

MINERALOGICAL PROPERTIES OF BULALA FLINT CLAY, CAMARINES NORTE, PHILIPPINES

E.J. Mamaril-Diegor* and K. Tomita*

(Received September 5, 1989)

ABSTRACT

Mineralogical studies by means of X-ray Diffraction Analysis (XRD), Scanning Electron Microscopy (SEM), Infrared Absorption Spectroscopy (IR) and Differential Thermal Analysis (DTA) have been conducted on a flint clay deposit found in Barrio Bulala, Camarines Norte, Philippines. Results were obtained from raw specimen as well as on specimens heated at 550, 650, 900, 1000, 1100, 1200, 1300°C.

Based on X-ray diffraction analysis, the Bulala flint clay is mainly composed of well-ordered kaolinite with minor amounts of alunite. SEM micrographs, DTA curves and IR spectra show that the clay is readily transformed to metakaolinite, γ -alumina, mullite and cristobalite by heat treatment.

INTRODUCTION

Several workers have conducted studies on a flint clay deposit found in Barrio Bulala, Capalonga, Camarines Norte, Philippines. Miranda first reported its occurrence in 1966 during a regional mapping of Camarines Norte. A follow-up detailed geologic study was subsequently conducted by Zepeda in 1967, and he discussed the probable origin of this clay deposit (Zepeda, 1968). Caleon (1974) also undertook a geological investigation with particular interest on its geologic reserves upon a paid request by Firestone Ceramics, Inc. These previous works, however, were mainly concerned with the geology, occurrence, origin and reserves with some reference on the mineralogical and chemical composition of this clay deposit. In this paper, we present the recent results of x-ray powder diffraction (XRD), differential thermal analysis (DTA), infrared absorption spectroscopy (IR) and scanning electron microscopy (SEM) studies on the changes in the mineralogical properties of this flint clay upon heat treatment. These findings are significant because they represent the first study on the thermal behavior of this type of clay which is the first of its kind in the Philippines.

GEOLOGIC SETTING

The flint clay sample used in this study came from Barrio Bulala, Capalonga, Camarines

* Institute of Earth Sciences, Faculty of Science, Kagoshima University, Kagoshima, Japan.

Norte, Philippines. The general geology of the Bulala area was described in detail by Zepeda (1968), Caleon (1974) and the UNDTCD (1987). The principal rock types consist of serpentized peridotites, greenschists and agglomerate pyroclastics with intercalated tuffaceous sedimentary rocks and chert. The flint clay deposit was reported to be a product of hydrothermal alteration of the volcanic and sedimentary rocks (Zepeda, 1968). It occurs as solution fillings along fractures and alteration products derived from the aluminous materials of the host rocks. Veinlets of flint clay vary in thickness from a millimeter to about 40cms.

METHODOLOGY

Chips (1×1cm) and powdered specimens of the flint clay were fired using an electric furnace at temperatures of 550, 650, 900, 1000, 1100, 1200, 1300, and 1400°C, and were kept constant at their respective temperatures for at least 1 hr. An oriented specimen was also prepared by the usual sedimentation method and was heated to 550°C in order to determine the effect of heat treatment on an oriented specimen of clay mineral, i.e. kaolinite. Raw and heated powdered and oriented specimens were analyzed on a Rigaku (Geigerflex) X-ray diffractometer using a Ni-filtered CuK α radiation at 30 kV and 15 mA. DTA curves were obtained with a Rigaku Thermoflex apparatus at a heating rate of 10°C per minute up to 1000°C. Raw and heated chips newly broken to expose fresh, natural fracture surfaces were used for SEM analysis in order to observe the morphological changes that took place during the heat treatment. SEM studies were carried out on a JEOL JSM-25 scanning electron microscope, after placing the samples in brass holders and coating them with sputtered Pd-Au for good electrical conductivity. IR analysis was conducted on a Nihon Bunko infrared spectrometer employing the potassium bromide tablet method of sample preparation in which a small amount of powdered specimens was mixed and ground with 300mg of potassium bromide and pressed into a disc.

RESULTS AND DISCUSSION

X-RAY DIFFRACTION DATA

X-ray diffraction patterns of raw and heated specimens of the flint clay are shown in Fig. 1. The flint clay consists dominantly of relatively well-crystallized kaolinite with minor amounts of alunite. Petrographic and x-ray studies of samples collected by Zepeda (1968) and the UNDP Group (UNDTCD, 1987) showed that other accessory minerals include quartz, magnetite, iron oxide (goethites?) and pyrite.

