

Mineralogy, Chemical Composition and Ceramic Properties of Clay Deposits in Southern Thailand

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ABSTRACT

The mineralogical, chemical composition and ceramic properties of clay deposits from southern Thailand were studied to assess their potential for use in the ceramics industry. Samples were collected from 11 localities where clay mining and processing plants are active in southern Thailand. X-ray powder diffraction patterns with sample treatments by glycolation and heat treatment were used to analyze the clay and non-clay minerals and the X-ray fluorescence method was used for elemental analysis. The data collected from these techniques showed that the clay minerals were kaolinite, halloysite and illite and the non-clay minerals consisted of quartz, microcline, gibbsite and anatase. The results from the chemical analysis of the clay samples showed that the most important components were SiO₂ (46.75–63.17%) and Al₂O₃ (20.01–37.03%), since they have a conclusive influence on the refractoriness and strength of the final product. Firing characteristics from 800 to 1,300 °C were used to determine firing shrinkage, color, bulk density, modulus of rupture, water absorption and phase transformation. Ranong clays had the necessary properties for the manufacturing of ceramic products. However, for clays from Nakhon Si Thammarat, Surat Thani and Songkhla, it will be necessary to add other components to enhance their workability.

Keywords: mineralogy, chemical analysis, ceramic properties, clay, Southern Thailand

INTRODUCTION

The Office of Industrial Economics (2009) reported that the ceramic industry is important in Thailand and is supported and promoted by the government because it uses mostly domestic raw materials and the production of ceramics employs many workers and contributes income to many local areas. In the past, the production of ceramics in Thailand was used to substitute for more costly

imports but the local technology has continually developed so that now Thailand has become one of the main ceramic manufacturers in Asia with ceramic products primarily exported to Japan, the United States, Australia, China, Germany and ASEAN; in 2009, the total export value of ceramic products was USD 538.23 million (The Office of Industrial Economics, 2009). The development of local ceramic industries in any area is dependent on the availability of a local good clay resource.

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Clays are used as raw materials in many industrial fields (ceramics, paper, paints, petroleum products, among others). Their applications depend on their structure, composition and physical attributes and knowledge of these characteristics can help to determine the best way to utilize any particular clay and may often lead to new areas of applications (Baccour *et al.*, 2008). Two types of clays are generally used—kaolin and ball clays. Kaolin is one of the most useful industrial minerals with a wide range of applications; kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is the main mineral in both clay types and this is composed of alternate octahedral gibbsite and tetrahedral silica layers to give a plate-like structure (Chandrasekhar and Ramaswamy, 2007). In kaolin, minor quantities of quartz and transition elements such as iron, titanium and manganese are generally present as additional minerals (Chandrasekhar and Ramaswamy, 2007). Ball clays are finer than kaolin and are often referred to as plastic clays as they provide a greater plasticity in the ceramic body (Das *et al.*, 2005).

The characteristics and quality of the clay are important for the best technical performance of the local products. Moreover, a specific deposit may have separate layers each associated with different clay. This provides opportunities to mix different clays in order to adjust the properties of both the

unfired ceramic body and the corresponding final product (Viera *et al.*, 2008).

Each ceramic product requires clays having particular and appropriate characteristics. However such characteristics of the material are still only poorly determined. The present paper discusses in detail, the processing of ceramics using clays from southern Thailand. The detailed studies of the physico-chemical properties, mineralogical composition, the effect of firing temperature and the characteristics of the ceramic bodies in each location were undertaken. The results can then be compared with standard criteria, phase transformations and utilization of the triaxial formula of clay. Thermal behavior is related to the mineralogical composition of the clays and is used to determine their possible use in ceramic production.

MATERIALS AND METHODS

Sources of clay samples

Clay samples were collected from 11 clay mining and processing plants situated in southern Thailand (latitude 6° to 11° N; longitude 98° to 102° E) as shown in Figure 1 and Table 1. The geology of the clay deposits in southern Thailand has been studied and mapped by the Department of

Table 1 Clay sample code, name and source of the clay samples.

Code	Name	Source
a	Kaolin	A. Muang Ranong, Ranong.
b	Kaolin	A. Muang Ranong, Ranong.
c	Kaolin	A. Muang Ranong, Ranong.
d	Kaolin	A. Muang Ranong, Ranong.
e	Kaolin	A. Muang Ranong, Ranong.
f	Kaolin	A. Muang Ranong, Ranong.
g	Ball clay	A. Chaloeiphra-kiat, Nakhon Si Thammarat.
h	Kaolin	A. Muang Surat Thani, Surat Thani.
i	Brick clay	A. Bangkam, Songkhla
j	Ball clay	A. Lansaka, Nakhon Si Thammarat
k	Kaolin	A. Lansaka, Nakhon Si Thammarat
C16	Compound clay	Compound Clay Co., Ltd. Khlongsamwa, Bangkok

