Geology, Mineralogy and Paragenesis of the Bentonite Deposit in Balamban, Cebu Province, Philippines

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Abstract

The bentonite deposit occurs as concordant, lenticular or podiform beds interstratified within the Middle Miocene Toledo Formation, in Balamban, Cebu Province, Philippines. Multiple analytical techniques reveal that the clay constitution of the bentonite is principally smectite minerals. Mixed-layer kaolinite/smectite is also indicative in some specimens. X-ray diffractograms of untreated $<2\mu$ m fraction oriented samples show that the basal dimension reflections are generally distinct at 16Å to 16.3Å. Ethylene glycol solvation promotes significant expansion of the basal distance to about 17.6Å to 18Å. Dehydration and rehydration capacities are attributes of the clays possessed at low temperature ranges but structure collapse and subsequent formation of new mineral phase are determinant characteristics observed at high temperature regimes. Scanning electron micrographs generally exhibit irregular smectite flakes resembling broken "potato chips". Kaolin, mica, and zeolite (probably clinoptilolite) are also found to be associated in minor amounts. The surfaces are uniformly rough and appear to be veneered by micro-scale dessication cracks. The non-phyllosilicates assemblage is dominantly of crystalline quartz, feldspar and calcite. Alteration process appears to be syngenetic and seems to be incident in a marine environment.

Introduction

The exploration of bentonite prospect in Barangay La Mesa, Balamban, Cebu Province, was pioneered by Momongan (1986) in line with the BMG Region 7 Project on canvassing and ore reserve evaluation of bentonite deposits of Cebu Island. His work established initial information on the general descriptions and ore reserves of the bentonite prospect.

Follow-up survey was also conducted by Aleta and Diegor (1995) in connection with bentonite reassessment in central Cebu.

This paper is tailored to offer a review and a general perspective of the bentonite deposit. The focus is on geology, mineralogy and paragenesis of the bentonite. Newly acquired data on x-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) will be partially presented. A more elaborate mineralogical analysis data and interpretations will be made in a separate paper.

Location and Access

The study area is located in Barangay La Mesa, about 9 aerial km or 11 road km east of Balamban township. It is bordered by geographic coordinates 10° 30′ 30″ to 10° 31′ 10″ North latitude and 123° 46 ′ 30″ to 123° 48′ 00″ East Longitude and encompasses roughly 3 square kilometers.

Major access to the area is available through a

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circuitous barangay road that splays into smaller feeder roads, consequently providing service to the other barangays or sitios in the hinterlands. Travel time takes about 1 hour by public utility vehicles plying from the town center to Barangay La Mesa. Road condition is relatively poor, particularly during wet seasons and one could expect rough travel through dirt- and gravel-surfaced roads.

Balamban Municipality is approximately 60 road kilometers northwest of Cebu City, the island Province's capital.

Topography

The study area, which is chiefly underlain by Toledo Formation, is generally undulating to rolling and has moderate relief. Some portions are hilly, with conspicuous isolated apices and linear ridges. Flatter grounds are converted to arable lands. Slope gradient probably varies from 5% to 15%. Within the immediate confines, peak elevations are about 300 to 360 meters above sea level. Towards the east, the topography gradually becomes rough and rugged. Valleys are more deeply incised and ridge slopes are steeper. The mountainous areas are generally underlain by volcanics and other older sediments and metamorphics. Towards the west, however, the terrain becomes gentler. Limestone areas do not demonstrate peculiar karstic features. Still farther west, the lowlands, basically underlain by alluvium, are defined by wide floodplains and flat landscapes.

GEOLOGY

The bentonite deposit is hosted by the Middle Miocene Toledo Formation. Figure 1 designates the specific locality of the deposit (and sampling stations) and its spatial and temporal relation to other formational units. Generalized descriptions of the rock formations are chiefly lifted and summarized from BMG, 1982.

Lithology and Stratigraphy

Serpentinized Peridotite

Serpentinized ultramafic and mafic rocks occurring as diapiric bodies along principal fault zones. The diapirs intrude younger formations. It can be seen in the northeastern corner of the study area.

Lutopan Diorite

Large elongated masses of diorite and related intrusives are mostly in central Cebu. They occur as stocks and dikes intruding the Cretaceous metasediments and metavolcanics. The diorites and the intruded metasediments and metavolcanics are occasionally cut by quartz veinlets carrying base metal sulfides and iron ore minerals, near the immediate contact. Coarsely crystalline acidic and basic differentiates of the diorite magma, range from dark, coarse grained or pegmatitic gabbros to almost pure plagioclase pegmatites (Santos-Ynigo, 1951).

Mananga Group

The Mananga Group consists of the Cansi Volcanics and Pandan Formation. The Cansi Volcanics is an assemblage of massive lava flows, pillow lavas and breccias. The composition ranges from basalt to basic pyroxene andesite. The Pandan Formation is composed generally of contorted, steeply dipping, metamorphosed limestone, shale, sandstone conglomerate and thin bedded chert.

Luka Formation

Interbedded sandstone and mudstone with conglomerate and limestone lenses. The age is placed as early Middle Miocene.

Uling Limestone

This limestone is generally massive and coralline. The color is typically white although some outcrops show variegated hues from beige to pink. The thickness is about 250 meters at the type locality. The abundance of Austrotrillina howchini (Schlumberger) defines the the age of this formation as early Middle Miocene.