Generally, kaolinite when heated to 550°C showed collapsed x-ray reflections. In the case of the flint clay, heating to this temperature indicated that only the intensity of the basal and related reflections of kaolinite were slightly reduced. Oriented specimen exhibited similar XRD pattern implying that the effect of heat treatment to 550°C is not dependent on the orientation of the clay. At 650°C, these reflections collapsed completely and were replaced by weak asymmetrical peaks (14 Å and 4 Å) broadening toward high angle θ 's; the 4 Å peak, however, persisted to higher temperature (1200). Some strong peaks, which are

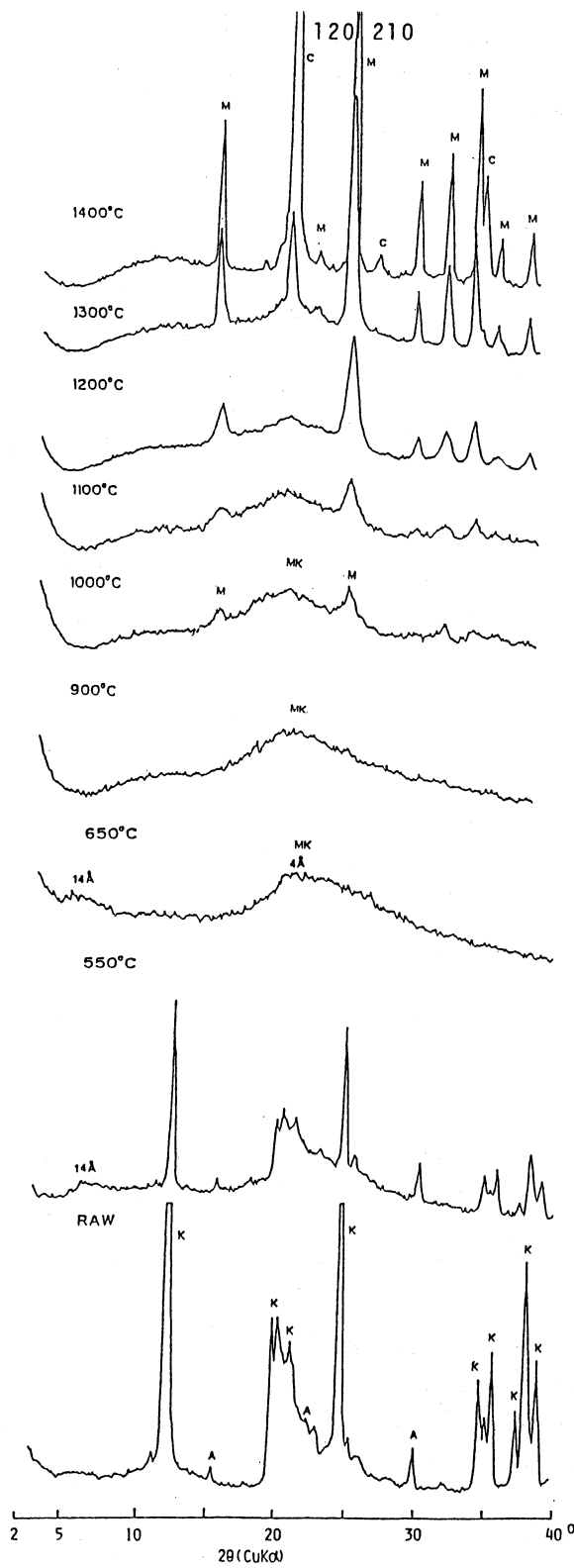


Fig. 1. X-ray diffraction patterns for Bulala flint clay.
 K : kaolinite ; A : Alunite ; MK : metakaolinite ; M : mullite ; C : cristobalite.

indicated in Fig. 2, appeared at 1000°C and were determined mainly to belong to mullite. Cristobalite, as indicated by its strongest peak (4.04Å), appeared at 1300°C. Well-defined x-ray patterns for mullite and cristobalite were observed at 1400°C.