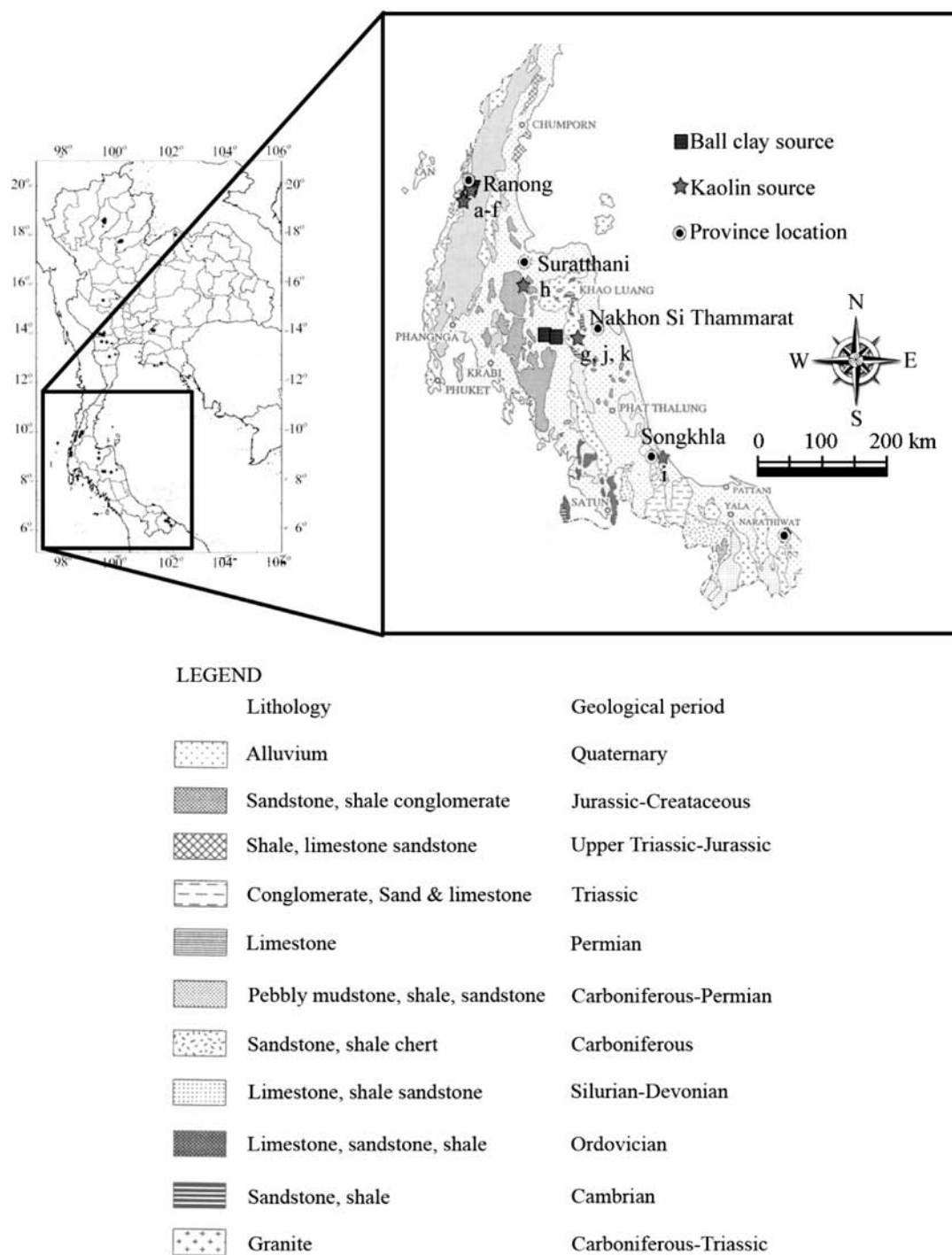


Figure 1 Map showing sampling locations of clay deposits (a–i) in southern Thailand; modified from DMR (2002) and Bhongsuwan (1993).

Mineral Resources (Figure 1). Kaolinitic deposits in this area contain two kaolin facies that result from 1) a residual deposit and 2) transport deposits. A residual deposit results from a hydrothermal alteration and a pneumatolithic process derived from granitic rock (Table 1, samples a-f; Ranong clays). Kaolinite and halloysite are the two major clays found in this area. They are formed by the pneumatolytic process occurring on medium-grained tourmaline granite with disseminated cassiterite (tin) occurring together with the clay minerals derived from the alteration of feldspar. These localities were well known as tin-producing areas forty years ago, but they are now producing clay instead, with the estimated clay resources being at least 30 million t (Keuntan, 1988).

Transport deposits are derived from rock sources consisting of shale, sandstone, mudstone or calcareous shale, such as samples g–k from Nakhon Si Thammarat, Surat Thani and Songkhla provinces. The Nakhon Si Thammarat clay deposit was located on the alluvial and flood plain areas of the Ta Pi River. The top layer was brownish yellow clay about 1.0 m in thickness, overlying dark brown ball clay 1.0–2.0 m thick. Locally, some pinkish clay deposits found as lenses or pockets of a few meters have also been recorded (Keuntan *et al.*, 1978). According to the mining lease, the ball clay reserve was estimated to be 126,000 t and the kaolin reserve was approximately 480,000 t. The Surat Thani clay deposit was located in west Khao Luang on a hill on the plain with a top soil thickness of 0.5 m. It comprised clay soil underlain by a layer of kaolin 8–10 m in thickness. The estimated clay resource was reported to be at least 4 million t (Keuntan *et al.*, 1978).

Mineralogical and chemical analysis

All clay samples were dried at 110 °C for 24 hr and desegregated through a 100-mesh sieve shaker (ANF -30; Dainippon Seito K.K.; Tokyo, Japan). The mineralogical analyses of clay samples were carried out by X-ray diffraction (XRD) techniques. To obtain a clay pattern more

clearly for XRD analysis, the less than 2 µm fraction was analyzed on glass slides. The less than 2 µm clay sample fraction was obtained by an oriented aggregated specimen preparation using a filter membrane technique (Drever, 1973; Poppe *et al.*, 2001). A 0.45 µm membrane filter was placed on a glass slide, mounted and placed over a suction flask. A pipette sample was added to the flask and suction was applied to force the sample onto the filter membrane. The filter membrane was then placed upside down on a glass slide, pressure was applied and the filter membrane removed, leaving the extract adhering to the slide. For clay mineralogical analysis, samples of these were dried at room temperature, while other samples were glycolated overnight at 65 °C for detection of expandable minerals, whereas further samples were heated for 3 hr at 400 and 550 °C to differentiate chlorite and kaolinite (Baccour *et al.*, 2009). The crystalline phases present in the materials were examined by X-ray powder diffraction, Phillips X'Pert MPD; PANalytical; Almelo, The Netherlands) using Cu-K_α radiation (λ = 1.5406 Å) with an Ni filter to get monochromatic Cu-K_α tube, 40 kV applied voltage and a current of 30 mA, a diffraction pattern spanning from 5°–90° (2θ) with a step size of 0.02° (2θ). Mineral phases were identified by the search-match method, using the JCPDS-ICDD data base and X'Pert HighScore software. The semi-quantitative analysis of crystalline phases was evaluated by the reference intensity ratio method (Chung, 1974). The normalization used in this method assumes that the sum of all identified phases is 100%. This means that only the crystalline phase would be identified with no amorphous phase present in the sample. Under these conditions, the semi-quantitative result is calculated by Equation 1:

$$X_{\alpha} = \frac{I_{(hkl)\alpha}}{RIR_{\alpha} I_{(hkl)\alpha}^{rel}} \left[\frac{1}{\sum_{j=1}^n (I_{(hkl)'j} / RIR_j I_{(hkl)'j}^{rel})} \right] \quad (1)$$

where X_α is the concentration of phase α ; $I_{(hkl)}$ and $I_{(hkl)}^{rel}$ are intensities of the selected Bragg reflection hkl, for phase α in the measurement and ICDD, respectively; $I_{(hkl)'j}$ and $I_{(hkl)'j}^{rel}$ are intensities of the selected Bragg reflection hkl for mixture in the measurement and ICDD, respectively; RIR_α and RIR_j are reference intensity ratio (RIR) values of phase α and the mixture, respectively.

The chemical composition was determined by wavelength dispersive X-ray fluorescence spectroscopy (WDXRF) in a Phillips PW2400 apparatus (PANalytical; Almelo, The Netherlands).

Microstructure analysis; SEM and LPSA

Microstructures of clay samples were examined using scanning electron microscopy (SEM), after coating with gold using a JEOL, model JSM-5200 (JEOL Ltd.; Tokyo, Japan). The particle size distribution of the clay samples was analyzed using a laser particle size analyzer (LPSA), with a model LS230 (Beckman Coulter Inc.; Brea, CA, USA).

Thermal analysis

A differential thermal analyzer (DTA; DTA7; PerkinElmer Inc., Waltham, MA, USA) and a thermogravimetric analyzer (TGA; TGA7; PerkinElmer Inc., Waltham, MA, USA) were used to study the kinetics of any phase transformation processes and chemical reaction mechanisms up to 1,300 °C with a heating rate of 10 °C.min⁻¹. The finely ground sample was introduced into a platinum crucible and placed in the furnace along with the reference sample.