Toledo Formation

The formation consists of fossiliferous conglomeratic limestone at the base and thick, calcareous, tuffaceous and locally bentonitic white shale and sandstone with occasional beds of sandy to conglomeratic limestone and gray brown shale at the
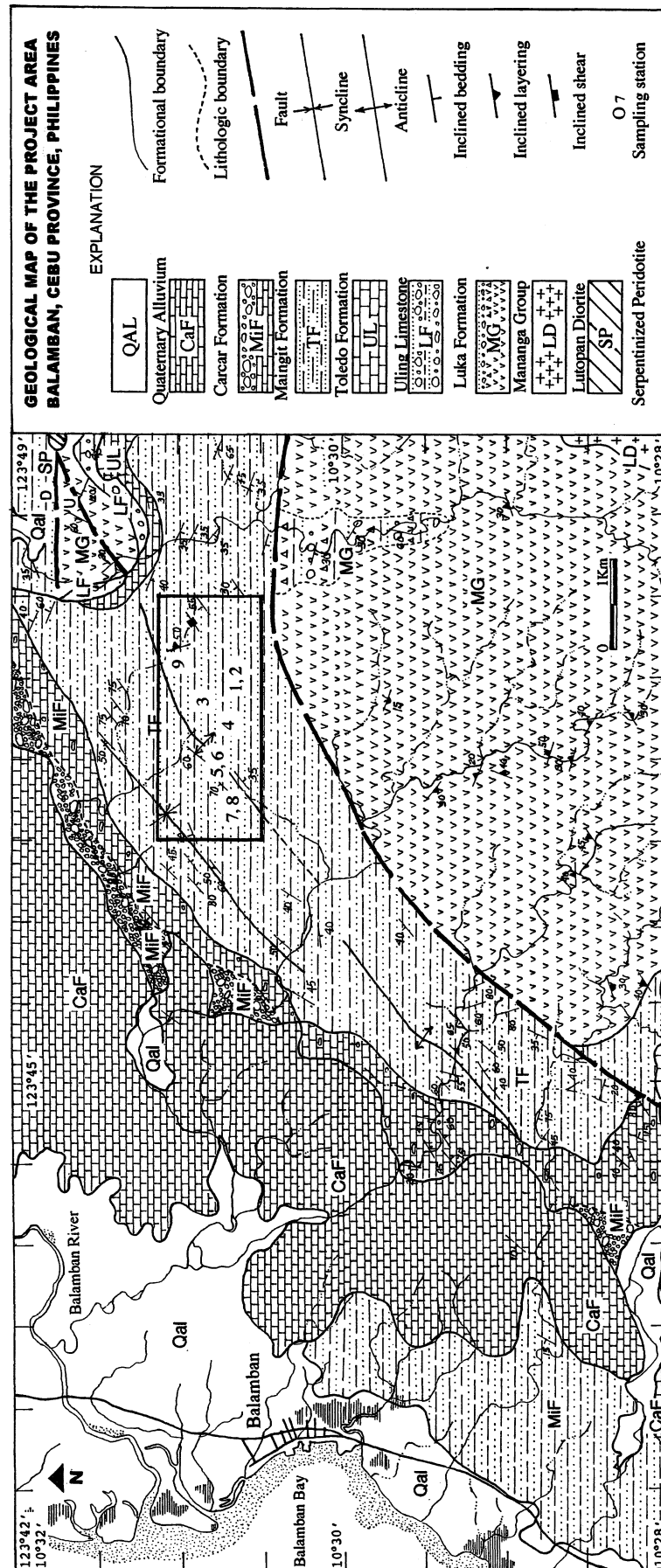
Fig. 1. Geological map of the bentonite area in Balamban, Cebu Province, Philippines. Adopted from the Philippine Bureau of Mines and Geosciences, geological maps of Balamban and Buanoy quadrangles, sheet nos. 3751-1 and 3751-2 respectively. Numerals in the rectangle correspond to sampling stations.

upper section. It appears to have a maximum thickness of about 250 meters. Middle Miocene age was given based on the dominance of planktonic Foraminifera which includes Orbulina universa d'Orgbigny, Globorotalia mayeri Cushman and Ellisor, and Sphaeroidinella seminulina Schwager.

Maingit Formation

The formation is divided into a lower limestone, middle conglomerate and an upper sandstone and shale unit. The basal white limestone occurs in lenticular beds and contains numerous corals and few microfossils. The conglomerate has pebbles of basement rocks and limestone set in a matrix of sands. Coal stringers and occasional thin beds of limestone are interbedded with the shale and sandstone in the upper part. The maximum thickness is about 2800 meters. A late Middle to Late Miocene age was given.

Carcar Formation

This Plio-Pleistocene limestone formation typically covers the coastal areas, hill ridges and low to moderate mountain slopes. The formation exemplifies gentle to moderate dips. Basically this carbonate mass is coralline, porous to massive, poorly bedded to well bedded, and rich in various fossils.

Quaternary Alluvium

Quaternary Alluvium consists of unconsolidated or detrital deposits of fine to coarse sedimentary materials derived from mass wasting of pre-existing rocks. It generally deposits along stream channels, tidal flats, beaches, deltas and marshes.