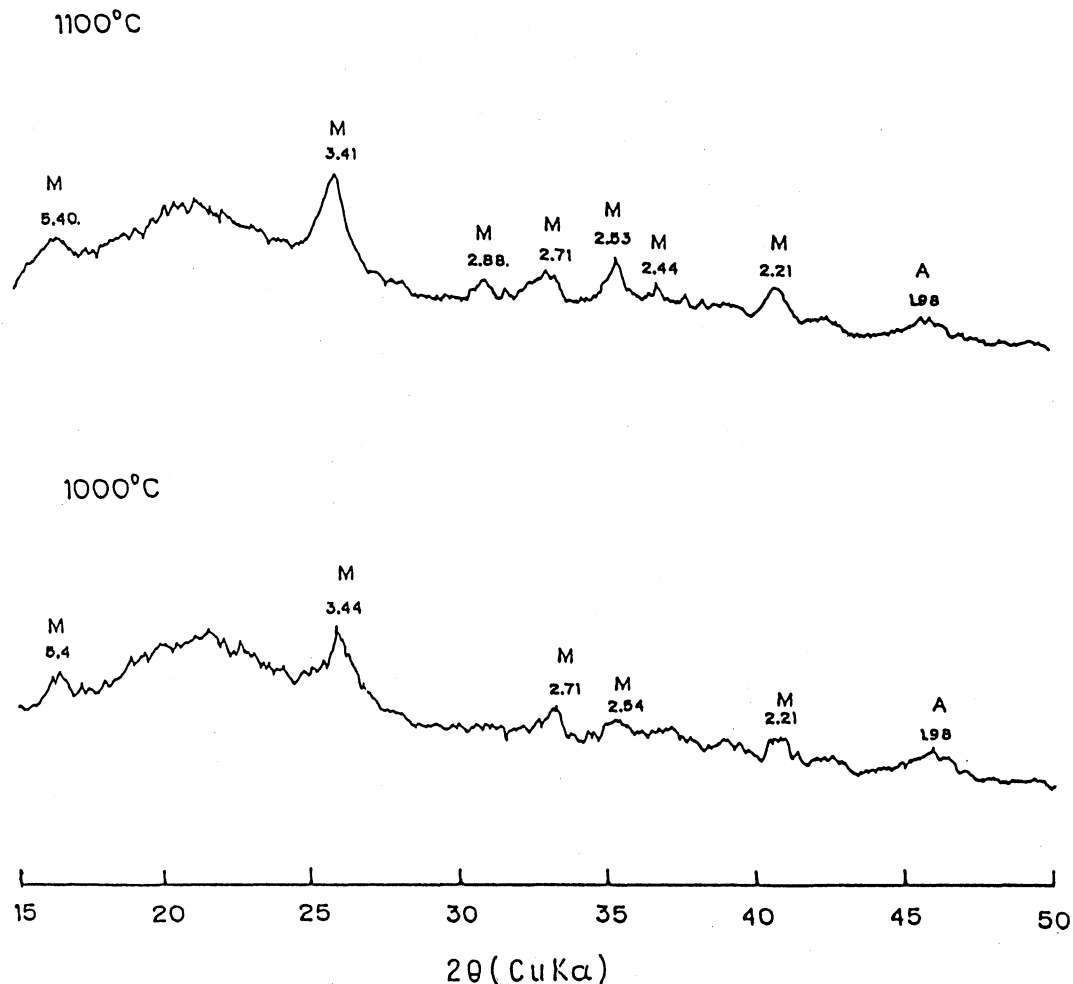
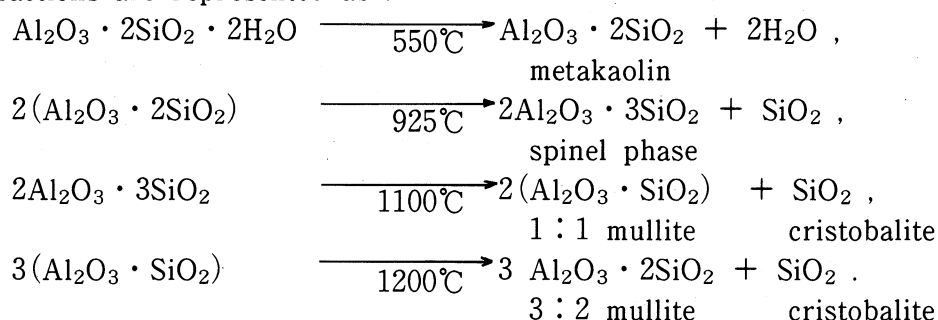


Fig. 2. X-ray diffraction patterns for specimens heated to 1000°C showing mullite (M) and γ -alumina (A) d-spacings in Å.

Based on the results of the XRD studies, the behavior of kaolinite to heat treatment could be attributed to its continuous transformation from one mineral phase to another. The slight decrease in intensity of kaolinite reflection at 550°C suggested that a loss of weight due to small amount of dehydroxylation must have occurred. Removal of water molecules and OH ions in kaolinite was completed at 650°C and caused a collapse in its crystal structure as reflected by the asymmetrical broad peaks at 14 Å and 4 Å. A similar observation was made by Brindley and Nakahira (1959) in their study of kaolinite. They attributed the unusual occurrence of a longer-order spacing (14 Å) after heat treatment to the crystal size of and expulsion of water in kaolinite. Likewise, Hill (1955) recorded the same result from the kaolin polymorph dickite when it was heated to 700°C. However, he

failed to obtain similar effect with kaolinite and ascribed this result to the different structure of dickite.

In his study of kaolinite and nacrite, Rinne (1924) found that the dehydration products (metakaolin and metanacrite, respectively) above 550°C gave weak patterns and that these products were amorphous or mixtures of amorphous substances. By applying single crystal X-ray techniques, Brindley and Nakahira (1958) showed that kaolinite is first transformed to metakaolin and subsequently to a cubic spinel-type phase by a process of orderly crystallization. According to these authors, when kaolinite is subjected to heat, the reactions are represented as :



Tsuzuki (1961) otherwise pointed out that the metakaolin is transformed into γ -alumina having a deficient spinel structure, in lieu of a cubic Al-Si spinel phase.