Ceramic properties

This study focused on the possibility of using clay in the ceramics industry so industrial tests were carried out as part of the evaluation process. Clay samples were dried at 110 °C for 24 hr and ground to a fine powder and sieved through -100 meshes. The fine powder was homogenized and 30 g lots were separated for preparation for

testing. The dry powders were mixed with 5–6% by weight of distilled water and rectangular bars were prepared using uniaxial compaction at a pressure on the clay bodies of 5,000 kg hydraulic presser (40 t; Carver Inc.; Wabash, IN, USA) to produce rectangular bars (14.90 × 89.90 mm). All clays were subjected to heating overnight at 110 °C in an oven (ED 240 (E2); Binder GmbH; Tuttlingen, Germany) then fired at temperatures of 800, 1,100, 1,200 and 1,300 °C in a kiln (model UAS16/10/24/16 CG; Lenton Thermal Designs Ltd; Derbyshire, UK). The fired samples were tested for color, loss on ignition, shrinkage after firing (using an in-house method, based on American National Standard, 1976), modulus of rupture (using an in-house method, based on American National Standard, 1981). Bulk density and water absorption (using an in-house method, based on American National Standard, 1977) were determined by a boiling water method (American National Standard, 1977). A universal testing machine (5503, 50 kN; Instron High Wycombe, UK) was utilized to determine the modulus of rupture. The color measurements were made by a scanner (Model HP Scanjet G2410; Hewlett-Packard Co.; Palo Alto CA, USA) attached to a computer for processing.

RESULTS AND DISCUSSION

Mineralogy analysis

Figure 2 shows the X-ray diffraction pattern of sample a of the studied clays. The following mineralogical phases were identified: kaolinite (International Centre for Diffraction Data (ICDD) reference pattern: 01-079-1570), quartz (ICDD reference pattern: 01-082-0511) and illite (ICDD reference pattern: 00-026-0911). The mineralogical compositions of the raw materials are summarized in Table 2 and indicate that the mineral associations are the same in all cases and correspond to a mixture of kaolinite, halloysite, quartz, illite, anatase, microcline and gibbsite.

Treatments including air drying, glycolation, heating at 400 °C and heating at 550 °C were necessary to identify the type of clay minerals.

Kaolinite was present in a small amount in the sample characterized by a 7.1 Å (001) reflection that did not expand during glycolation, but completely disappeared after heating at 550 °C (Figure 3). In the kaolinite group, two clay minerals, kaolinite and halloysite had similar characteristics in the X-ray diffractogram after treatment. In order to identify them, SEM was

used (Figure 4). Tubular grains present in sample k indicated the presence of halloysite (Figure 4b) whereas sample a consisted of both platy (kaolinite) and tubular (halloysite) grains (Figure 4a).

Illite is a group name for a non-expanding mineral. It is structurally similar to muscovite (Poppe *et al.*, 2001) and is characterized by intense 3.3 Å (002) and 10 Å (001) peaks that remain unaltered by ethylene glycol treatment and heat treatment to 400 °C and 550 °C, as shown in Figure 3.

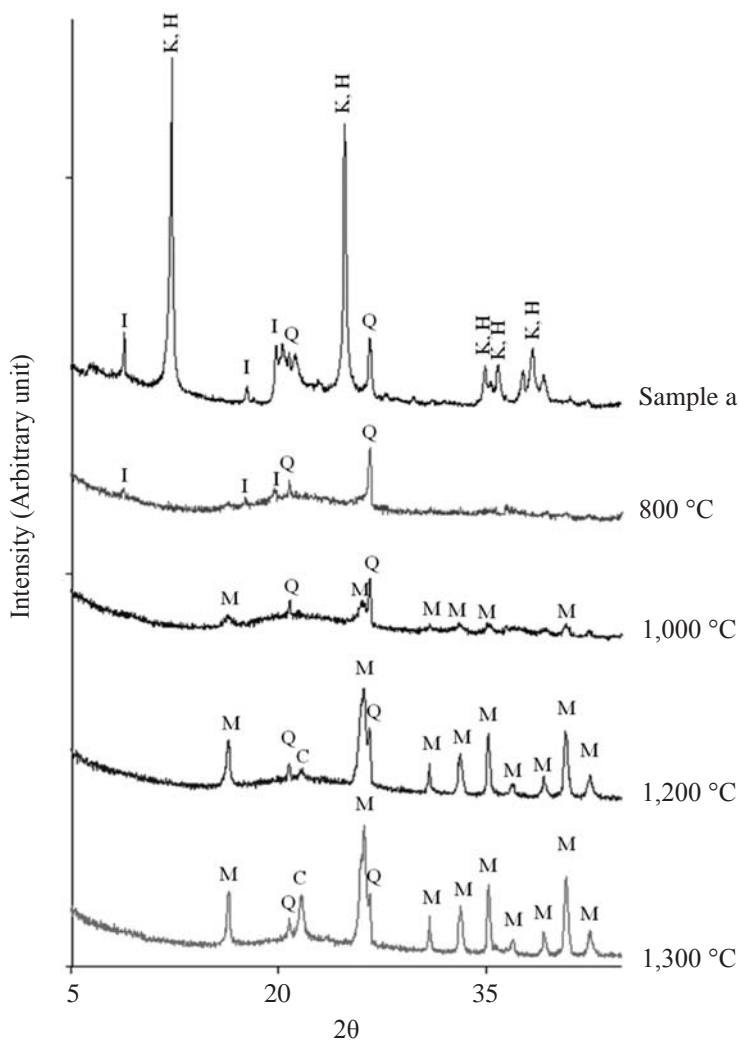
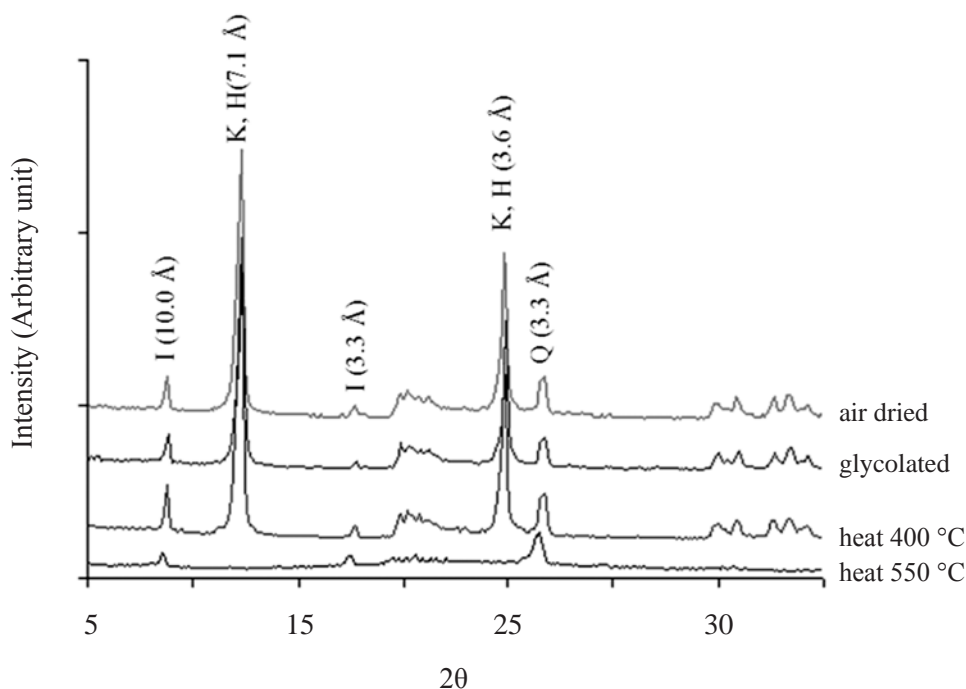


Figure 2 X-ray diffraction patterns of kaolin Ranong (sample a) sintered at various temperatures. (I = Illite, K = kaolinite, H = Halloysite, Q = Quartz, M = Mullite, C = Cristobalite. Sample a curve is based on room temperature of 25 °C.