Structure

Structural features in the project area are generally in a NE-SW orientation. Varied degree and intensity of structural events and deformations are reflected in the fault and fold patterns recognizable in the study area. Fault contact is distinct between the Mananga Group and the Toledo Formation and implies the dislocation or truncation of other clastic strata. Anticline and syncline that trend NW-SE are prominent within the Toledo Formation. The folded strata of most of the sedimentary formations display varied dips from low to moderate to high angles. Strikes generally follow NE-SW direction in the central part of the area, however, some strikes also exhibit NW-SE trend as seen in the northern corner. Inclined layerings are chiefly observed in Mananga Group.

General Description of the Bentonite Deposit

The characterization and description are essentially abridgement from the findings of Momongan (1986) and Aleta & Diegor (1995). The bentonite deposit is generally delineated as seams, concordant with the interstratification of calcareous and tuffaceous shale and sandstone and other argillaceous sediments. The seams oftentimes exhibit pinch and swell characteristic. Several other outcrops depict discontinuous lenses or pods that are vertically and laterally separated. The size of seams basically varies from one outcrop to another. Some measurements conducted suggest that on the average, width ranges from 4-20 meters and length from several meters to roughly 150-200 meters. Smaller beds are about 2-4 meters wide and elongation of 6-10 meters. The biggest single seam measured so far, has a width of about 50 meters and a length of approximately 250-300 meters (Momongan, 1986). Thickness of the seams is from few centimeters (10-20 cm) and barely exceed one (1) meter. The color displays variegated tones of gray, green, cream, and yellow. Fresh outcrops give waxy or soapy appearance and texture. Fissility is commonly well defined and conchoidal fracture is normally conspicuous, especially in fresh samples. On brief exposure to air, the bentonite easily develops shrinkage cracks due to drying and eventually turns disaggregated and pulverized. Some samples readily slake and disperse in water, while other more indurated and silicified varieties take longer time to disaggregate. Wet specimens give slight to moderate plasticity. Previous XRD analysis (Momongan, 1986), showed that the minerals of bentonite grade from pure montmorillonite to a bentonite consisting of montmorillonite, zeolite (?), and other accessory minerals of calcite, plagioclase, and quartz. Cation

exchange capacity (CEC) values range from 70-95 meq.

MINERALOGY

Multiple combination of analytical techniques and various treatments have been carried out on bentonite samples. However, detailed results of the mineralogical analyses will be published in a separate journal. Only partial outputs on x-ray diffraction tests and scanning electron microscopy will suffice for discussion in this paper.

The x-ray diffraction analysis indicates smectite minerals as the dominant constituents of the bentonite. Minor amounts of mixed-layer kaolinite/ smectite, kaolin, mica, and zeolite (possibly clinoptilolite) are also identified and characterized in the clay fraction. Discrete crystalline quartz, feldspar and calcite are the major minerals in the non-phyllosilicates component.

Fine oriented $<2\mu$m aggregate fraction displays 16 Å to 16.3 Å basal dimension (Fig. 2a). Generally, smectite clay show basal spacings of about 15 Å to 15.5 Å in untreated state (Brown, 1961). The discrepancy in the observed spacings may have been due to intergrade of some clay minerals in the smectite. Solvation treatment with ethylene glycol promotes expansion of the basal size to 17.6 Å to 18 Å (Fig. 2b). Ethylene glycol (EG) treatment generally
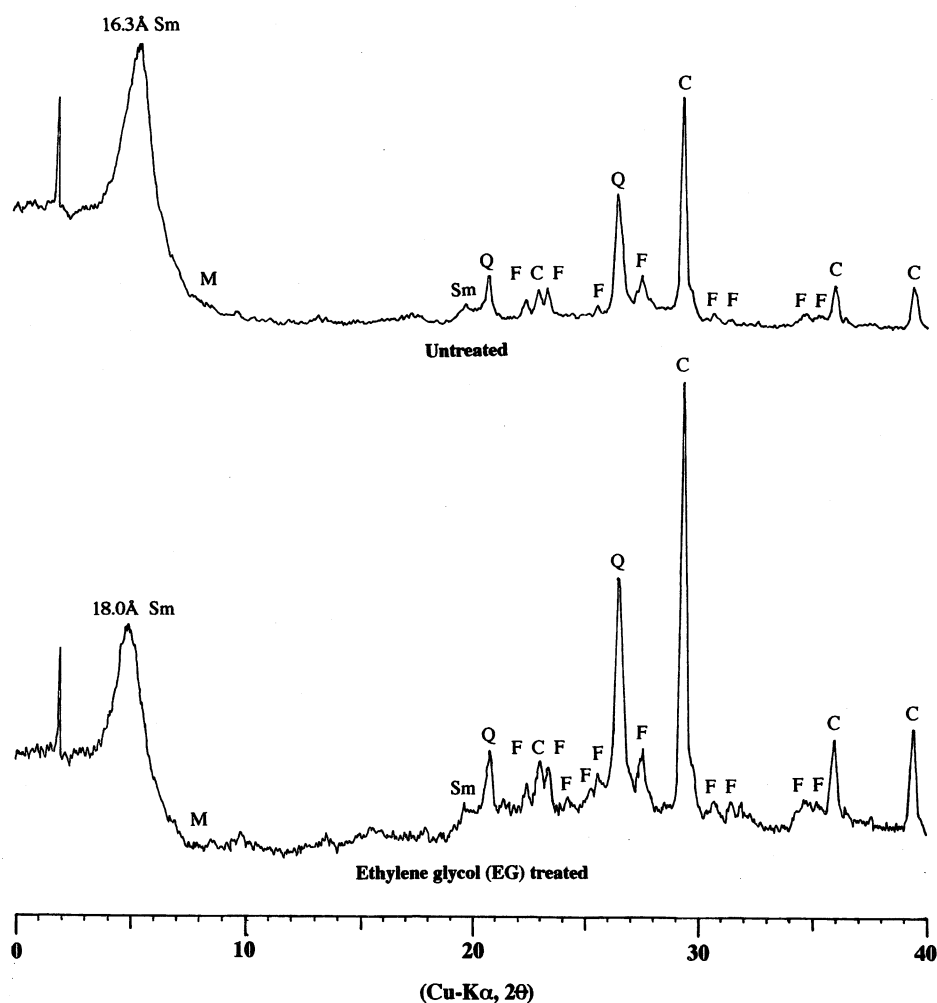