In the present study, neither the Al-Si spinel nor the γ -alumina were clearly observed as only x-ray powder diffraction technique was used. It is quite interesting to note here, however, that a broad peak at 1.98Å (Fig. 2) was observed when the sample was heated to 1000°C, which could indicate the formation of γ -alumina (Torillo *et al*, 1982). Furthermore, some indistinct peaks of mullite began to appear at this temperature and became enhanced at advanced temperatures. These observations could be explained by the fact that kaolinite is transformed first into metakaolin which is not wholly amorphous but still retains some crystallinity (Brindley and Nakahira, 1959). According to Tsuzuki (1961), the packing of oxygen layers is loose but the contraction of these layers advances as the temperature rises and this probably gives impetus to the formation of a framework of oxygen for γ -alumina. Although the regular arrangement of the oxygen of the γ -alumina follows that of metakaolin, the regularity of the atomic arrangement is still not sufficient to yield x-ray diffraction. Generally, cations migrate more easily than oxygen ions, and therefore, they are more numerous in the most suitable positions in the oxygen framework at such higher temperatures. As further migration and rearrangement of cations proceeds, almost all aluminum ions are consumed in the formation of γ -alumina, in the case of poorly crystallized kaolin minerals. But in a well-crystallized kaolin minerals such as the kaolinite present in the flint clay, aluminum ions remain because the rearrangement and migration of ions is more difficult, and they readily combined with silicon and oxygen ions forming mullite. Thus, the ratio of mullite to γ -alumina tends to increase with an increase in crystallinity of the original kaolin mineral. These conclusions made by Tsuzuki agreed with the observations of the present authors in which the γ -alumina, as indicated by the

weak peak at 1.98Å, occurs only in a relative minimal amount between 1000 and 1100°C as compared to that of mullite. On the other hand, the residual silicon and oxygen ions form amorphous silica (or "diffused" silica by Brindley and Nakahira) as shown by the persistence of the broad peak at 4Å. As the temperature increases, a corresponding increase in the concentration of silica occurs that facilitates the formation of cristobalite. At still higher temperature, the crystallization of mullite and cristobalite improves remarkably and is accompanied by the disappearance of the amorphous pattern. The double reflections of the former, (120) and (210), are also resolved (Fig. 1.)

DIFFERENTIAL THERMAL DATA

DTA curves (Fig. 3) of the flint clay further support the observations based on the XRD results. Raw sample showed double endothermic peaks at 598°C and 624°C. The authors attribute this to the presence of two types of kaolin minerals. However, further studies are needed. The small exothermic peak at 701°C indicates the presence of alunite. The rapid transformation of the γ -alumina to mullite was indicated by the sharp exothermic peak at around 977°C and 983-985°C for the raw and heated samples, respectively. The difference in the exothermic peaks of the raw and heated samples could be due to the presence of impurities, i.e. alunite, that lowers the exothermic peak of the former. Moreover, the K^+ ions released from the destroyed alunite probably markedly reduced the rate of formation of cristobalite from kaolinite (Holdridge, 1957). Unfortunately, this could not be confirmed since the formation of cristobalite occurs above 1000°C which is beyond the temperature range of the differential thermal analyzer used in the present study.

INFRARED ABSORPTION SPECTROSCOPY DATA

The infrared spectrum of the flint clay (Fig. 4) is dominated by the absorption bands of kaolinite at 3675, 3650, 1100, 1000, 940, 905, 795, 530, 430 cm^{-1} (Table 1). The sharp doublet at 3675 and 3650 cm^{-1} are assigned to OH-stretching modes whereas a weak band at 1625 cm^{-1} , to the OH-vibrating mode. The bands at 940, 905 cm^{-1} arise from the vibrations of inner and inner surface OH groups, respectively (Russell, 1987). The strong broad absorption near 1100 cm^{-1} and supporting bands between 400 and 800 cm^{-1} are due to (Si-O)-(Al-O) modes.

Heat treatment produced a number of significant changes in the spectrum. Increasing the temperature to 550°C brought no distinguishable changes except that the intensity of the absorption bands was slightly reduced and the 1000 cm^{-1} shifted to higher wavenumber. At 650°C, dehydroxylation occurred as reflected by the disappearance of all OH vibrational modes. Furthermore, the (Si-O)-(Al-O) bands in the region between 1000-1100 cm^{-1} merged and became a broad peak at 1100 cm^{-1} . The relatively sharp peaks between 400-800 cm^{-1} , likewise assigned to (Si-O)-(Al-O), disappeared and were replaced by a peak at 470 cm^{-1} . These results suggest that the crystalline structure of the kaolinite was largely destroyed and was being replaced by a partially amorphous phase of metakaolinite.