Table 2 Results of chemical composition, loss on ignition (LOI) at 900 °C, and mineralogy of clay samples.

S	Chemical composition (%)									Mineralogy					
	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	LOI	Q	K&H	I	G	A	M
a	0.05	0.04	37.03	47.13	1.65	0.01	0.03	0.78	13.2	✓	✓✓✓ _(K,H)	✓	✗	✗	✗
b	0.18	0.05	34.66	48.17	2.43	0.02	0.05	1.25	12.9	✓	✓✓✓ _(K,H)	✓	✗	✗	✗
c	0.15	0.09	33.53	47.54	4.82	0.07	0.08	1.93	11.3	✓	✓✓✓ _(K,H)	✓	✗	✗	✓
d	0.11	0.06	35.24	47.34	1.23	0.02	0.09	1.68	14.1	✓	✓✓✓ _(K,H)	✓	✓	✗	✗
e	0.05	0.10	35.33	46.75	1.14	0.01	0.06	2.21	14.2	✓	✓✓✓ _(K,H)	✓	✗	✗	✗
f	0.04	0.05	34.71	47.13	2.49	0.03	0.11	2.48	12.8	✓	✓✓✓ _(K,H)	✓	✗	✗	✗
g	0.26	0.37	27.27	50.18	2.56	0.39	1.00	4.65	13.2	✓✓	✓✓✓ _(K)	✓	✗	✗	✗
h	0.08	0.13	29.75	53.79	1.38	0.08	1.86	2.66	10.2	✓✓	✓✓ _(K)	✗	✗	Tr	✗
i	0.05	0.39	20.01	63.17	2.77	0.09	0.93	4.90	7.5	✓✓	✓ _(K)	✗	✗	✗	✓
j	0.16	0.27	25.94	49.65	3.75	0.68	0.56	3.42	15.4	✓✓	✓✓ _(K)	✓	✗	✗	✓✓
k	0.05	0.08	34.10	46.86	0.80	0.13	2.72	2.27	12.6	✓✓	✓✓✓ _(H,K)	✗	✗	Tr	✗
C16	0.71	0.24	22.98	61.87	2.46	0.58	0.41	2.13	8.5	✓✓	✓✓✓ _(K)	✓	✗	✗	✓✓

S = Sample identifier, Q = Quartz, A = Anatase, K=Kaolinite, I = Illite, M = Microcline, G = Gibbsite, H = Halloysite (identified from scanning electron microscopy). ✓✓✓ = dominant (more than 50%), ✓✓ = moderate (20–50%), ✓ = minor (5–20%), Tr = trace (less than 5%), ✗ = not found.

**Figure 3** X-ray diffraction patterns of oriented aggregate of kaolin Ranong (sample a); I = Illite, K = kaolinite, H = Halloysite, Q = Quartz.

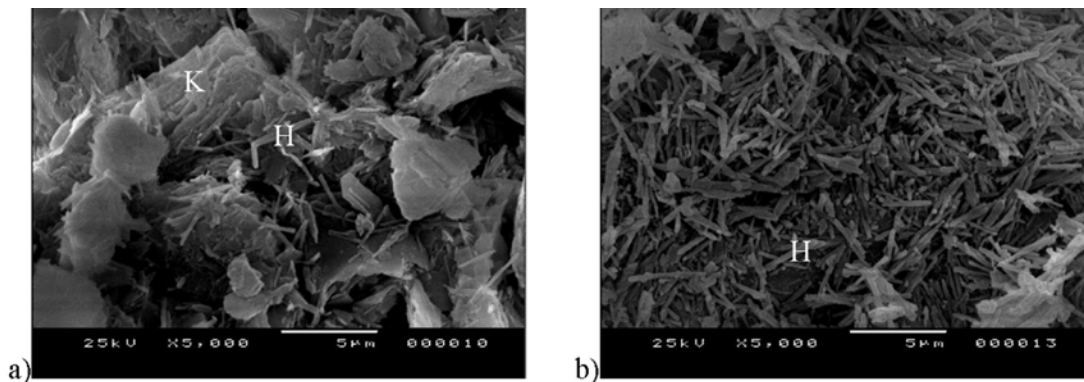


Figure 4 Scanning electron microscope micrographs of: a) kaolin Ranong (sample a); and b) kaolin Nakhon Si Thammarat (sample k). K = kaolinite and H = Halloysite. White scale bar = 5 μm .

Based on the X-ray diffraction patterns, it is possible to describe the transformations undergone by the clay at different temperatures (Figures 2 and 3).

At 550 $^{\circ}\text{C}$, (Figure 3) the peak of kaolinite was not seen; kaolinite was transformed into metakaolinite by the removal of the hydroxyl groups of the silicate lattice above 450 $^{\circ}\text{C}$. The peaks of quartz and illite were still observed.

Above 800 $^{\circ}\text{C}$, (Figure 2), the densification behavior of clay was influenced by the presence of flux materials such as K_2O , Na_2O and CaO that favored the formation of a glass phase (amorphous materials).

At 1,100 $^{\circ}\text{C}$, (Figure 2) the main phases present were quartz and mullite. In the X-ray diffractogram, it can be observed that the characteristic peaks of the kaolinite, illite have disappeared. A mullite phase (ICDD reference pattern: 00-001-0613) can be observed, as indicated by metakaolinite being decomposed into mullite and an amorphous phase by firing.

Above 1,200 $^{\circ}\text{C}$, (Figure 2) the amount of residual quartz decreased with the higher temperature, due to conversion of a part of SiO_2 into cristobalite (ICDD reference pattern: 01-082-0512). At 1,200 $^{\circ}\text{C}$, free SiO_2 transformed to cristobalite.

Particle size

The results of particle size distribution of clay samples are shown in Figure 5. All particles passed through 149 μm , whereas only approximately 85% of particle sizes were smaller than 44 μm . In Figure 5, the corresponding clay, silt and sand fractions are indicated according to the International Society of Soil Science (Baccour *et al.*, 2009). The clay and silt fraction (approximately 40%) was associated with clay minerals that were responsible for the plasticity.

Thermal analysis

Figure 6 shows the DTA/TGA curves recorded. First, a weight loss occurred that is related to the removal of adsorbed water up to ~ 250 $^{\circ}\text{C}$. The second weight loss up to ~ 550 $^{\circ}\text{C}$ is attributed to the combustion of the pressing organic additives and correlated with an endothermic reaction, due to the dehydroxylation. The curves decrease slightly at about 800–850 $^{\circ}\text{C}$ and this correlates with the endothermic reaction, as at this temperature the illite structure breaks down. The last exothermic peak occurs at $\sim 1,000$ $^{\circ}\text{C}$ and is attributed to a transformation in which an SiO_4 group combines with an AlO_6 group to form the Al-Si spinel phase, the precursor of the mullite crystallization (Carbajal *et al.*, 2007).

