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## Mineralogy of Clay Raw Materials from Côte d'Ivoire: Case of the Deposit from Katiola

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**Abstract:** This study deals with two clays referenced  $K_1$  and  $K_2$ , used in the local and traditional manufacture of pottery ware at Katiola. Those samples were analysed by X-rays diffraction, infrared spectroscopy and thermal differential and chemical techniques. The results show that the samples ( $K_1$  and  $K_2$ ) are mainly composed of montmorillonite, kaolinite and illite. Only  $K_1$  is inter-stratified. The mineralogical balance achieved from the reflection (001) of the oriented film, indicate for  $K_1$ : 74.5% of montmorillonite; 13.5% of inter-stratified clay; 7% of kaolinite and 5.4% of illite and for  $K_2$ : 73.4% of montmorillonite; 23.5% of kaolinite and 3.1% of illite. The results also indicate that the raw material may not be use only for pottery. It can be consider in the protection of the environment, cosmetic industry, vegetable oil treatment, medicine etc.

**Key words:** Clayey materials, mineralogy, chemical analysis, x-rays diffraction, thermal analysis, montmorillonite, environment

### INTRODUCTION

Clay has always played a major role in human life since it has a wide range of applications. The technological properties of clay raw materials depend on its mineralogical composition (Konta, 1995; Montes *et al.*, 2003). Several studies have demonstrated the relationship between crystal structure or crystal chemistry of the dominant phyllosilicate and the technological properties of clay: in the production of foods, beverage, paper, rubber, plastics, artificial leather, protective coatings for interior or exterior use, pharmaceuticals, cosmetics, paints, porcelain, fine ceramics, coarse ceramics and various branches of the chemical, petroleum and cement industries, agricultural, health, water treatment, civil engineering and environment (Ferrandon *et al.*, 1998; Elkebrokk and Saltnes, 2001; Cases, 2002; Hizal and Apak, 2006; Liang-Guo *et al.*, 2007; Assaad *et al.*, 2007).

The Bentonite was proposed as a barrier to protect against nuclear waste storage at its very high swelling-shrinkage and water adsorption potentiality (Pusch, 1992; Kacha *et al.*, 1997; Al-Tabbaa and Aravinthan, 1998). The experimental absorption reveals that clay may be quite effective in removing basic dyes like methylene blue and Congo red (Dipa *et al.*, 2002; Mumin *et al.*, 2007).

More knowledge about clay raw materials is needed to sustain the application suitable domains in Côte d'Ivoire, it is necessary to gather as much as possible all the information on the raw materials.

The clayey deposits from Côte d'Ivoire have been studied in detail, except that of the city of Katiola (Andji *et al.*, 2001; Andji, 2006; Konan, 2006). However clay raw materials of Katiola (in center of Côte d'Ivoire) are abundantly being used in pottery by the women (called Mangoros) organized in cooperative for several decades. The characteristics of these raw materials are completely unknown by the Mangoros who still use traditional techniques to produce the wares of pottery with a high rate of loss due to the drying technique they applied. This loss implies a drastic reduction in their income.

The present study investigates with different techniques the physicochemical and mineralogical characteristics of the raw materials of Katiola.

### MATERIALS AND METHODS

Two samples of clays ( $K_1$  and  $K_2$ ) used in this study are from the deposit of Katiola, a city located in the centre of Côte d'Ivoire. The accurate geographic coordinates of the samples  $K_1$  and  $K_2$  obtained from a Global Positioning

System are, respectively K<sub>1</sub>(N: 08° 14.709'; W: 005°06.505') and K<sub>2</sub> (N: 08°08.945'; W: 005°05.959 ').

A quantometer Jobin-Yvon 70-P equipped with ICP (Inductively Coupled Plasma) plasma was used to make the chemical analysis in total rock.