Fig. 2. X-ray diffractograms of oriented $<2\mu$m fraction, showing x-ray powder reflections in untreated and ethylene glycol (EG) treated states. **Sm**-smectite; **Q**-quartz; **F**-feldspar; **C**-calcite; **M**-mica.

expands the basal size of ordinary smectite to constant values of 17 Å (Brindley and Brown, 1980). This observation further points to the possibility of admixture of various clay minerals in the predominantly smectite assemblage. Thermal treatment at selected temperature settings shows the dehydration and rehydration capacity and behavior of the oriented fines. At 300℃ for 1 hour heat treatment, no significant change in x-ray patterns was observed for the loss of interlamellar water, consequently, basal size maintains 18 Å upon ethylene glycol saturation (Fig. 3). At 500℃ for 1 hour heat treatment, the peak reflection shifts to 9.82 Å suggesting expulsion of interlayer water (Fig 4a). Upon water treatment,

partial intake of H_2O molecules is suggestive from peak reflection shifts at 9.93 Å and 17.6 Å (Fig. 4b). Ethylene glycol treatment still bring back the basal distance to 17.6 Å (Fig. 4c). Temperature treatment at 700 ℃ (Fig. 5a) finally dehydrates and dehydroxylates the clay, and the structure eventually contracted to 9.93 Å. No amount of expandability is observed even after saturation with water and ethylene glycol as shown by peak reflections constantly arrested at 9.93 Å (Fig. 5b & 5c). The high intensity peak at 37.4° 2Θ with value of about 2.40 Å is still unknown as to what mineral species it belongs (Fig. 5a). The peak is recognized to have developed only after 700℃ temperature exposure.
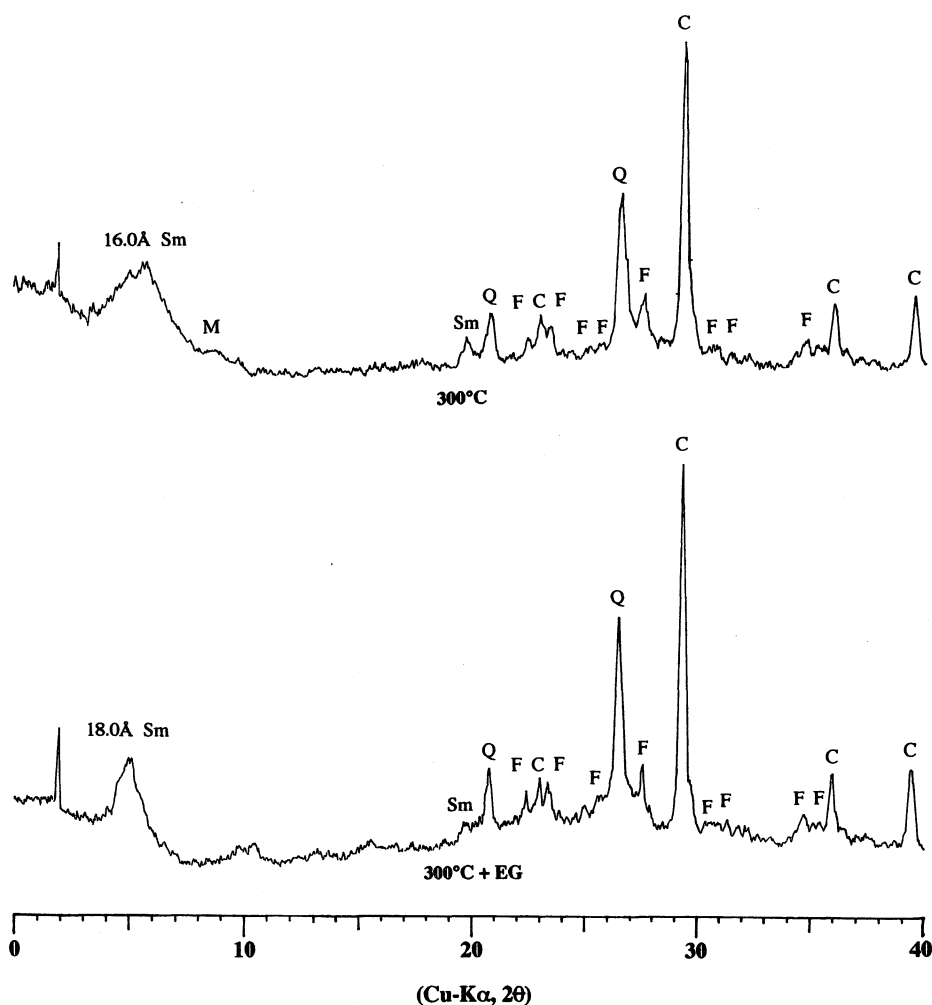

Fig. 3. X-ray diffractograms of oriented <2μm fraction, showing x-ray powder reflections of thermal treatment at 3
00℃ for 1 hour. **Sm**-smectite; **Q**-quartz; **F**-feldspar; **C**-calcite; **M**-mica.

