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Mineralogical Studies of the Bentonite Deposits in Homapon, Legazpi City, Philippines

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ABSTRACT

Mineralogical studies utilizing X-ray Diffraction Analysis, Scanning Electron Microscopy, Infrared Spectroscopy and Differential Thermal Analysis methods were conducted on the samples collected from the bentonite deposits in Legazpi City, Philippines. Results show montmorillonite as the main clay constituent, with mixed layer illite/ montmorillonite mixed layer and 7 Å halloysite. Non clay components are quartz, cristobalite and feldspar.

Based on geological evidences along with this present mineralogical findings, the deposit is considered to have been formed by ground water alteration accompanied by the chemical weathering of probably low hydrothermal action of the underlying rhyodacitic rocks.

INTRODUCTION

Bentonite deposits occur in Homapon, Legazpi City, Philippines (Fig. 1). Previous studies on this deposits have been made of gross physical properties and general mineralogy like the works of Ronan and Magpantay (1985) and Ronan (1986). Investigation was likewise undertaken by Carranza (1987), mainly aimed on the occurrence and reserves with relatively few mention on the mineralogical character.

In the discussions that were presented in the above mentioned studies, it can be stated that the Homapon bentonite deposits have been considered but not definitely proved to be formed by low hydrothermal alteration. Relative to this, the present study discusses the findings on the mineralogical analysis of Homapon bentonite with focus on the character of the clay mineral formations in order to define any indications of the minerals to the mode of occurrence of the deposit.

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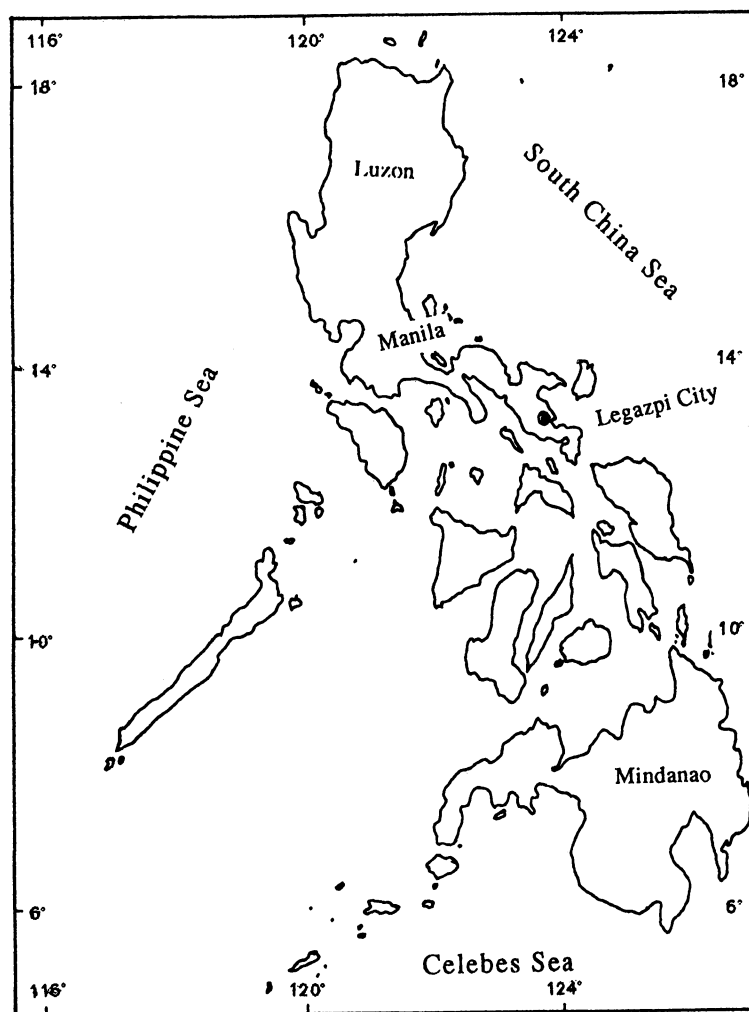


Fig. 1 Location Map of the Bentonite Deposit.
 ● bentonite deposit

GEOLOGY OF THE AREA AND BRIEF DESCRIPTION OF THE DEPOSITS

The area is generally underlain by andesite flows and rhyolitic flows. Intercalated with the andesite are tuffaceous pyroclastics and minor agglomerates.