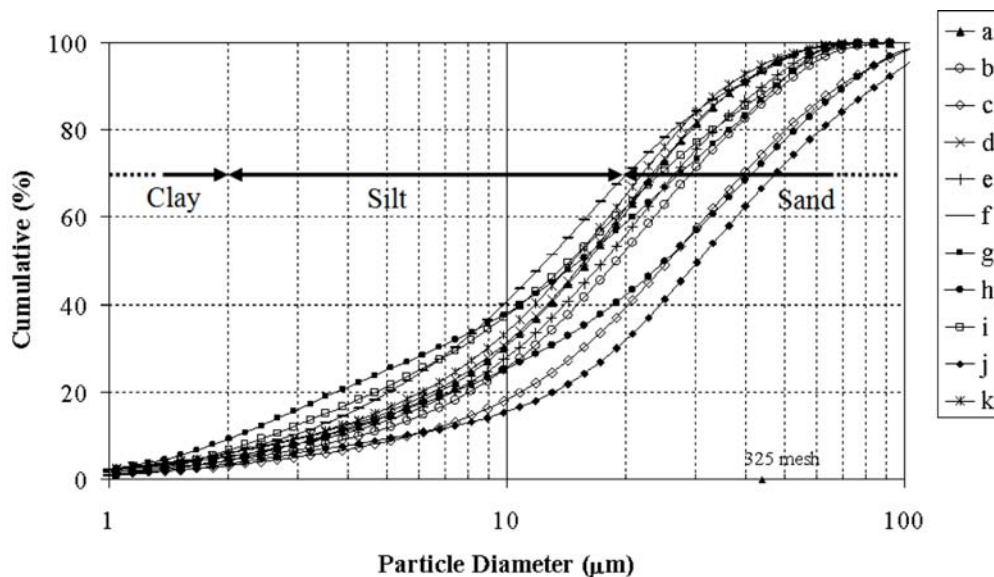


Figure 5 Particle size distribution of the representative clay samples (a – k = sample code from Table 1).

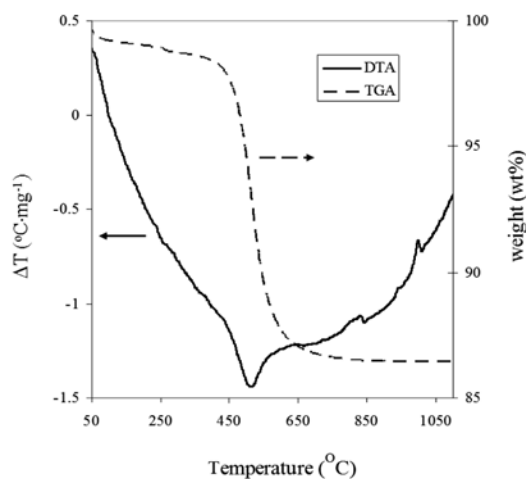


Figure 6 Differential thermal and thermogravimetric analysis of kaolin Ranong sample a. (wt% = Weight as a percentage of original weight, DTA = differential thermal analyzer, TGA = thermogravimetric analyzer.)

Chemical analysis

The chemical composition and the loss on ignition at 900 °C are shown in Table 2. The major

elements are SiO_2 (46.75–63.17 %) and Al_2O_3 (20.01–37.03 %) because of the presence of clay minerals and quartz. A substantial amount of iron oxide, which is responsible for the typical red color of unfired clays and fired clays at 800–1,300 °C, was present (Figure 7). The content of Fe_2O_3 was relatively high (on average 2.53%) but acceptable for use in the ceramics industry. However, Fe_2O_3 is not the only factor responsible for the coloration of ceramic wares, as there are also other components such as CaO , MgO and TiO_2 . After firing the representative samples to 1,300°C, the colors of the clays brightened due to the removal of the organic matter from the samples. Ranong clays (samples a–f) were somewhat white in color, which is good for ceramic products, whereas the color of Nakhon Si Thammarat, Surat Thani and Songkhla clays (samples g, h, i, j and k) were dark brown-grey (shown as darker shades in Figure 7). Another important component of the studied clays was the high content of K_2O (2.77–4.82%) in the clay samples c, i and j that was probably due to the presence of residual feldspar (microcline) and illite (Ligas *et al.*, 1997).

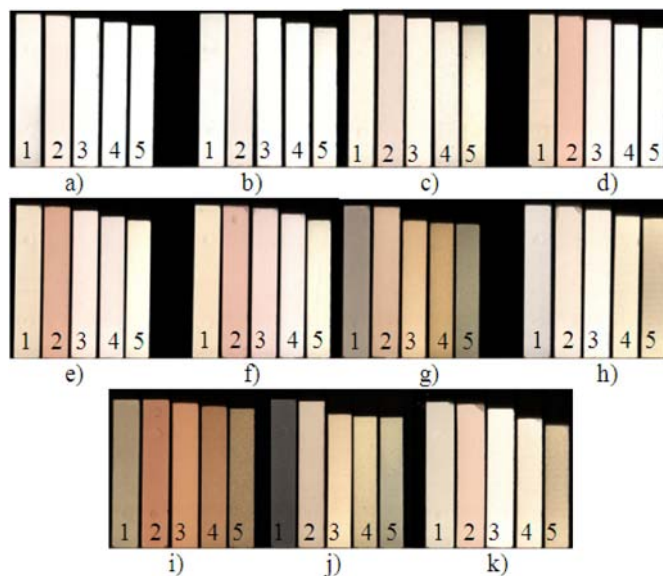


Figure 7 Fired and unfired clay at 800–1,300 °C. (1 = 110 °C, 2 = 800 °C, 3 = 1,100 °C, 4 = 1,200 °C, 5 = 1,300 °C (a – k = sample code from Table 1).

The loss on ignition (LOI) was related to the presence of substantial volatiles in the clay mineral, decomposition of carbonate, organic matter oxidation, and sulfides and hydroxides, among others (Baccour *et al.*, 2008; Viera *et al.*, 2008). Most clay samples had a higher LOI (11–15 %) associated with the presence of clay minerals and organic matter with the exception of the Songkhla clays (sample i), Surat Thani clays (sample h), and sample C16 which ranged from 7–10% (Table 2), probably due to the higher quartz content in these samples. The amount of earth-alkaline (CaO and MgO) was low, implying that the clays contained a small amount of carbonate.

The chemical compositions in the clays are presented as ternary diagrams of silica-alumina-other oxides (Figures 8a and 8b).