The difficulty in identifying this peak is compounded by its occurrence as a single peak wherein it could hardly be correlated with other known peaks near this 2θ region. This peak disappeared (or just probably shifted to 2.63Å?) after H_2O and EG treatments. But after H_2O and EG saturation however, there is again a noticeable appearance of new peak at around 18° 2θ and value of about 4.92Å (Fig. 5b & 5c). The ascription of this peak reflection is still dubious. It is also suspicious whether it is a (002) reflection of the contracted smectite. Provisional explanation, at this instance, attributes this peak

as either an effect of rehydroxylation or a change in aggregate orientation. Should this be rehydroxylation, it therefore suggests that minimal sorption of OH ions in the clay lattice is still possible at this temperature and subsequently produced a sharp peak highly visible in the x-ray patterns. The change in aggregate orientation is also likely to produce similar peak due to some rearrangement of clay particles after resedimentation in the quartz slide. Inclusion of organic impuritites as caused of the appearance of the peak at 18° 2θ may be possibly ruled out since most organic materials may have
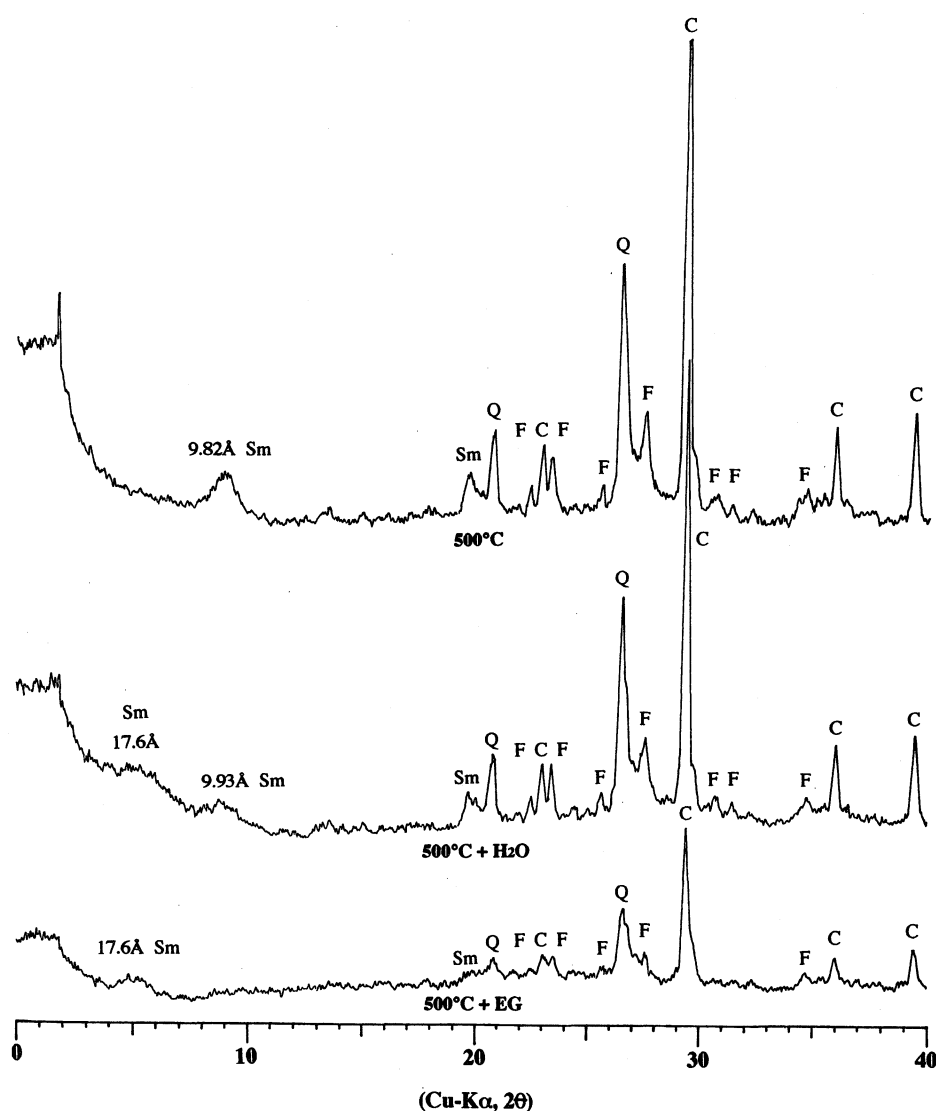

