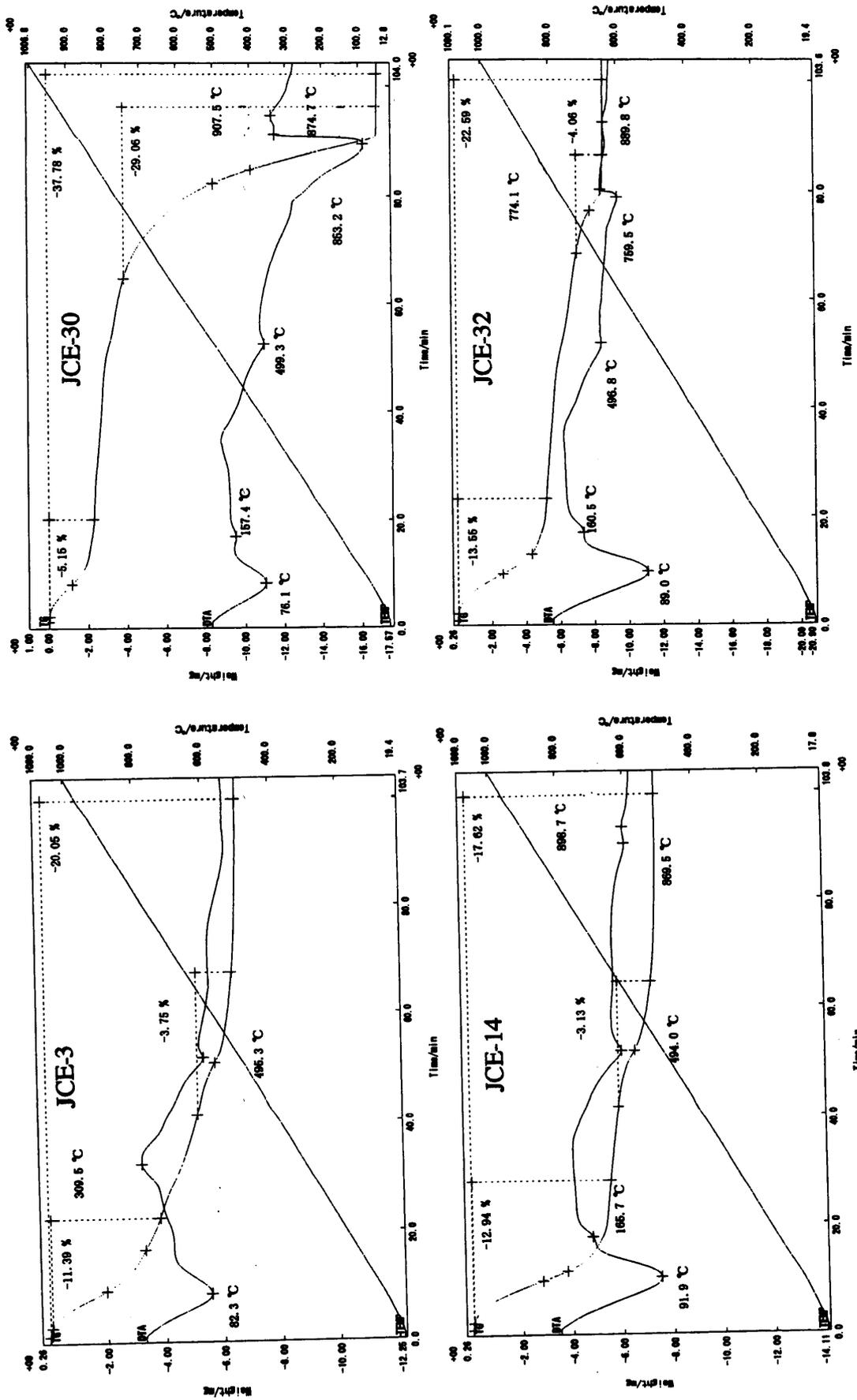
Figure 8. Examples of the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) derived from JCE-3, JCE-14, JCE-30 and JCE-32 of the Paghumayan samples.

and exothermic reactions may be ascribed to smectite clay since the other associated non-sheet silicates do not show these behaviors to this type of treatment due to their relative thermal stability. Very prominent endothermic reaction near the range 760℃ − 853℃ relates to calcination of the calcite crystallites especially contained in JCE-30 and lesser intensity in JCE-32.