The clays had a wide range of silica and alumina content. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio ranged between 1 and 2 with the exception of clay sample i, which indicates that these two dominant component of the clays are mixed in a 1:1 ratio (dioctahedral phyllosilicates) close to the theoretical ratio of pure kaolinite (Baccour *et al.*,

2008). The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is slightly different from the theoretical ratio probably as a result of the presence of some quartz, illite, gibbsite and feldspar. Ranong and Nakhon Si Thammarat clays (samples a–f, k) are similar to those from Latium, central Italy and some parts of (AKW) Bavaria, Germany which are used in high quality products when the clays are mixed with quartz and feldspar (Ligas *et al.*, 1997). Surat Thani clay (sample h) was higher in SiO_2 (53.79%) and lower in Fe_2O_3 (2.66%) and was similar to the Klardorf clay from Bavaria, Germany (Figure 8a). Songkhla clay (sample i) and Nakhon Si Thammarat clay (samples g and j) had a higher SiO_2 content (63.17, 50.18 and 49.65%, respectively) and a lower Al_2O_3 content (20.01, 27.27 and 25.94%, respectively), and were similar to a typical commercial ball clay, as shown in Figure 8a (Dondi *et al.*, 2001). Thai commercial compound clay (sample C16) was similar to the clays from Saxony, Germany (Figure 8a), Clays should be modified in order to make their chemical composition closer to the ideal. The chemical composition of samples a–f, h and k was within the range nominated for white

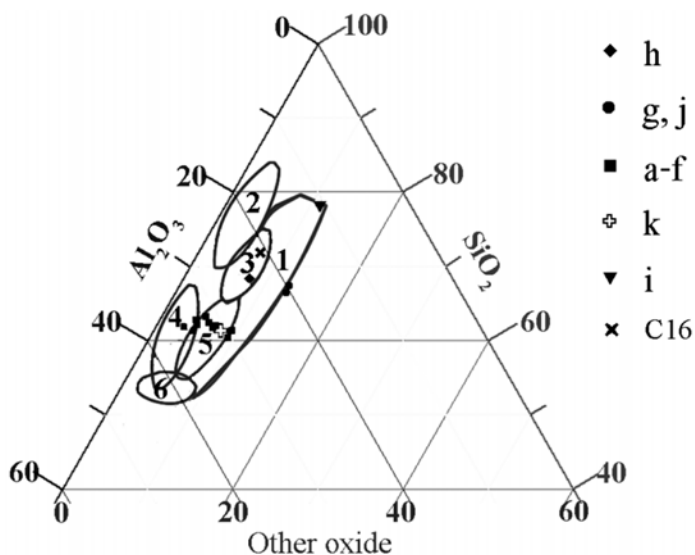


Figure 8a Ternary diagram of silica-alumina-other oxide for clay samples and comparison with the chemical composition of commercial kaolin (Ligas *et al.*, 1997) and ball clays (Ligas *et al.*, 1997; Dondi *et al.*, 2001, Nkoumbou *et al.*, 2009). The numbers (1–6) refer to different clays (1 = commercial ball clay, Italy, 2–6 = commercial kaolin; 2 = Latium, Italy, 3 = Saxony Germany, 4 = (AKW) Bavaria, Germany, 5 = (Klardorf) Bavaria, Germany and 6 = Devonshire, UK and Bretagne, France) (a – k = sample code from Table 1).

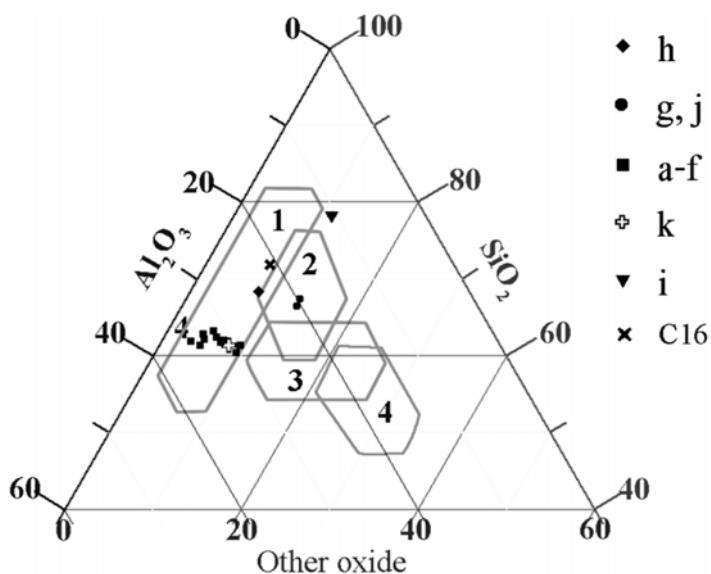


Figure 8b Ternary diagram of silica-alumina-other oxide for clay samples in comparison with raw materials currently used by Italian tile-makers (Strazzera *et al.*, 1997; Türkmenoğlu; Yavuz-Işık, 2008). The numbers 1–4 refer to clays for stoneware tiles (1 = white bodies, 2 = red bodies) and porous tiles (3 = cottoforte, 4 = majolica) (a – k = sample code from Table 1).

stoneware. The clay sample i from Songkhla was rich in alkaline-earth elements and had an Fe_2O_3 content within the range for red stoneware (Figure 8b). The chemical composition of Thai compound clay (C16) was within the range for white stoneware and near-red stoneware ceramic products. Samples j and g were just outside the borderline values for white stoneware and porous tiles (cottoforte). Therefore, most of the clay from southern Thailand can be used as raw materials for the ceramic industry. All samples were suitable for stoneware products (white and red bodies).

Ceramic properties

After drying for 24 hr, the clay samples were fired from 800 to 1,300 °C, and measurements taken of the bulk density, water absorption, modulus of rupture and firing shrinkage. The results are shown in Figure 9. All properties showed a dependence on the firing temperature. However there were no substantial differences in the results between 800 and 1,100 °C, but upon heating above 1,100 °C the bulk density, modulus of rupture and firing shrinkage continued to increase and water absorption continued to decrease.

The results indicated that water absorption is a function of temperature (Figures 9e and 9f). For all clays, the water absorption values decreased when the firing temperatures increased. It is well known that water absorption is closely related to densification, and the amount of quartz influences the quantity of the amorphous phase after sintering (Baccour *et al.*, 2009).

At 800°C, the firing shrinkage was small (0.11–1.15%). At this temperature the illite structure breaks down (illite peaks not seen in XRD) and the vitreous phases begin to form. Above 1,100°C, the curves of firing shrinkage show a sudden change (2.34–14.66%) associated with liquid phase formation. This phase penetrates the pores closing them and explains the decrease in water absorption in this temperature range (Monteiro and Vieira, 2004; Baccour *et al.*, 2008).

Above 1,100°C, the densification behavior of clay is influenced by the presence of flux materials such as K_2O , Na_2O and Fe_2O_3 in the clay materials that may contribute to vitrification (Iqbal and Lee, 2000). Considering the Thai Industrial Standard (TIS) for clays used in the pottery industry based on test fired clay at 1,200 °C (TIS 485-1999), the firing shrinkage values must be less than 12% (Thai Industrial Standard, 1999). The results showed that all the studied clays had a shrinkage value that complies with the standard. The shrinkage values of samples a–f and sample h ranged from 4 to 7%, and of samples g and k ranged from 10 to 12%, which were quite high when compared to the others. The brick clay (sample i) had a higher firing shrinkage (12.93%) at 1,300 °C while it was only 5% at 1,200 °C.