The deposits are stratum, non-swelling bentonite. Host rock to this bentonite is flow tuff of rhyolitic composition probably predominantly glass. The bentonite occur in lensoid shapes which are found to be deposited in topographic low areas where surface run-off collects and ground water is abundant. There are at least five delineated deposits but neither are found to be a lateral extension of the other. The five deposits are observed to have similar character. Geological mapping of the area shows that the bentonite rest upon cavities in rhyodacitic flow; there were depressions in the rhyodacitic flow that were filled up by tuffaceous ash flow which were later altered to bentonite.

The deposit generally grades from highly argillized rock to bentonitic clay to

bentonite. The highly argillized rock shows stratification suggesting that the original rock is the bedded tuffaceous pyroclastics intercalated in the andesite flows. Some bentonite layers contain pebble to sand size altered volcanic fragments.

MATERIALS AND METHODOLOGY

This present mineralogical work was carried out on the samples collected from the upper 3 layers of the bentonite exposed in the quarry site in Homapon. Samples that represent the pink and cream color varieties were collected. One sample was also taken from the zone which contains pebble to sand size altered rock fragments indicating its volcanic origin. This volcanic origin was cited by Carranza (1987) who offered proof that textural characteristics of the volcanic tuffs have been retained in the bentonite layers.

Nine strata previously identified (Carranza, 1987) are reviewed in this paper (Table. 1).

Table 1 Description of the different strata observed in drill core in the bentonite quarry in Homapon, Legazpi City.

STRATUM	DEPTH	DESCRIPTION	CLAYS DETECTED
1	0.06-0.50	Overburden	
2	0.50-2.00	Dirty white to cream bentonite W/scattered sand sized fragments.	mont., 7A halloysite, I / mont., quartz, cristobalite
3	2.00-2.50	Pink colored bentonite. Relict shard structure still discernible.	mont., I / mont., cristobalite, quartz, 7A halloysite
4	2.50-2.80	Dirty white to cream bentonite. Coarse and sand sized altered rock fragments present.	mont., I/ mont., cristobalite, feldspar, 7A halloysite, clinoptilolite
5	2.80-2.81	Green colored bentonitic (?) layer or probably a thin layer of andesitic flow.	—
6	2.81-3.50	Dirty white in color with laminations of pink and grayish bentonite, coarse and fine sand sized altered rock fragments present.	mont., I / mont., quartz, clinoptilolite, feldspar.
7	3.50-3.60	Dull light gray colored with lots of silt and sand sized colored bentonite. No altered rock fragments observed.	mont., quartz, I/mont
8	3.60-3.70	Dull light gray colored bentonite with silt and sand size rock fragments.	mont., quartz, I / mont, clinoptilolite.
9	3.70-3.90	Light gray brown bentonite grading downwards to a tuffeous textured brownish gray bentonite. No rock fragments observed.	mont., quartz, I/mont.
10	3.90-4.20	Cream colored bentonite with fine sand sized altered rock fragments.	quartz, mont., I/mont

The mineral contents of the samples were determined by the Rigaku (Geigerflex) X-ray diffractometer (30kV, 15mA) instrument. Results were obtained from the raw samples as well as from treated specimens of the less than 2 microns fractions, prepared as oriented aggregates through the usual sedimentation process. Scanning electron microscopy (SEM) was carried out with the JEOL JSM-25SII instrument. Raw samples used for SEM were first coated with sputtered Pd-Au before observations were undertaken. Differential thermal data (DTA) were obtained with the Rigaku Thermoflex apparatus by heating samples at the rate of 10°C/ min up to 1000°C temperature.

Infrared absorption (IR) analysis was undertaken with the Nihonbunko Infrared Absorption Spectroscopy using the KBr method.