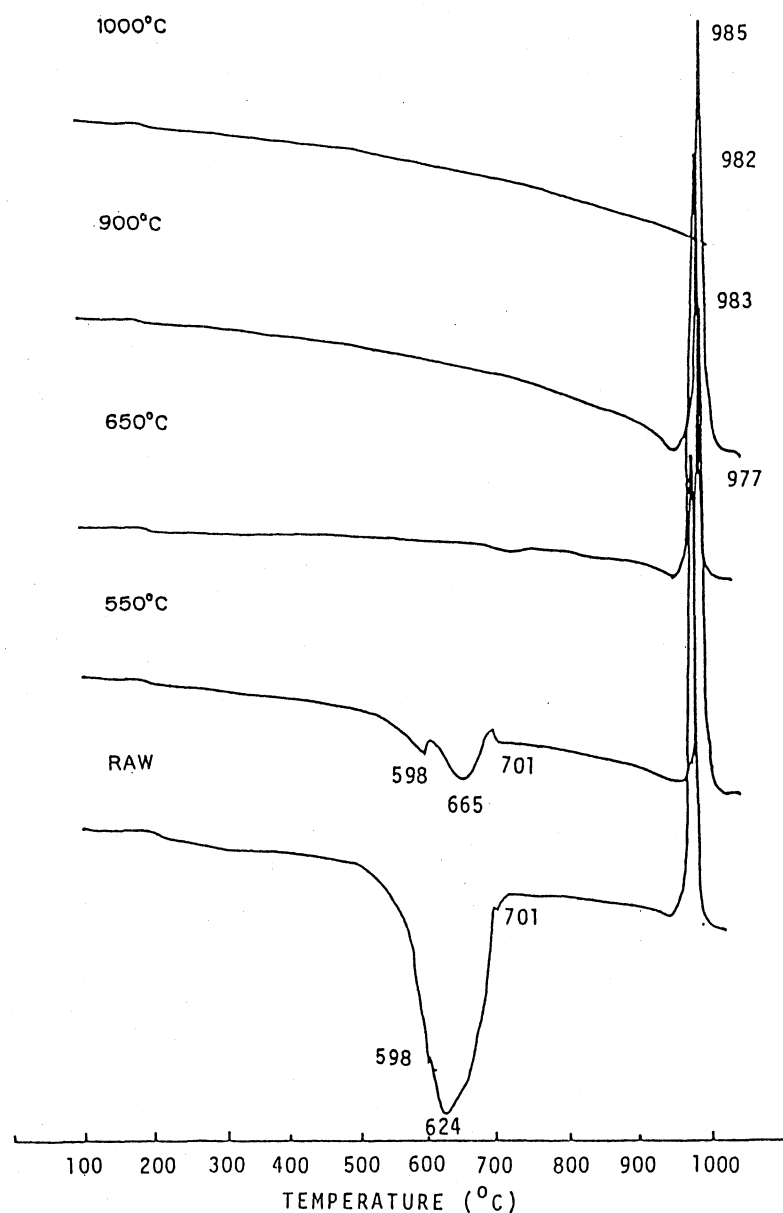


Fig. 3. DTA curves for Bulala flint clay.

Aside from the sharpening and shifting of peaks to higher wavenumbers, a similar spectrum is observed at 900°C. As the temperature was raised to 1000°C, new broad peaks at 550 and 730 cm^{-1} began to appear and were enhanced at further heating, indicating that mullite was being formed at this point. The single band at 470 cm^{-1} can be assigned to (Al-O)- and (Si-O)-bending modes in a random arrangement of (AlO₄)- and (SiO₄)-tetrahedra (Freund, 1974). As the crystallization of mullite advances, silica and Al/Si ordering causes the band to split into separate bands (470, 550 and 730 cm^{-1}) which shift apart and gain sharpness at about 1300°C. A weak shoulder peak of the 1100 cm^{-1} absorption band