Fig. 4. X-ray diffractograms of oriented <2μm fraction, showing x-ray powder reflections of thermal treatment at 5 00℃ for 1 hour. **Sm**-smectite; **Q**-quartz; **F**-feldspar; **C**-calcite.
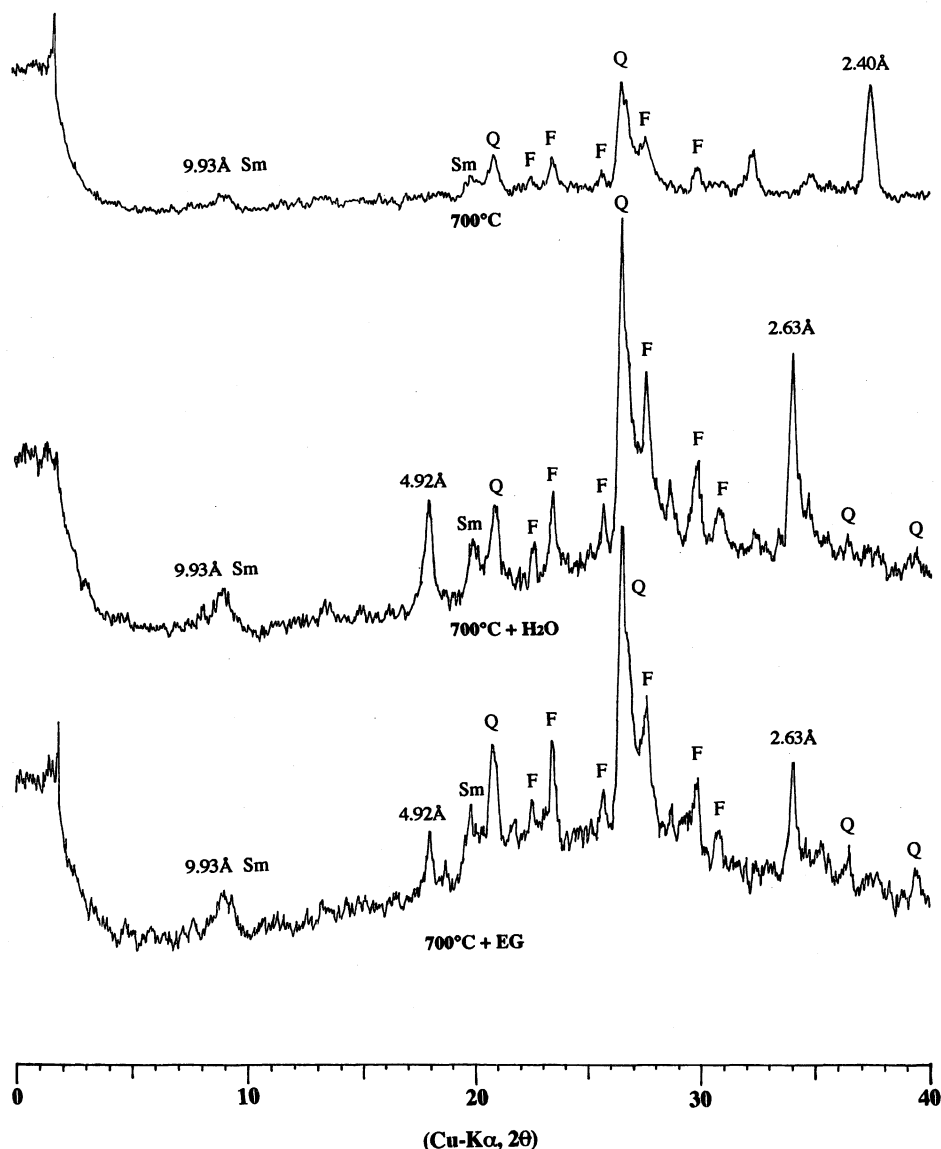
Fig. 5. X-ray diffractograms of oriented <2μm fraction, showing x-ray powder reflections of thermal treatment at 500℃ for 1 hour. **Sm**-smectite; **Q**-quartz; **F**-feldspar; **C**-calcite.

already decomposed before reaching 700℃. Further analysis is still needed to define this kind of x-ray pattern behaviour. Acid treatment using 6N HCl, disintegrates calcite peaks and confirms the non-inclusion of chlorite minerals (Fig.6).

Scanning electron micrographs of the gold-palladium sputtered, <2μm fine samples generally exhibit irregular clay flakes resembling broken "potato chips". The flakes are relatively thick and the edges are curly and wavy, which seem to be indicative of some mixture or interstratification of other clay species with smectite minerals. The surfaces are uniformly rough and appear to be veneered by micro-scale dessication cracks (Fig. 7).

PARAGENESIS

Momongan (1986) briefly described the origin of the bentonite seams as product of alteration of the ash fall tuff.