Thermogravimetric Analysis (TGA)

The TGA graphs are shown in Figure 8. Weight decrease is illustrated with 2 slopes that jibe with the endotherms. The first slope is generally steep, relating to abrupt weight loss usually in the range of 9% to 16% transpiring at ambient temperature to about 200℃. This is primarily sympathetic to dehydration. The second slope is gentle to moderate, relating to gradual weight decrease in the range of 2% to 5% occurring at 400℃ to 600 ℃. This is essentially cognate to dehydroxylation. These features are reversed for sample JCE-30 which contains predominantly calcite with smectite. In this case, the weight loss is about 5% in the first reaction and about 29% in the second reaction and typified by gentle slope and steep dip respectively. The 5% is harmonious to dehydration particularly of smectite while the 29% to CO_2 expulsion from the calcite. Weight loss minima-maxima of the samples is in the range of 13% (JCE-27) to 38% (JCE-30).

Scanning Electron Microscopy (SEM)

Figure 9 shows the morphology of the samples JCE-3, JCE-14, JCE-30 and JCE-32. The mineral assemblages generally show porous aggregates of poorly developed crystals. Figure 9A illustrates the conversion reaction of volcanic glass fragments into smectitic clay from JCE-3. Figure 9B exhibits broken crystal of zeolite surrounded by irregular flaky masses of smectite from sample JCE-3. Sample JCE-14 in Figure 9C also shows the glass to clay conversion. The reaction appears taking place more rapidly and profoundly along the edges of the shards than at the faces. Figure 9D shows smectite with the usual irregular flaky outline. The flakes seem rather thick with less curling of the edges. The calcite-rich assemblage of JCE-30 in Figure 9 E and F shows incoherent aggregation of varied dimensions of laths and blocks of calcite richly coated with smectite. Sample JCE-32 in Figure 9 (G and H) exhibits fluffy to flaky masses of smectite with associated crystals.