RESULTS

X-RAY DIFFRACTOMETRY (XRD)

Shown in Fig. 2 are diffraction patterns of raw and treated bentonite samples. Results show that clay minerals present are montmorillonite, mixed layer illite/montmorillonite, and 7 Å halloysite. Non clay minerals detected are quartz, cristobalite and feldspar. The dif-

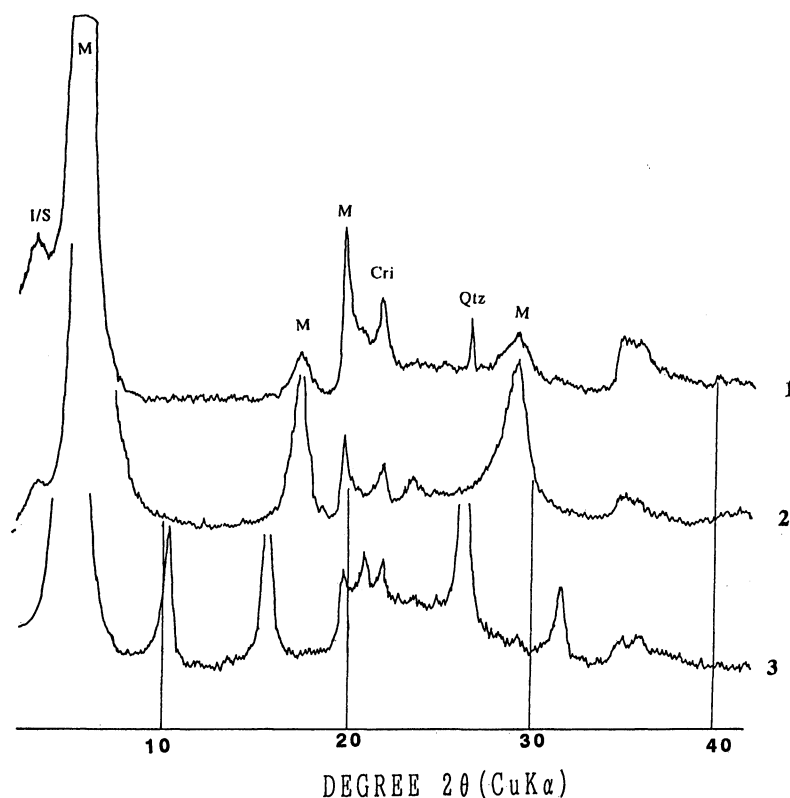


Fig. 2a X-ray diffraction patterns of bulk samples from layer 2.

1. raw sample, 2. oriented samples

3. treated with ethylene glycol

(M-montmorillonite, Cri-cristobalite, Qtz-quartz I/ S-illite/ montmorillonite)

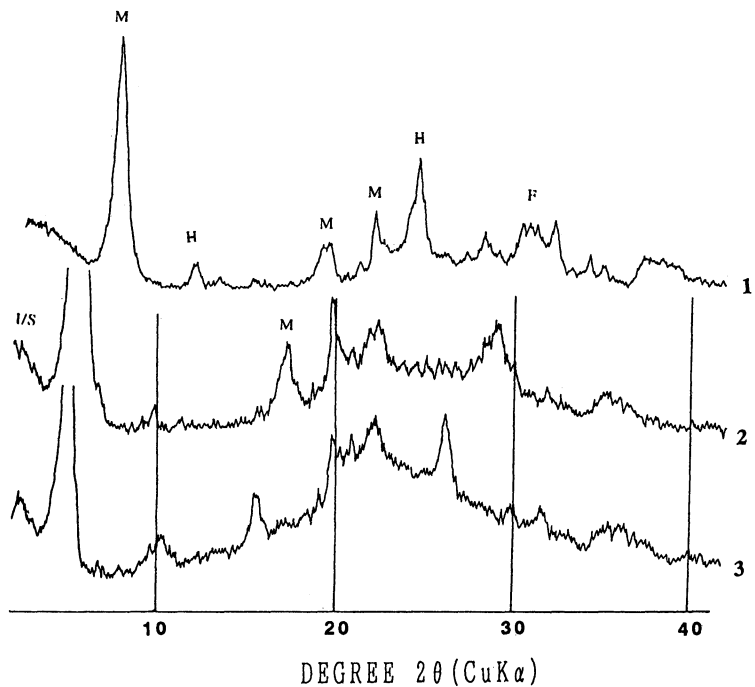


Fig. 2b X-ray diffraction patterns of bulk samples from layer 3.
 1. raw sample, 2. oriented samples
 3. treated with ethylene glycol
 (M-montmorillonite, H-7 Å halloysite, F-feldspar cli-clinoptilolite)