Figures 9a and 9b display the variation in the modulus of rupture of the studied clays with temperature. An increase in the modulus of rupture is related to the temperature increase when the sample becomes denser as a result of increasing bulk density. Up to 1,100 °C, only slight changes occurred. The increase was more pronounced above 1,100 °C except for samples h, j and k and a very pronounced slope was found with clays sample b and e. Ranong Clays (samples a–f) had high values of bending strength (13–31 MPa at 1200 °C) when compared to the Songkhla clay (sample i; 17 MPa), and Surat Thani (h) and Nakhon Si Thammarat clays (samples g, j and k) in the range of 5–9 MPa. The average modulus of rupture for the Ranong clays was significantly higher than those from other localities at the 95% confidence level at every firing temperature (data not shown).

Figures 9g and 9h show the variation in bulk density related to the firing temperature. No significant variation was observed in the bulk density values with a firing temperature lower than 1,100 °C (except for samples g and j). At firing temperatures higher than 1,100 °C, there were sudden increases in the bulk density (except for samples g and j).

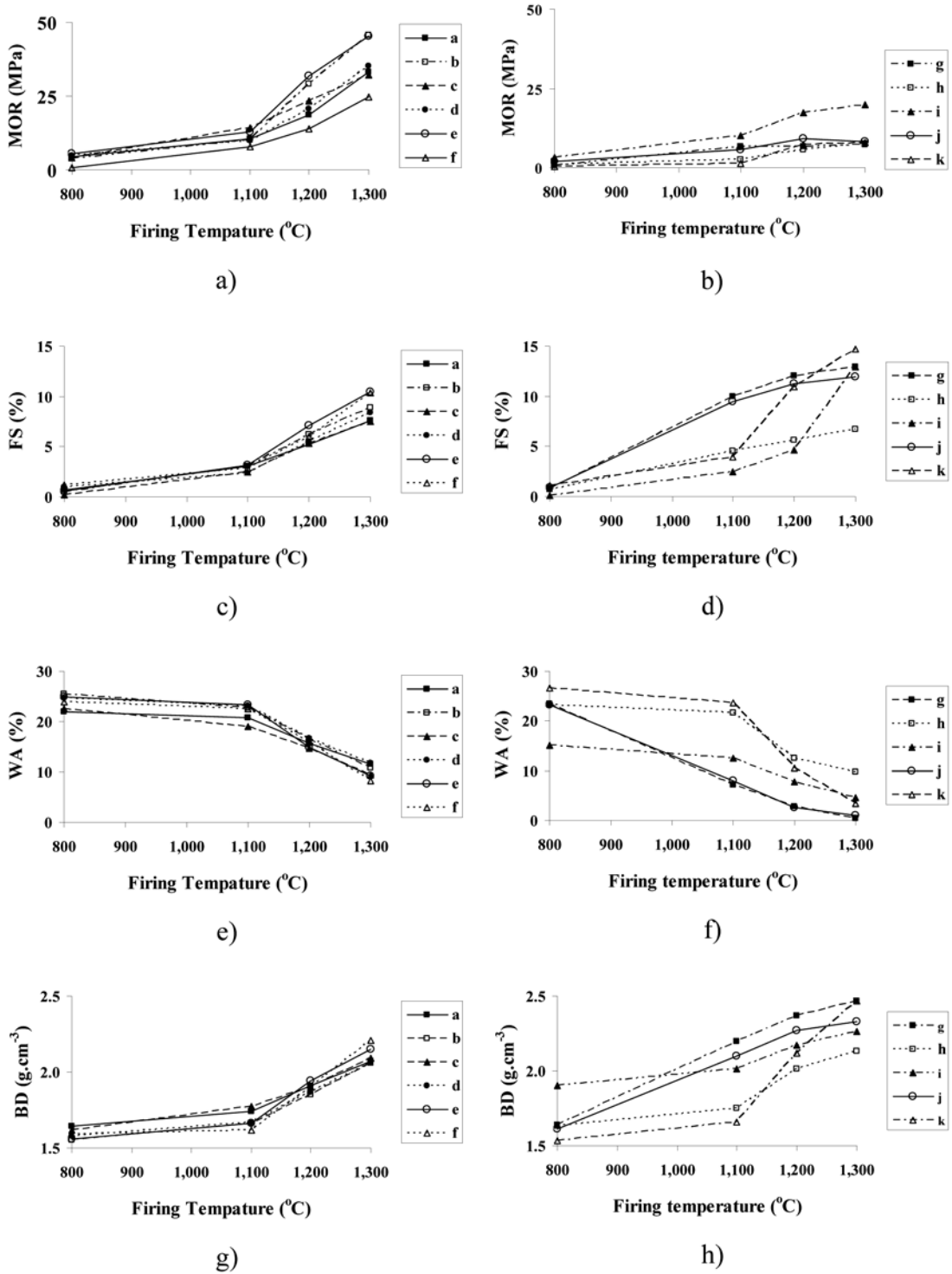


Figure 9 Physical properties of samples resulting from different firing temperatures. (MOR = modulus of rupture, FS = firing shrinkage, WA = water absorption and BD = bulk density) (a – k = sample code from Table 1).

The relationships between firing shrinkage and water absorption were strong (correlation coefficient (r) > 0.9) and there was a highly significant ($P < 0.01$) linear relationship on average between the variables (Figure 10). Comparisons were made between the properties of the clays in southern Thailand with commercial marketed kaolin. The water absorption and firing shrinkage values of local clays in southern Thailand were mainly characterized by lower values of shrinkage and water absorption than the commercial marketed kaolin (the shaded zone in Figure 10). This behavior may be explained by the abundance of mica (illite), feldspar (microcline) and silica that have lower values of shrinkage and water absorption (Siddiqui *et al.*, 2005).

CONCLUSION

Clays from southern Thailand were characterized by chemical, thermal and mineralogical analysis. The clays consisted of quartz, anatase, kaolinite, illite, microcline, gibbsite and halloysite. Chemical analysis showed that the most important components were Al_2O_3 and SiO_2 , since they have a conclusive influence on the refractoriness and strength of the final product.

During sintering, the phase transformations that occurred in the minerals present were mainly mullite, cristoballite and quartz. Sintering processes occurred and led to an improvement in the ceramic properties.

The present investigation can help to improve the main clays used for ceramics as well as contributing to correct exploration to facilitate the optimization of ceramic fabrication methods. Clays from southern Thailand are suitable for ceramic use in terms of their mineralogical and chemical composition and physical properties, inclusive of their firing shrinkage, color, bulk density, modulus of rupture and water absorption behavior.

Kaolin from Ranong (samples a–f), with a prominent modulus of rupture showed the best qualities. The fired clays were white in color and exhibited low firing shrinkage which is an interesting potential for use in the white ware ceramics industry. When the clays were fired to 1300 °C, their modulus of rupture and water absorption improved.

Kaolin from Surat Thani (sample h) showed medium quality. It was somewhat white in color but had a low modulus of rupture and so is suitable for ceramic white ware raw materials, which do not require a high bending strength.