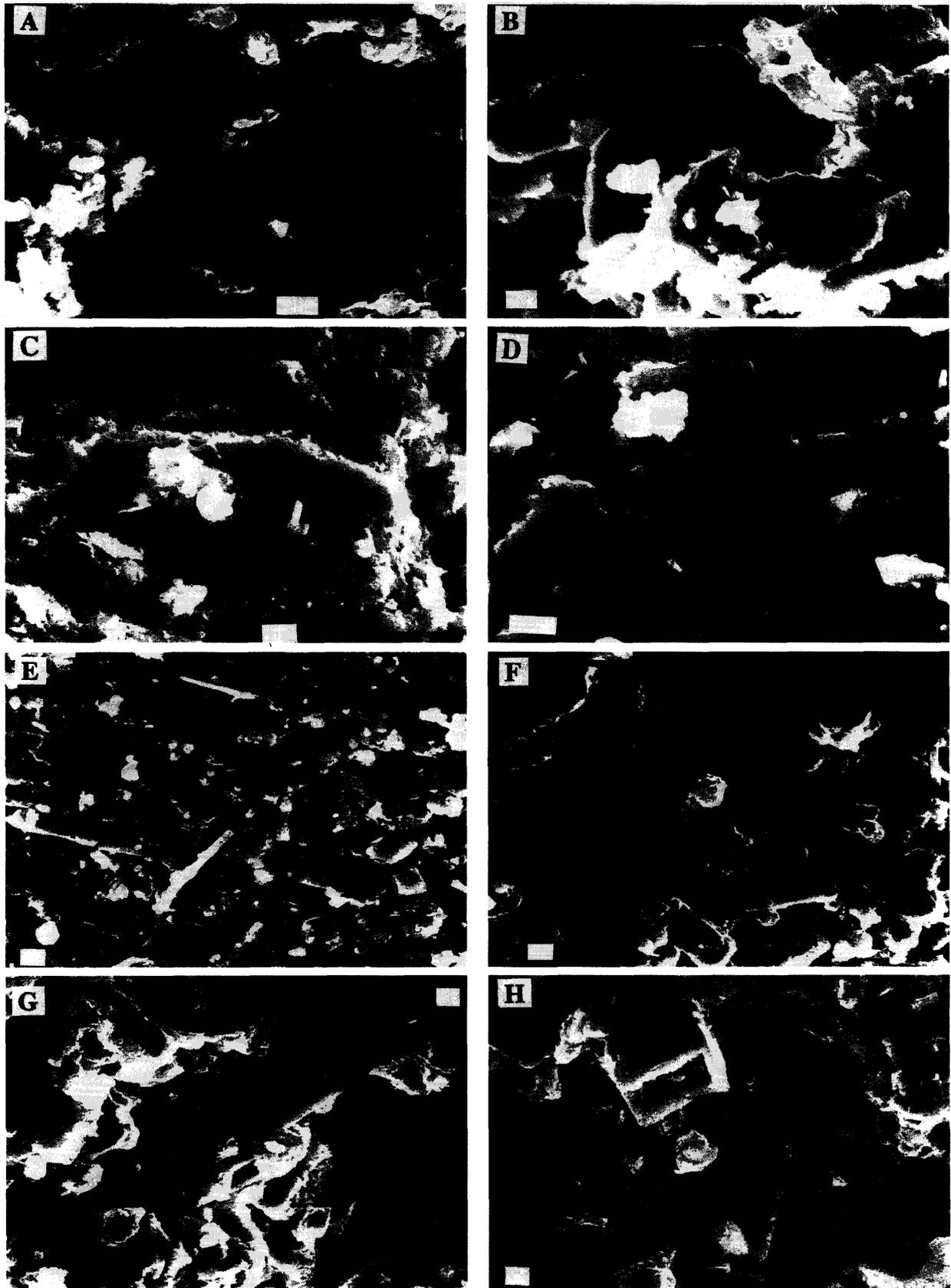
Figure 9.   Examples of scanning electron microscopy (SEM) derived from JCE-3 (A&B), JCE-14 (C&D), JCE-30 (E&F) and JCE-32 (G&H) of the Paghumayan samples. Bar scale=2 μm.

Energy Dispersive X-ray (EDX)

The semi-quantitative chemical analyses of the samples using EDX are shown in Table 1. The samples are generally SiO_2-rich and moderate in Al_2O_3 except JCE-30. SiO_2 range is highest in JCE-3 while Al_2O_3 range is highest in JCE-14. TiO_2 content is low and sometimes not detected. FeO is appreciably high for most samples except JCE-30. JCE-32 shows highest range reaching about 11 to 16% FeO. MgO is insignificant except in JCE-32 where it posted 12.80% which seems to be spurious. CaO is present in all the samples. It is highest in JCE-30 where it ranges 76 to 91%. Na_2O goes almost undetected for all the samples. K_2O is usually present in all the samples and is highest in range in the calcite-rich sample of JCE-30.

DISCUSSIONS

Green tuff and associated mudrocks in various sedimentary rock formations across the globe were investigated by many researches. In Japan, the conventionally known Green Tuff occurs as thick beds in strata of the Miocene epoch (Sudo and Shimoda, 1978). This Green Tuff has been geologically, stratigraphically, petrologically and mineralogically studied extensively by many workers such as Sudo and Ota (1952), Kohyama, Shimoda and Sudo

Table 1   Approximate chemical compositions of Paghumayan samples JCE-3, JCE-14, JCE-30 and JCE-32 based on EDX analyses. * = <2 Sigma. ND=not detected.