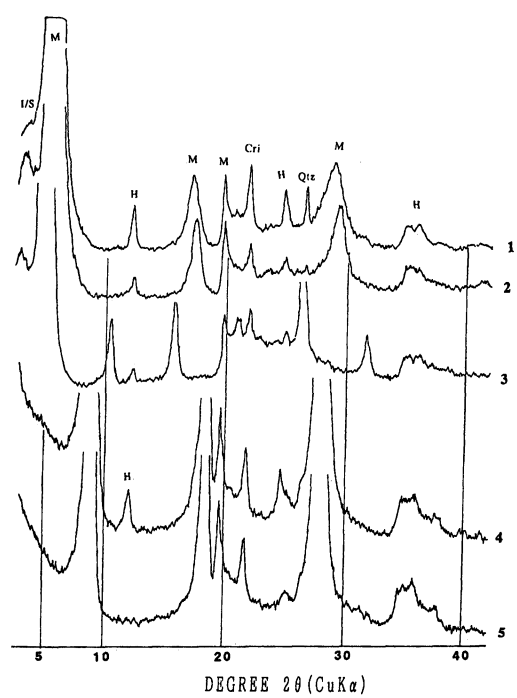


Fig. 2c X-ray diffraction patterns of bulk samples from layer 4.
 1. raw sample, 2. oriented samples
 3. treated with ethylene glycol, 4. heated at 400°C, 5. heated at 550°C
 (M-montmorillonite, Cri-cristobalite, Qtz-quartz H-7 Å halloysite, I/S-illite/montmorillonite, cli-clinoptilolite)

fraction traces of the untreated specimens have broad 001 reflections for montmorillonite clay at 15.8 Å that shifted to about 17 Å on glycolation. This spacing at 001 reflection give an indication whether the predominant exchangeable cation is sodium or calcium/magnesium (Mielnz et. al, 1955), i. e. calcium and/or magnesium if the spacing is about 15.4 Å (Papke, 1969). The mixed layer illite/montmorillonite is identified at the range from 10.16 Å to 13.19 Å. Moreover, the broad 001 reflections at 7.2 Å -7.4 Å, often with distinct asymmetry towards the low angle side, is typically the diffraction pattern of halloysite mineral. A similarly broad 002 peaks at 3.6 Å of this halloysite mineral is also evident in most of the samples. Heating to 400°C-550°C for one hour collapses halloysite causing the basal reflection at 7 Å to disappear, and the 15.8 Å peak of montmorillonite to shift to 9.98 Å (Fig. 2).

Minimal amount of clinoptilolite is detected in some samples.

SCANNING ELECTRON MICROSCOPY (SEM)

The bentonite samples are almost wholly composed of montmorillonite with some halloysite as revealed in the SEM micrographs. The characteristic thin flakes appearance of montmorillonite is clearly observed in Fig. 3a. The halloysite minerals on the other hand show spherical rather than the typical tubular shape. From this textural character, it can be considered that halloysite may have been transformed from montmorillonite minerals. In micrographs of Fig. 3b, it is obviously visible, as indicated by arrows, the transformation of halloysite with stages from (1) thin flakes of montmorillonite, (2) transforming into a rose bud-like appearance and (3) further developing into spheroidal halloysite.

DIFFERENTIAL THERMAL ANALYSIS (DTA)

DTA curves (Fig. 4) of bentonite raw samples show peaks at 120°C, 148°C, 690°C and 880°C. The DTA curves in the temperature range 100°C-300°C is considered the sorbed water region and the 600°C-700°C temperature range is due to dehydroxylation of halloysite and mixed layer illite/montmorillonite. The endothermic peak between 800°C and 900°C is due to the dehydroxylation of montmorillonite.

INFRARED SPECTROSCOPY (IR)

Infrared spectra of the samples in Fig. 5 are dominated by the absorption of montmorillonite and halloysite. The 3640cm⁻¹ band is due to the OH-stretching frequency of halloysite and smectite. Broad band at about 3600cm⁻¹ is due to the interlayer water of montmorillonite. Sharp band at 1640cm⁻¹ is assigned to OH-bending modes of montmorillonite.

CHEMICAL DATA

The chemical composition of bentonite is shown in Table 2. Based on the soda ash content (about 0.075%) of the samples, it is clear that the bentonite deposit is composed of calcium montmorillonite.