The x-rays diffraction was done with a Brucker's D8 diffractometer that use Co-K $\alpha$  monochromatic radiation ( $\lambda = 1.7889 \text{ \AA}$ ) at ambient temperature over the domain  $3 \leq \theta \leq 35$ .

The absorption spectra are carried out in the field of the mean infrared, that is to say for numbers of wave ( $\nu = 1/\lambda$ ) ranging between 400 and 4000  $\text{cm}^{-1}$ . Measurements were taken in diffuse reflection). In order to minimize the loss of energy, the samples are diluted in a KBr (70 mg of sample for 370 mg of KBr). The device used is a Fourier transform infrared spectrometer (Brucker YEWS 55). This device has a laser He-Ne and a high sensitive large bandwidth of wavelength (6000-600  $\text{cm}^{-1}$ ) detector of type MCT (Cadmium and Mercury Telluride).

The DTA-TGA was carried out with a device ATD Linseis, an entirely automated differential thermal analyser. The samples have been ground to a granulometry lower to 100  $\mu\text{m}$ . The reference is a charred alumina and the trial mass is 70 mg for the sample and the reference. The powders are packed slightly and the measures were carried out in identical platinum crucibles according to a programme for heating, run at  $10^\circ\text{C min}^{-1}$  under an air atmosphere.

**RESULTS AND DISCUSSION**

**Chemical analysis:** The chemical analysis results are presented in Table 1. From the analysis, one can see that the samples (K<sub>1</sub> and K<sub>2</sub>) have similar composition. Silica, alumina and iron are the main constituents of those samples. However, the percentage of alumina and iron is higher in K<sub>2</sub> than in K<sub>1</sub>. The results also reveal the presence of a relatively important amount of Mg in the samples. Nevertheless, the percentage of Mg is higher in K<sub>1</sub> than in K<sub>2</sub>. For what concern the chemical elements Ca, Na and K, the percentage is not negligible for K<sub>1</sub> but quasi inexistent for K<sub>2</sub>.

**X-rays diffraction:** Figure 1 shows the results of the analysis made with the X-rays diffraction. The diagrams were obtained from normal films and Ethylene Glycol (EG)

saturated films. The patterns exhibit predominantly the presence of inflating minerals in K<sub>1</sub> and K<sub>2</sub> (Brindley and Brown, 1980; Caillère *et al.*, 1982; Bouchet *et al.*, 2000). The wavelength of the major ray is shifted from 14.36  $\text{Å}$  to 17.132  $\text{Å}$  on the EG test. The diagram also shows a peak for K<sub>1</sub> at the wavelength 12.243  $\text{Å}$  confirming the presence of inter-stratified clay, probably illite-montmorillonite (Brindley and Brown, 1980; Caillère *et al.*, 1982).

The results of the Hofmann and Klemen (1950) test on K<sub>1</sub> and K<sub>2</sub> are shown in Fig. 2. It can be seen that the samples exchanged with lithium and heated at 300°C does not inflate anymore after saturation with glycerol. This structural modification can be explained as an irreversible closing of intrafoliar due to the migration of the Li<sup>+</sup> cations toward emptied octahedral cavities, characterizing the presence of montmorillonite clay.

**Infrared spectroscopy:** Inside the domain corresponding to the elongating vibration of the hydroxyl (3750-3500  $\text{cm}^{-1}$ ), the spectrogram shows a large massive complex that reflects the diversity of the hydroxyl groups environment (AlAlOH, AlMgOH, AlFeOH, FeFeOH etc.) (Fig. 3). The remarkable bands around 3696 and 3620  $\text{cm}^{-1}$  wavenumber confirm the presence of Kaolinite (Farmer, 1974). At low frequencies corresponding to the range 1000 to 600  $\text{cm}^{-1}$ , it is observed bands around 915, 890 and 795  $\text{cm}^{-1}$ . This can be attributed to the distorting vibrations of AlAlOH, AlFeOH and FeFeOH, respectively. This is characteristic of the presence of dioctahedral smectite. The other characteristic frequencies around the bands 1109 and 1017  $\text{cm}^{-1}$  correspond to the distortion vibrations of the SiO (Fripiat, 1970; Famer, 1974).