Comp. %	Sample Nos.			
	JCE- 3	JCE-14	JCE-30	JCE-32
SiO_2	70.79	67.85	1.33	51.91
	71.67	68.01	6.85	59.38
	74.99	64.89	10.38	54.71
TiO_2	2.23	ND	0.92*	ND
	2.23	ND	0.07*	ND
	ND	3.95	0.31*	1.84
Al_2O_3	11.32	21.30	0.12*	13.11
	13.86	20.24	2.15	13.05
	11.66	15.16	3.53	3.68
FeO	8.51	5.40	0.76*	11.15
	7.07	7.17	2.57*	16.80
	7.78	10.71	4.67	14.07
MgO	ND	ND	ND	ND
	ND	1.75	ND	ND
	ND	ND	ND	12.80
CaO	3.01	3.19	91.16	21.04
	3.15	2.60	83.30	8.82
	3.44	4.08	76.78	11.77
Na_2O	ND	1.34	ND	ND
	ND	ND	ND	ND
	ND	ND	ND	ND
K_2O	4.15	0.92	5.71	2.79
	2.02	0.24*	5.05	1.95
	2.13	1.21	4.33	1.13

(1973), Yoshimura (1964), Iijima (1971) and Kimbara (1973) among others. Their studies suggest the very complex nature of the tuff and the mineral assemblages and origin are too varied.

In contrast, the clay mineralogy of tuff and mudrocks of the Paghumayan sedimentary rocks in the study area appears to be relatively uniform or homogeneous. Minerals consist principally of phyllosilicate montmorillonitic smectite, with poor amount of kaolinite and non-phyllosilicates feldspar, zeolite, silica polymorphs of cristobalite and quartz, and calcite. Similar mineral assemblages are displayed in both bulk and fine fractions despite the variation in ratios of each component. However, the non-phyllosilicates appear greater in the bulk than in the fine suggesting that the minerals occur generally as coarse particles and dwindle with decreasing particle size. The feldspar is essentially ubiquitous mineral and seems to exist in almost equal amounts in both the coarse and fine fractions. It may be plagioclase in composition based on the x-ray peak position of $3.18 Å$. The zeolite may be the clinoptilolite or heulandite species as indicated by the x-ray peak reflection at $8.96 Å$. The silica polymorphs of cristobalite ($4.04 Å$) and quartz ($3.34 Å$) may either exist together or not in certain assemblages and one polymorph may be observed to be more dominant than the other. Cristobalite, however seems to be more ruling. Calcite is very sporadic in the assemblages and its appearance is discerned only in 2 samples (JCE-30 and JCE-32). Smectite-feldspar-zeolite-silica assemblage generally reigns the mineral constitution of the sedimentary rock formation. Smectite- calcite assemblage is only shown in one sample and this may correlate well with the arenaceous limestone.

Halmyrolysis generates marine zeolite and authigenesis of clay minerals (Larsen and Chilingar, 1983) and the coexistence of these minerals are common (Velde, 1985). These silicates correspond to alkaline conditions (Chamley, 1989). Particles arrive wind-borne as fall-out (pyroclastic ash) from volcanic eruptions, and chemical reaction with seawater begins immediately after the sediment reaches the ocean, and continues while it moved over the bottom or is swept along by currents as it settles from suspension (Larsen and Chilingar, 1983). The devitrification and hydration of the volcanic glass would likely be the primal and significant chemical reactions (Chamley, 1989, Larsen and Chilingar 1983, Velde, 1985). The rate of glass dissolution increases with both salinity and alkalinity (Hay, 1966). Silica and alkali activities in solution, pH, temperature and time are of great importance to determine the type of mineral formation (Tomita and Kawano, 1992; Tomita and Kawano, 1993; Tomita et al., 1997; Iijima, 1975; Read and Eisbacher, 1974; Sheppard and Gude, 1971; Honda and Muffler, 1970). The basaltic to andesitic green tuff and mudrocks of the Paghumayan Formation may be inferred to have undergone these styles of deposition and alteration processes.