Hewett (1917) and Ross and Shannon (1926) made early appraisal of several clays which had been formed by the alteration of ash and redefined
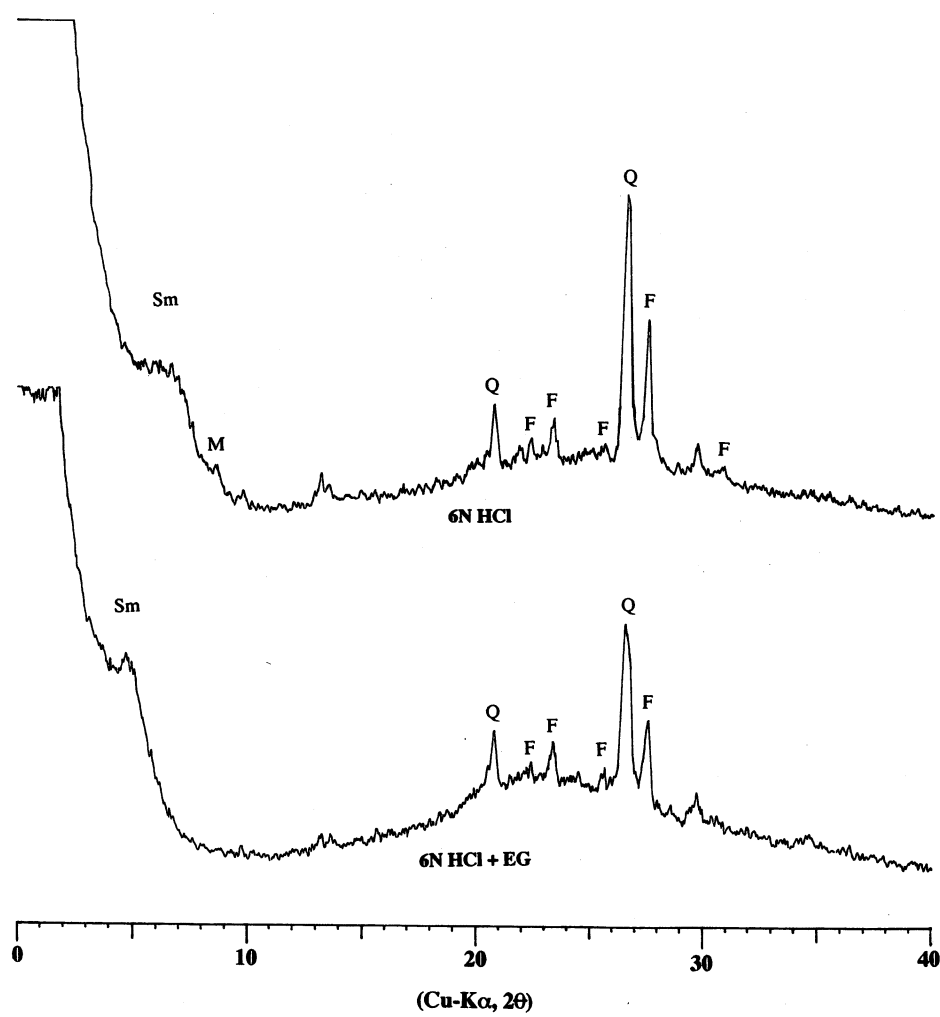
Fig. 6. X-ray diffractograms of oriented <2µm fraction, showing x-ray powder reflections of 6N HCl treatment. **Sm** -smectite; **Q**-quartz; **F**-feldspar; **C**-calcite; **M**-mica.

the term bentonite to limit it to clays produced by the alteration of volcanic ash *in situ*. They emphasized that such clays are largely composed of montmorillonite clay minerals and that they are generally highly colloidal and plastic. Borchardt (1977) defines that bentonite is a rock term referring to altered deposit of volcanic ash usually in prehistoric lakes or estuaries, and the major alteration constituent mineral is smectite and substantial impurites of quartz and feldspar. The ash contains glassy material of very high Si contents necessary for smectite formation. It appears certain therefore that almost all bentonites are derivative of alteration

of volcanic ash, enriched in silica and alumina. However, the specific mechanisms and conditions necessary for bentonite formation are still until now, not firmly established.

Grim (1953) elaborates that in order for bentonite to form, it is necessary for the ash to fall in water. The kind of water, i. e., fresh or saline, is important in determining whether bentonite forms at all and, if it does, the precise character of the resulting montmorillonite. Since much bentonite is associated with marine formations, it seems certain that the alteration can take place in seawater. The composition of the ash must have a moderate content
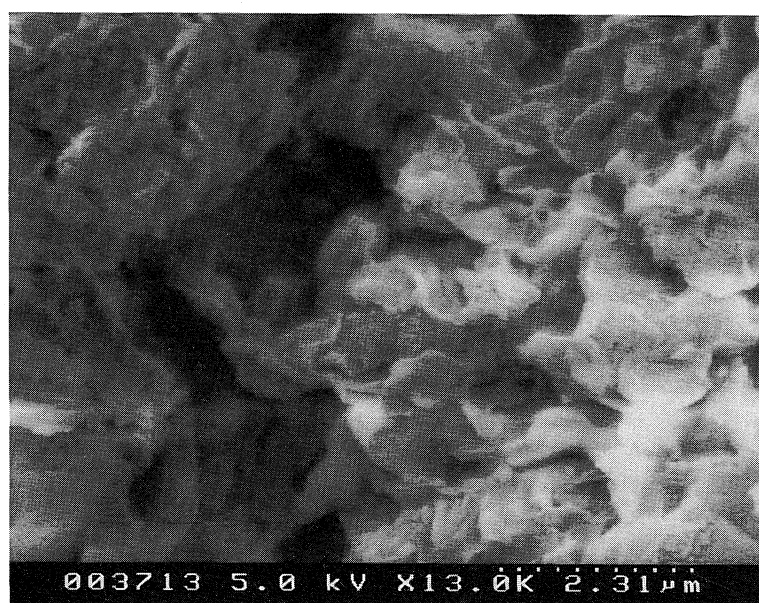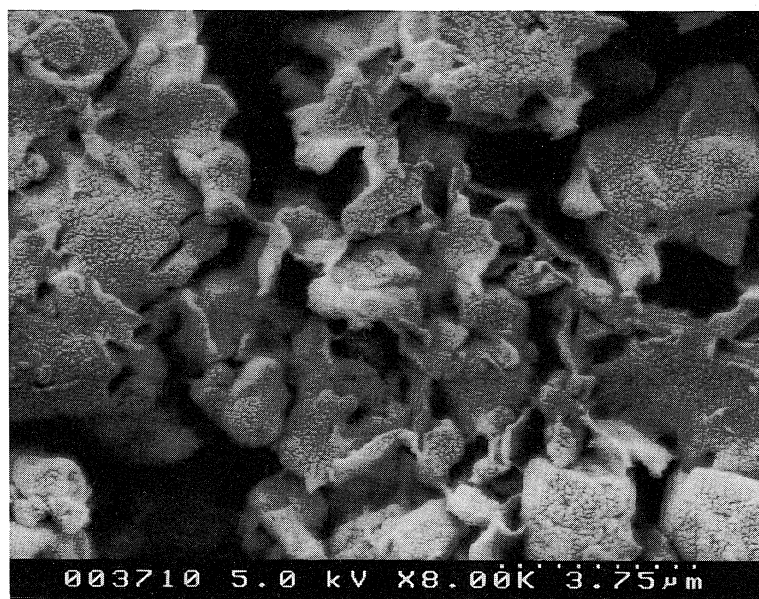
Fig. 7.   Scanning electron micrographs of the <2μm fraction. General appearance of the clay assemblages resembles broken or crumpled "potato chips".