Table 2 Chemical Data of Homapon Bentonite

Mineral Composition	Legazpi Bentonite		Japan (Sanwa)	US (Wyoming)
	Sample 1	Sample 2		
SiO ₂	63.73%	62.82%	61.32%	58.80%
Al ₂ O ₃	19.60	20.32	12.66	20.28
Fe ₂ O ₃	1.62	1.96	2.72	3.99
TiO ₂	0.36	0.33	—	—
CaO	1.69	1.64	1.60	1.39
MgO	3.83	4.27	1.47	2.78
Na ₂ O	0.07	0.08	1.88	2.04
K ₂ O	0.10	0.05	0.45	0.12
LOI	8.61	8.64	5.78	4.90

LOI: Ignition loss

DISCUSSIONS

The evidence of volcanic origin of the deposit appears to be substantiated by the pebble to sand size volcanic fragments present and the volcanic structures retained during the alteration of ash to clay. Alteration of volcanic materials have apparently taken place in depressions in the rhyodacitic rocks where pyroclastic materials were deposited. There is no indicative proof of any marine deposition; it is most likely that the depressions in the andesitic and rhyodacitic rocks contain abundant surface run-off and ground water to permit deposition of volcanic ash materials which were later altered to clay. The mode of formation of the deposit is however unclear, whether it was formed by low hydrothermal alteration or by alteration of volcanic ash by groundwaters where geologic or topographic conditions did not permit thorough leaching. To consider alteration by ground water rather than low hydrothermal alteration, which they geologically resembles, would be based on two (2) factors: (1) the lack of structural control and (2) the lensoid occurrences of the deposit.

In the reported zeolitized rock (Gibbons *et. al*, 1960) that were formed from unwelded tuffs by mildly alkaline, meteoric waters, it was concluded that alteration was accomplished in the vadose zone by ground water whose downward circulation was impeded by the impermeable rock. A somewhat similar process is postulated for the bentonite deposit Homapon, except that it is probably accompanied by the chemical weathering with probable low hydrothermal alteration of the underlying rocks. According to Keller (1966), volcanic ash on lands tends to alter to montmorillonite in the same way that it does in water. The partly stagnant ground water, trapped in depressions in andesitic or rhyodacitic rocks, is necessary to prevent the complete leaching of alkalis from permeable rocks. Calcium, sodium and magnesium are released during hydrolysis of the unstable glass, and the ions produce an alkaline environment