The alteration involved seems to bear semblance to the bentonite formation in Balamban (Aleta et al. 2000) which follows the mechanism trend of Hay (1963), Karlson (1979), Surdam and Hall (1984) and Wensaas et al. (1989). It is very evident from the SEM microphotographs (Figure 9 A and C) that vitric shards are the precursor materials in the clay formation.

The division of the zeolite facies assemblages is made in three groups: low, medium, and high temperature and pressure for "closed" systems where mass of the elements K, Na, Al and Si determines the presence of the different phases for a given P-T range (Velde, 1985). With reference to this, the smectite-feldspar-zeolite-silica is exactly one of the 5 facies distinguished in the low P-T group. The other 4 assemblages of this group cited by Velde (1985) are:

1- natrolite — analcime — zeolite - kaolinite
2- natrolite — analcime — zeolite - illite, smectite (solid solution interlayered with illite)
3- analcime — kaolinite - illite, smectite s.s. — zeolite
4- analcime — smectite — zeolite — silica

Minerals and assemblages in the medium P-T and high P-T groups will not be discussed.

Low temperatures give maximum solid solutions where all of the so-called "diagenetic" zeolites are stable.

This forms the initial zeolite paragenesis (Velde, 1985). An 80℃ temperature limit is placed on the initial alkali zeolite paragenesis where solid solution is maximum (Velde, 1985). Iijima (1970) reports an observed upper thermal limit of the alkali zeolites to be near 90℃ at about 1 Kbar lithostatic pressure. Boles (1971) give a 100 ℃ value at 2-3 Kbars based on his experiments. The minerals and assemblages of Paghumayan may correlate within these regimes with consideration to the assumptions that sedimentation of the tuffs and mudrocks was normal type and without influence of heat caused by igneous intrusion, unlike some of the green tuffs in Japan.

Kawano and Tomita (1997) conducted synthesis study of zeolites entailing the interactions of obsidian and NaOH and KOH solutions at 150℃ and 200℃. They obtained almost similar mineral assemblage with the current one but the mineral species are not the same. Phillipsite type was shown to be the dominant zeolite product they obtained compared to clinoptilolite or heulandite in this study. The former type is more alkaline than the other two.

CONCLUSIONS

The sheeted clay mineral of green tuff and mudrocks of the Paghumayan Formation is almost monomineralic, consisting dominantly of dioctahedral smectite. Kaolinite exists sporadically in trivial amount. The smectite clay always coexists and forms some assemblages with non-sheeted clay minerals consisting predominantly of feldspar, zeolite, cristobalite, quartz and calcite. Each mineral component varies in amounts and proportions in the assemblages of both bulk and fine fractions and from one sample to another. Frequently, 1 or 2 components may be observed lacking in an assemblage. The smectite-feldspar-zeolite-cristobalite appears to be the dominating association, and smectite and feldspar are always diagnostic and persistent. Smectite-calcite association appears only in one sample and affirms the intercalation of calcareous horizon or horizons in the predominantly tuffaceous column.

Halmyrolysis and diagenesis in early stage seem to be the central engines in the mineral accumulation and formation. The minerals and mineral assemblages reflect independence from extreme thermodynamic influence and depict "closed" system in marine depositional environment. Apparently, no minerals or mineral assemblages were identified that give indications or trends that tell advanced stage and deeper burial diagenetic alteration.

This study correlates well with the generality of published data that strongly point to these kind of mineral assemblages to be typical and have significantly numerous occurrences worldwide.

It is instructive to note that this research covers only small-scale area of the Paghumayan Formation. It may not be known at this point whether the minerals and mineral assemblages will show lateral and stratigraphic similarity or diversity in other locations with the same lithology if regional dimension is put into consideration. This argument will only be elucidated by further studies.

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