of MgO, since ash devoid of magnesia does not seem to alter to montmorillonite. The alteration of the ash to montmorillonite takes place soon after accumulation or possibly almost contemporaneously with accumulation. It does not seem, at least in most cases, to be a later process and certainly is not a weathering process. The process of formation of the montmorillonite is essentially a devitrification of the natural glass of the ash and the crystallization of the montmorillonite. The ash probably in most cases contains an excess of silica and alkalies. Most bentonites carry Ca as the most abundant ion and only a few are known which carry Na as the dominant ion.

More recent studies by Weaver (1989) suggests significant difference in the time mode factor of the bentonite formation. He explains that the late-stage alteration of volcanic tuff deposits is of interest from the standpoint of the origin of ancient bentonites and K bentonites. The usual tendency is to envisage volcanic ash beds altering to montmorillonite shortly after deposition and while they retain some contact with the overlying water. It now appears that these ash beds, particularly the more acid types, were probably buried to a considerable depth. They altered after they no longer had direct contact with circulating ocean waters, but presumably were exposed to circulating and expressed water. Most marine bentonites are presumably diagenetic (or epigenetic) in origin rather than authigenic (or syngenetic).

Nemecz (1981) indicates that bentonites, apart from the instances of hydrothermal origin, are the hydrolysis products of feldspars and volcanic glass fallen into water, such as typified by some Hungarian Bentonites. However only a smaller percentage can be considered lacustrine, a major part is regarded as marine. Magnesium (Mg) and calcium (Ca) ions are mostly absorbed to the detriment of sodium (Na) which leads to the assumption that bentonites largely containing alkali earths are of marine origin. The much scarcer original Na-bentonites were presumably found in lakes poor in Ca and Mg and rich in Na ions.

Hence, in contrast and in correlation to the explanations of the above authors, it may be well stated that the formation of the bentonite deposit in Balamban was strongly the result of devitrification of volcanic glass fragments contained in the tuff member of the Toledo Formation. Considering all indications of geological and paleontological records, the process of bentonite formation ensued in a marine environment. The association of fossiliferous conglomeratic limestone at the base and another sandy to conglomeratic limestone and shale at the upper section of the Toledo Formation points that the accumulation took place in marine waters. Furthermore, the inclusion of Miocene index foraminifera, in the Toledo Formation, namely Globorotalia mayeri, Orbulina universa and Sphaeroidinella seminulina highly suggests that the marine deposition took place in relatively deep waters in the outer neritic zone. The alteration of the ash and the eventual crystallization of smectite seem to proceed concomitantly with the accumulation since the thickness of the Toledo Formation of about 250 meters, probably could not afford to cause alteration by burial diagenesis. The bentonite possesses Ca as the dominant ion based on XRD and EDX results and the silica and alumina are observed to be appreciably high.

CONCLUSIONS

The bentonite deposit occurs as seams concordant with stratification of host rock of the Middle Miocene Toledo Formation. The bentonite lenses or pods are generally clay mineral associations of smectite, minor interstratified kaolinite / smectite, kaolin, mica, and zeolite. Crystalline quartz, feldspar and calcite are notably the accessory minerals of non-phyllosilicates fraction. Electron scanned micrographs display irregular configurations of clay flakes and aggregations suggestive of moderate degree of crystallinity or structural order. The manifestation of micro-scale dessication cracks on larger crystal surfaces appears to be intergrowths of kaolin minerals. The origin is probably from the alteration of tuff by devitrification of volcanic glass, containing very high amounts of silica and alumina. The alteration process of the ash to smectite is inferred to be

almost concomitant with accumulation in an aqueous saline environment.

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