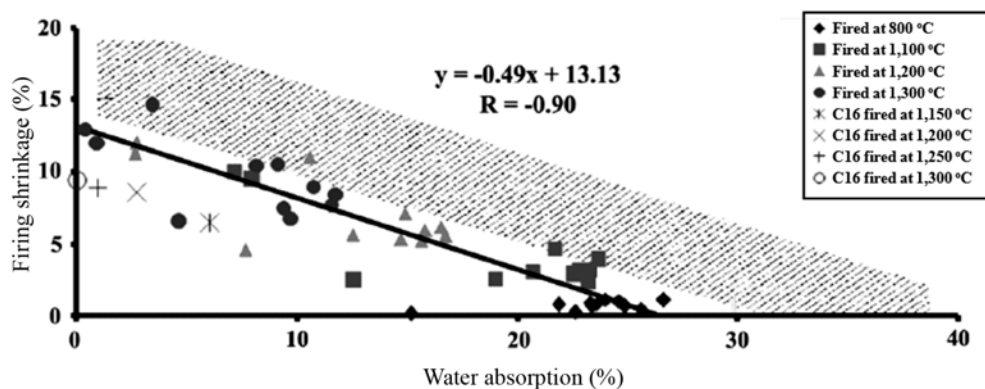


Figure 10 Relationship between water absorption and shrinkage after firing in kaolin for clays in southern Thailand and kaolin commercially marketed in Italy (the shaded zone) (Siddiqui *et al.*, 2005).

Brick clays from Songkhla (sample i) showed medium quality and should be suitable for ceramic products requiring a medium modulus of rupture, no white color and firing below 1,300 °C due to its high firing shrinkage.

Ball clays from Nakhon Si Thammarat (samples g and h) showed medium quality. They were suitable for ceramic raw materials that do not depend on the modulus of rupture and on having a white color. Their properties were probably due to the main composition of the ceramic mixture.

Kaolin from Nakhon Si Thammarat (sample k) was different as it mainly consisted of halloysite, because of the tubular structure morphology. Although the ceramic properties were not prominent, it is interesting from other points of view such as for the production of porous ceramics, use in water purification, use as a filler, for drug delivery and in ceramic nanotubes.

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LITERATURE CITED

- American National Standard. 1976. ASTM C 326-76: Standard Test Method for Shrinkages of Ceramic Whiteware Clays After Drying and Firing. **ASTM**. 271–272.
- American National Standard. 1977. ASTM C 373-72, Reapproved 1977: Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products. **ASTM**. 313–314.
- American National Standard. 1981. ASTM C 674-81: Standard Test Method Flexural Properties of Ceramic Whiteware Materials. **ASTM**. 674–678.
- Baccour, H., M. Medhioub, F. Jamoussi and T. Mhiri. 2009. Influence of firing temperature on the ceramic properties of Triassic clays from Tunisia. **J. Mater. Process. Tech.** 209: 2812–2817.
- Baccour, H., M. Medhioub, F. Jamoussi, T. Mhiri and A. Daoud. 2008. Mineralogical evaluation and industrial applications of the Triassic clay deposits, Southern Tunisia. **Mater. Charact.** 59: 1613–1622.
- Bhongsuwan, T. 1993. **Palaeomagnetic Investigations in Thailand**. Ph.D. Thesis, Luleå University of Technology, Sweden. 128 pp.
- Carbajal, L., F. Rubio-Marcos, M.A. Bengochea and J.F. Fernandez. 2007. Properties related phase evolution in porcelain ceramics. **J. Eur. Ceram. Soc.** 27: 4065–4069.
- Chandrasekhar, S. and S. Ramaswamy. 2007. Investigation on a grey kaolin from south east India. **Appl. Clay Sci.** 37: 32–46.
- Chung, F.H., 1974. Quantitative interpretation of X-ray diffraction patterns, I. Matrix-flushing method of quantitative multicomponent analysis, **J. Appl. Cryst.** 7: 513–519.
- Das, S.K., K. Dana, N. Singh and R. Sarkar. 2005. Shrinkage and strength behaviour of quartzitic and kaolinitic clays in wall tile compositions. **Appl. Clay Sci.** 29: 137–143.
- Department of Mineral Resources. 2002. **Map and Data of Mineral Sources**, Department of mineral resources, Bangkok, Thailand. 1 map sheet.
- Dondi, M., G. Guarini, P. Ligas, M. Palomba and M. Raimondo. 2001. Chemical, mineralogical and ceramic properties of kaolinitic materials from the Tresnuraghes mining district

- (Western Sardinia, Italy). **Appl. Clay Sci.** 18: 145–155.
- Drever, J.I. 1973. The preparation of oriented clay mineral specimens for X-ray diffraction analysis by a filter-membrane peel technique. **Am. Mineral.** 58: 553–554.
- Iqbal, Y. and W.E. Lee 2000. Microstructural evolution in triaxial porcelain. **J. Am. Ceram. Soc.** 83: 3121–3127.
- Keuntan, J., T. Pungrassami and P. Wasuwanich. 1978. **Clay**. Department of Mineral Resources, Bangkok, Thailand. 282 pp.
- Keuntan, J. 1988. **Clay Deposits in Thailand**. Conference on Mining 1988. Department of Mineral Resources, Bangkok, Thailand. August 17-19, 1988, 63-70 pp.
- Ligas, P., I. Uras, M. Dondi and M. Marsigli. 1997. Kaolinitic materials from Romana (north-west Sardinia, Italy) and their ceramic properties. **Appl. Clay Sci.** 12: 145–163.
- Monteiro, S.N. and C.M.F. Vieira. 2004. Influence of firing temperature on the ceramic properties of clays from Campos dos Goytacazes, Brazil. **Appl. Clay Sci.** 27: 229–234
- Nkoumbou, C., A. Njoya, D. Njoya, C. Grosbois, D. Njopwouo, J. Yvon and F. Martin. 2009. Kaolin from Mayouom (Western Cameroon): Industrial suitability evaluation. **Appl. Clay Sci.** 43: 118–124.
- Siddiqui, M.A., Z. Ahmed and A.A. Saleemi. 2005. Evaluation of Swat kaolin deposits of Pakistan for industrial uses. **Appl. Clay Sci.** 29: 55–72.
- Strazzera, B., M. Dondi and M. Marsigli. 1997. Composition and ceramic properties of Tertiary clays from southern Sardinia (Italy). **Appl. Clay Sci.** 12: 247–66.
- Thai Industrial Standards Institute. 1999. **Thai Industrial Standard, White Clay for Ceramic Industry**. Thai Industrial Standards Institute. Thailand. 7 pp.
- The Office of Industrial Economics. 2009. **Summary of Thailand's Industrial Economy in 2009 and Trends for 2010**. The Office of Industrial Economics Ceramic Industry. Thailand. 140 pp.
- Türkmenoğlu, A.G. and N. Yavuz-Işık. 2008. Mineralogy, chemistry and potential utilization of clays from coal deposits in the Kütahya province, Western Turkey. **Appl. Clay Sci.** 42: 63–73.
- Poppe, L.J., V.F. Paskevich, J.C. Hathaway and D.S. Blackwood 2001. **A Laboratory Manual for X-Ray Powder Diffraction**. USA. 88 pp.
- Vieira, C.M.F., R. Sanchez and S.N. Monteiro. 2008. Characteristics of clays and properties of building ceramics in the state of Rio de Janeiro, Brazil. **Construction and Building Materials** 22: 781–787.