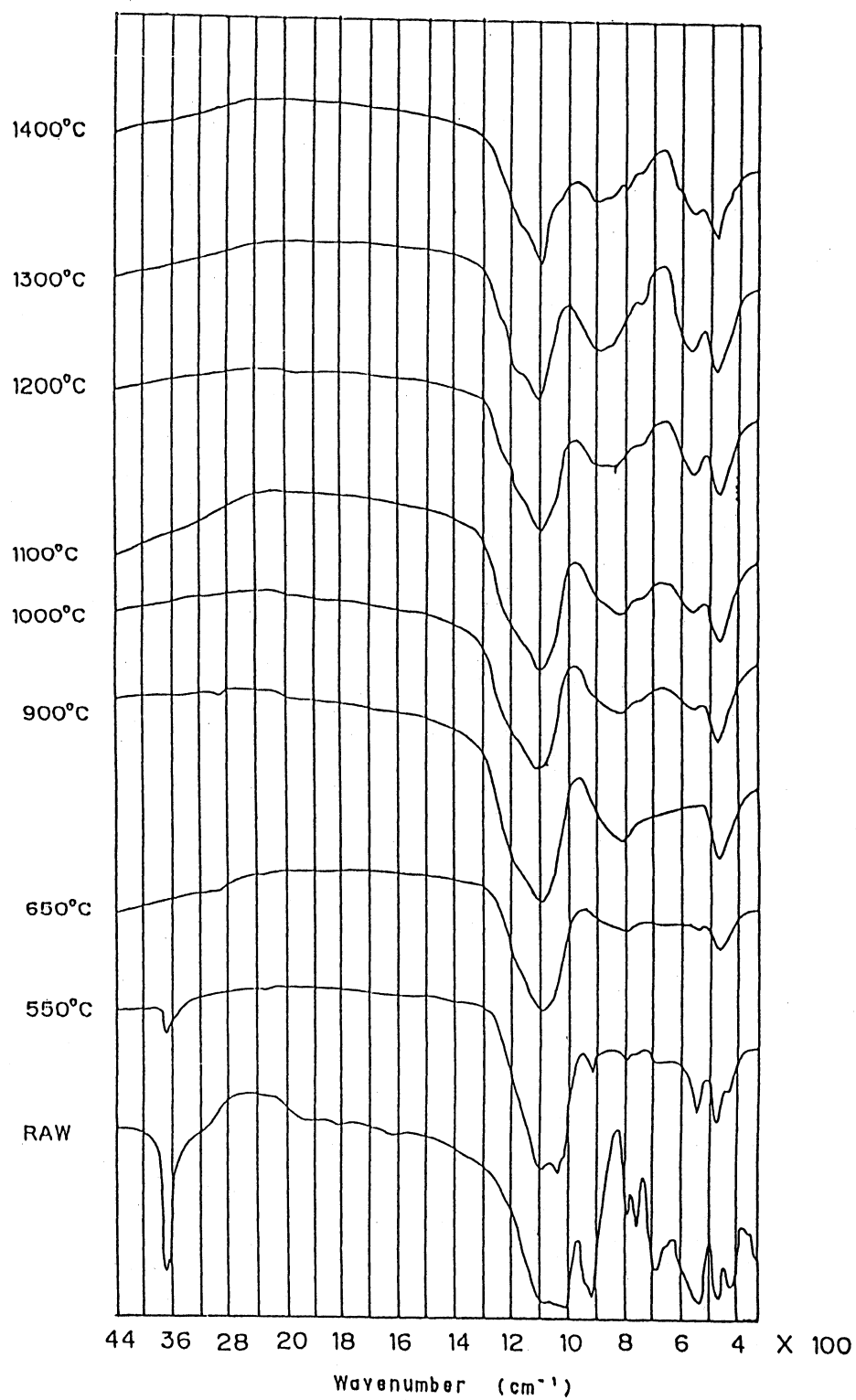


Fig. 4. Infrared spectra for Bulala flint clay.

Table 1. Infrared absorption data (in cm^{-1}) of raw and heated specimens of Bulala flint clay.

Raw	3690	3650	1100	1000	940	905	795	758	700	530	470	430
550°C	3700		1100	1040		920	795		695	540	470	430
650°C			1100				800			540	470	
900°C			1100				810				470	
1000°C			1100				810			560	470	
1100°C			1100				820	730		560	470	
1200°C			1100				910-820	730		560	470	
1300°C		1170	1100				900-830	730		560	470	
1400°C		1170	1100			920-880	800	740	620	560	470	

(1170cm^{-1}) also started to show and was determined to be part of the spectrum of cristobalite. Additional absorption bands ($620, 800\text{cm}^{-1}$) of cristobalite were finally obtained at 1400°C . The results of the IR analysis confirmed those that were obtained from X-ray diffraction.

SCANNING ELECTRON MICROSCOPY DATA

Scanning electron micrographs show that kaolinite occurs as interlocking spherical crystals (Fig. 5a) and as hexagonal plates (Fig. 5b). By heating to 650°C minute fractures within the crystals were developed that smaller, irregular grains were also noted (Fig. 5d). At increasing temperature, the subsequent loss of interlayer OH in the structure of kaolinite brought about a gradual change in morphology from individual crystals into a coalesced mass (Fig. 5 e-h); but retention of some original flaky shapes of the kaolinite crystals were still clearly visible at 1200°C . The initial development of a mosaic structure was observed at 1100°C (Fig. 5g) which became pronounced at 1300°C with the appearance of some rounded particles (Fig. 6). At 1400°C , a few needle-like crystals occurred in random orientation as shown in Fig. 7.

The above-observed changes in morphology with increasing temperature could be attributed to the formation of different crystal phases which was confirmed by the results of X-ray analysis. The change from kaolinite to metakaolin due to removal of structural water brought about the coalescence of individual crystals. Although the transformation of the latter to γ -alumina was not clear, it was probably indicated by the later development of the mosaic texture. Mullite and cristobalite were hardly distinguished at lower temperatures but rounded particles probably of cristobalite and a network of needle-like crystals of mullite became prominent at 1300°C and 1400°C , respectively.