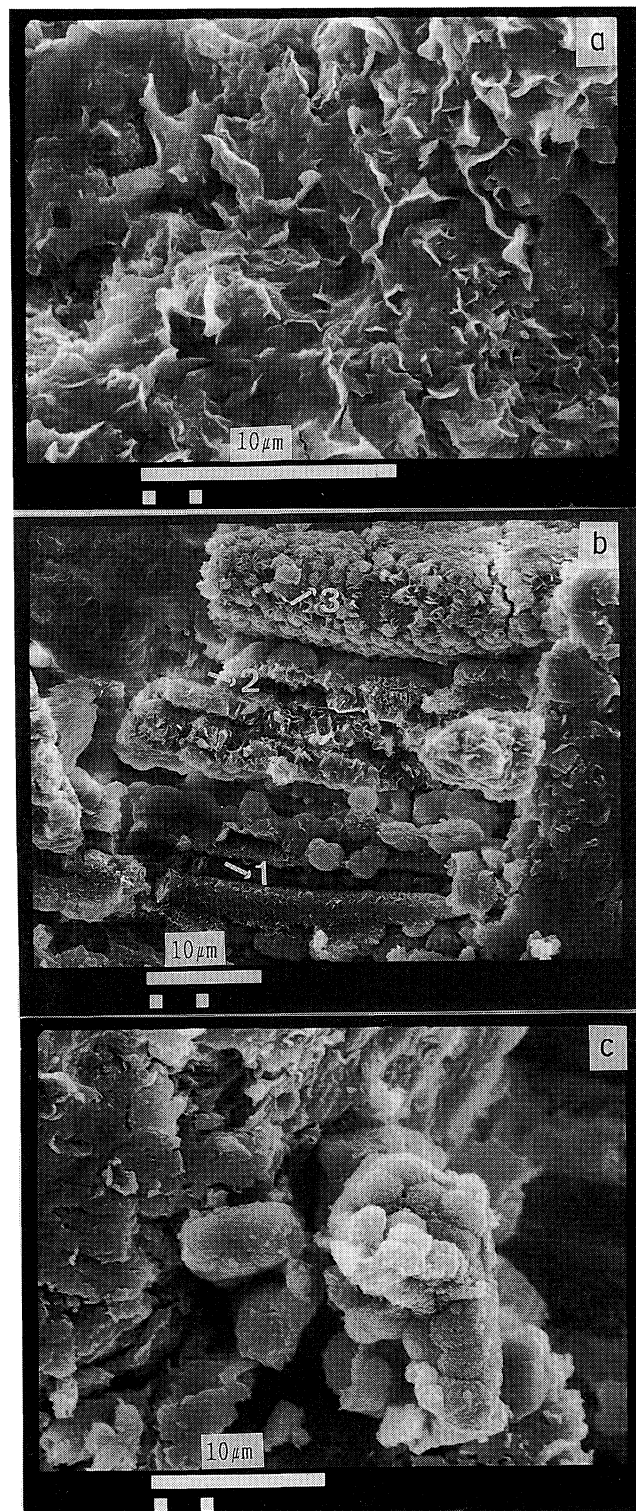


Fig. 3 SEM micrographs of the bentonite samples, showing transformation of montmorillonite to halloysite
a. Thin flakes of montmorillonite mineral.
b. Development of montmorillonite into a rose-bud like form, then transforming to halloysite.
c. Spheroidal-shaped halloysite formed from montmorillonite.

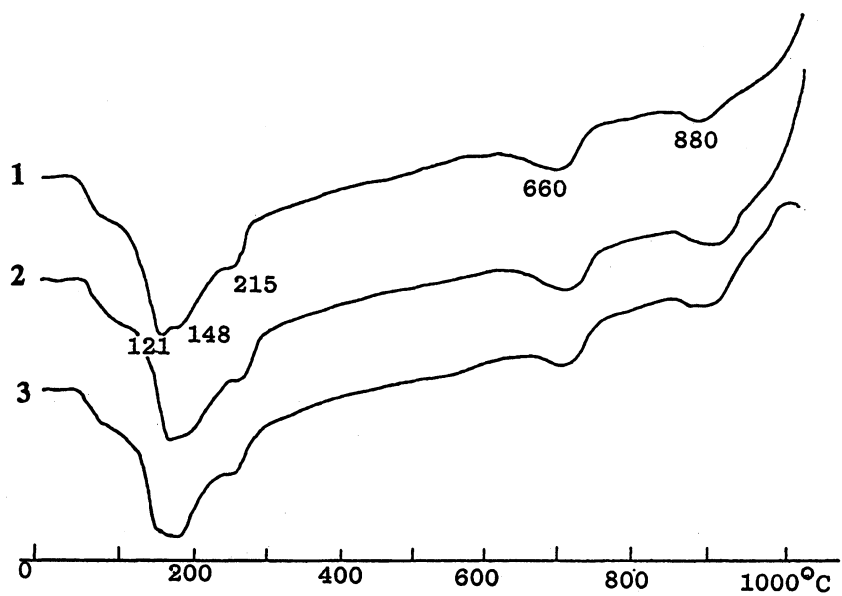


Fig. 4 DTA curves of Homapon Bentonite
 1. Sample from layer 2.
 2. Sample from layer 3.
 3. Sample from layer 4.