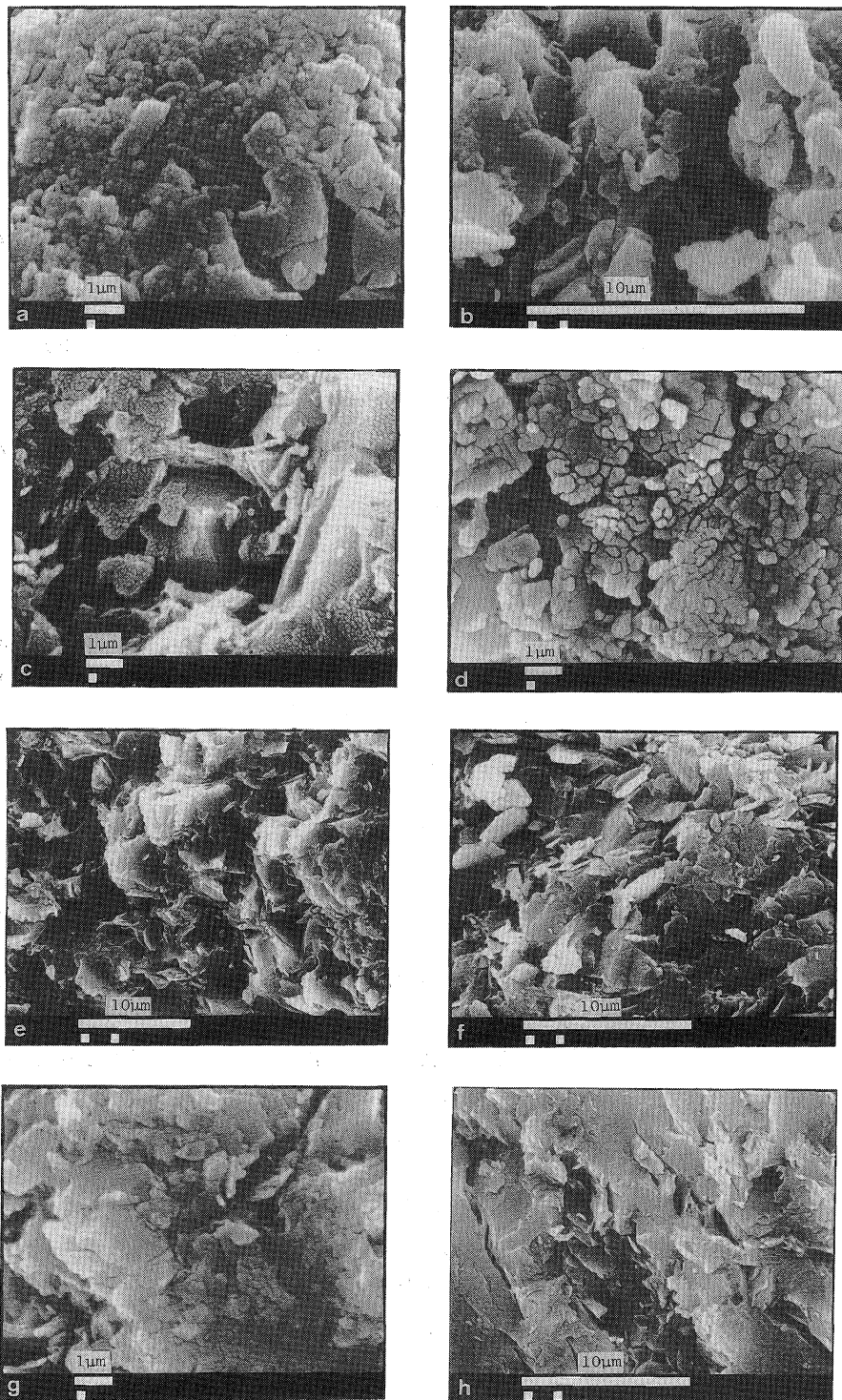


Fig. 5. Scanning electron micrographs for Bulala flint clay heated at different temperatures. a : raw 1 ; b : raw 2 ; c : 550°C ; d : 650°C ; e : 900°C ; f : 1000°C ; g : 1100°C ; h : 1200°C.

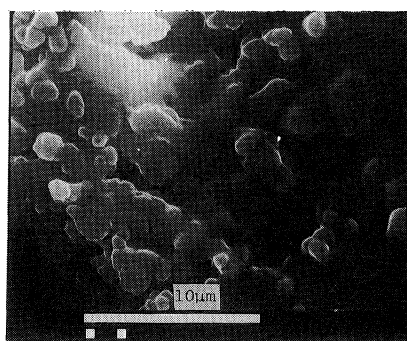
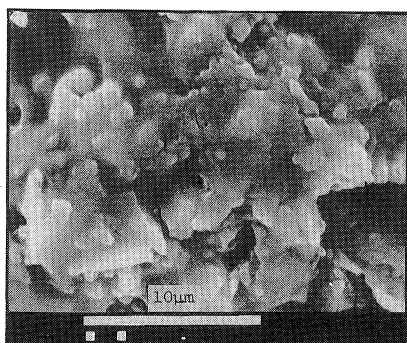
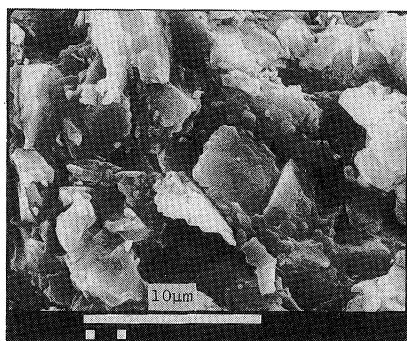


Fig. 6. Scanning electron micrographs for specimen of Bulala flint clay heated to 1300°C.