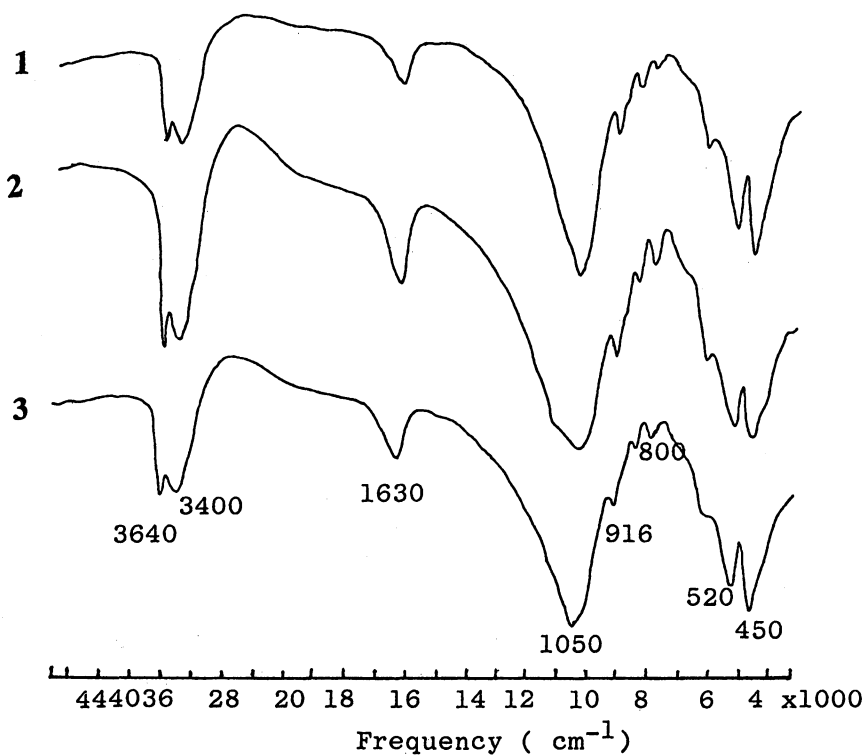


Fig. 5 Infrared Spectra of Homapon Bentonite
 1. Sample from layer 2.
 2. Sample from layer 3.
 3. Sample from layer 4.

around volcanic particles and aid in the flocculation of silica, thus, providing development of montmorillonite.

Transformation of montmorillonite to halloysite is favored by the above conditions whereby montmorillonite minerals tended to transform to halloysite by surface water or acidic ground water leaching. The clay mineral occurrences listed in Table 1 show that halloysite occur only in the upper portions indicating near surface weathering. This transformation of montmorillonite to halloysite is considered a major geochemical process; much silica was liberated to enrich the ground water that explains the presence of quartz and cristobalite on the upper section in the layerings of the deposits.

SEM micrograph in Fig. 3b clearly shows the transformation of halloysite from montmorillonite, and weathering must have been responsible for this transformation to take place. Transformation apparently proceeds by intracrystalline leaching of tetrahedral silica layers by slightly acidic ground water. This process of transformation is best illustrated in the proposal of Sudo and Shimoda (1978) on the process of formation and weathering of acid clay (bentonite) in Japan. Furthermore, the spherical morphology of the halloysite is distinctively observed in this deposit (Fig. 3c). A similar morphological feature of weathered halloysite also derived from volcanic ash was described by Kirkman (1981).

Based however on the physical character such as relict flow bandings suggests that deposits have been influenced by chemical weathering and alteration of the underlying rhyodacitic flow. It is assumed that the deposition of the original rocks (i. e., the tuffaceous ash flow) preceded the deposition of rhyodacitic and andesite flows. The rhyodacitic and andesite flows are still presumably hot to cause chemical weathering and alteration on the tuffaceous ash flows by low hydrothermal solutions. This assumption is then supported by the abundance of quartz particularly at the lower portions in the layerings observed from the drill core obtained in the bentonite quarry in the area (Table 1).

In the formation of montmorillonite to illite from volcanic ash, on the other hand, the common genetic sequence of transformation especially in intense hydrothermal alteration seems to be the conversion of volcanic glass to Ca-montmorillonite followed by potassium fixation, then the formation of mixed layer illite/montmorillonite, and finally, illite (Steiner, 1968). The findings in this paper does not show fully contineous sequence of the conversion. Transformation proceeded only from Ca-montmorillonite to mixed layer illite/montmorillonite. Hydrothermal alteration was probably weak that is, the hydrothermal temperature was very low and the hydrothermal solution was probably defficient of potassium concentration that limit the sequence to reach the final stage of transformation. Should there be prevailing low hydrothermal conditions all throughout the period of transformation as the case maybe, development of illite may have been possible. As pointed out by Hower, *et al* (1976) who concluded that montmorillonite/ illite transformation process proceeds over a predictable temperature range and that it progresses through a series of mixed layer phases. The absence of illite therefore suggest an involvement of certain complicated conditions related to transformations such as temperature and weathering.

The presence of clinoptilolite (which was detected in small amount), indicates high

silica activity in the chemical environment (Verde, 1992). This statement supports the assumption that acidic ground water probably derived from the underlying rhyodacitic rocks prevailed at the time of transformations of some clay minerals in the bentonite deposits in Legazpi City.

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