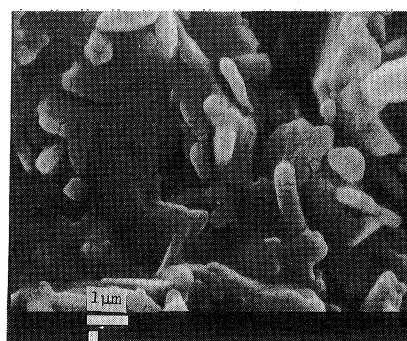
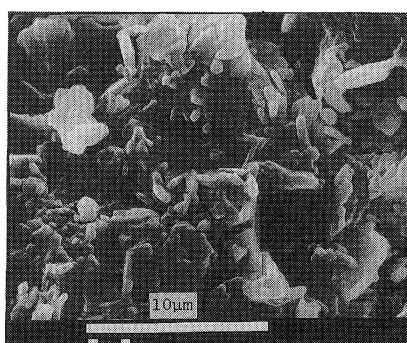
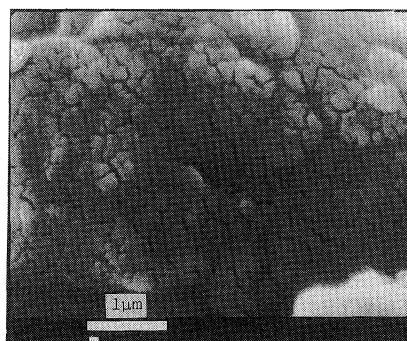


Fig. 7. Scanning electron micrographs for specimen of Bulala flint clay heated to 1400°C under different magnifications.

CONCLUSION

Based on the above discussion, the flint clay is composed dominantly of well-crystallized kaolinite with small amount of alunite (and some accessory minerals), that responded to heat treatment by continuously changing into new mineral phases, i.e. kaolinite \rightarrow metakaolin \rightarrow γ -alumina + mullite \rightarrow mullite + cristobalite, as shown by XRD, DTA and IR analyses. On the other hand, scanning electron microscopy revealed that these transformations were accompanied with corresponding changes in morphology from individual spherical and platy particles of kaolinite into masses of metakaolin and γ -alumina, and in turn into well-crystallized mullite and cristobalite crystals.

ACKNOWLEDGMENT

The authors wish to express their thanks to the Bureau of Mines and Geo-Sciences, Philippines for allowing us to use their facilities during the sample collection and providing us some of the unpublished reports ; and to Conrado Miranda, Lorna Vicente, Lydia Rajas and Bella Pandi for accompanying the senior author in the field. We are also grateful to the staff of the Institute of Earth Sciences, Kagoshima University for allowing us to use their laboratory equipment ; to Mr. Tetsuo Kobayashi of the same Institute and Professor N. Miyauchi of the Faculty of Agriculture for the use of the computer of the Volcanology Laboratory for word processing and the infrared absorption spectrometer for analysis. The moral support and valuable comments of Mr. Wilfredo G. Diegor, Mr. Constante B. Belandres and Mr. Laurence P. James are also gratefully acknowledged.

REFERENCES

- Bates, T.F. (1971) The Kaolin Minerals : in *Electron-Optical Investigation of Clays*, J.A. Gard, ed., Mineralogical Society, London, 109-158.
- Brindley, G.W. and Nakahira, M. (1958) New Concept of the Transformation Sequence of Kaolinite to Mullite, *Nature*, 181, 133-34.
- _____ (1959) The Kaolin-Mullite Reaction Series : I, II, and III, *J. Am. Ceram. Soc.*, **42**, 311-324.
- Caleon, P.C. (1975) Geologic Reserves of the Flint Clay Property of Firestone Ceramics, Inc. at Bulala, Capalonga, Camarines Norte : Unpublished Report, Bureau of Mines, Philippines, 13pp.
- Freud, F. (1974) Ceramics and Thermal Transformations of Minerals : in *The Infrared Spectra of Minerals*, V.C. Farmer, ed., Mineralogical Society, London, 465-482.
- Hill, R.D. (1955) 14 A Spacings in Kaolin Minerals *Acta Crystallographica*, **8**, 120.
- Holdridge, D.A. and Vaughan, F. (1957) The Kaolin Minerals (Kandites) : in *The Differential Thermal Investigation of Clays*, R.C. Mackenzie, ed., Mineralogical Society, London, 99-139.
- Llave, C.A. (1971) Geological Investigation of the 13 Mining Claims (PLA-4912-D to PLA-4924-D) in Barrio Bulala, Capalonga, Camarines Norte for Firestone Ceramics, Incorporated : Unpublished Report, Bureau of Mines, Philippines, 7pp.
- Rinne F. (1924) Rontgenographische Diagnostik beim Brennen von Kalkstein, Dolomit, Kaolin, und Glimmer *Z. Krist.*, **61**, 113-124.
- Russell, J.D. (1987) Infrared Methods : in *A Handbook of Determinative Methods in Clay Mineralogy*, M.J. Wilson, ed., Blackie and Sons Ltd., London, 133-173.
- Torillo, A.R. et al. (1982) Kaolin-rich Clays of the Philippines : A Critical Study of its Behavior on Heating *J. Geol. Soc. Phil.*, **36**, 32-46.
- Tsuzuki, Y. (1962) Mechanism of the 980°C exotherm of kaolin minerals *J. Earth Sci., Nagoya Univ.*, **9**, 305-344.
- United Nations Department of Technical Cooperation for Development (1987) *Geology and Mineralization in the Panganiban - Tabas and Bulala Areas, Camarines Norte*, Manila, DP/UN/PHI-85-001/1, 43pp.
- Zepeda, Z.C. (1968) The Geology of the Flint Clay Deposits in Bulala, Capalonga, Camarines Norte : Unpublished Report, Bureau of Mines, Philippines, 12pp.