**Thermal analysis:** The plots of thermal analysis of K<sub>1</sub> and K<sub>2</sub> (Fig. 4, 5) are similar. Indeed, it can be observed:

- An intense and large endothermic peak around 130°C, corresponding to the starting point of the intra-sheets water.
- An endothermic accident of low intensity around 200°C, corresponding to the starting point of the hygroscopic water of associated minerals.
- From 450 to 600°C, an outstanding endothermic peak corresponding to the deshydroxylation explained by the following chemical equation:  $2(\text{OH}) \rightarrow \text{O} + \text{H}_2\text{O}$ .

Table 1: Chemical composition in total rock of the studied samples

Sample	Mass content													
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Slot	H <sub>2</sub> O <sup>+</sup>	H <sub>2</sub> O <sup>-</sup>	PF
	(%)													
K <sub>1</sub>	48.35	14.36	13.43	0.10	5.08	3.82	2.05	1.41	0.88	0.15	0.01	5.24	4.66	10.37
K <sub>2</sub>	47.98	17.58	13.81	0.04	3.23	0.76	0.31	0.50	0.84	0.00	0.01	8.68	5.46	14.90

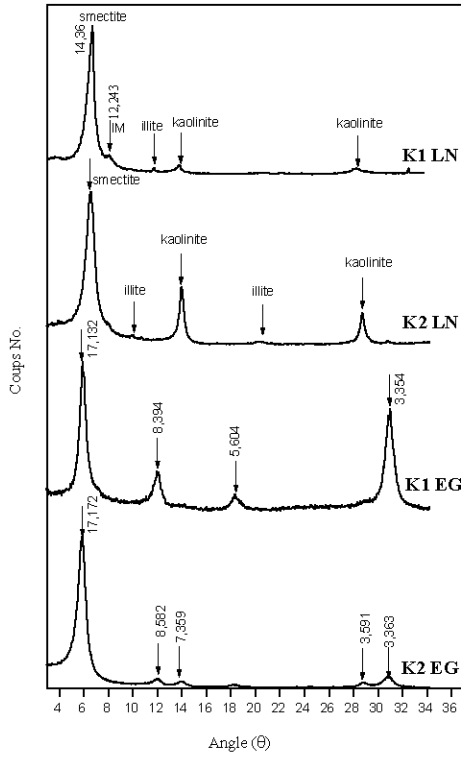


Fig. 1: Comparison of X-rays patterns of K<sub>1</sub> and K<sub>2</sub> obtained by normal thin films and saturated EG

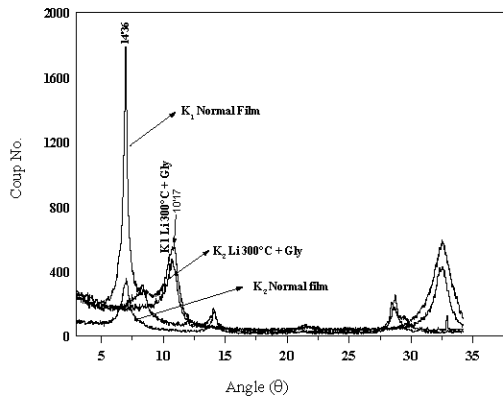


Fig. 2: Study of Hoffmann-Klemen effect on K<sub>1</sub> and K<sub>2</sub> samples

At 800°C, we also observe a relatively marked endothermic accident due to the emergence of an amorphous, followed by an exothermic peak which characterized the recrystallization toward 900°C (Greene, 1957). The position of the experimental peaks as described above (dehydration around 130°C and deshydroxylation between 450 and 600°C) corresponds to the phenomenon reported by several authors during

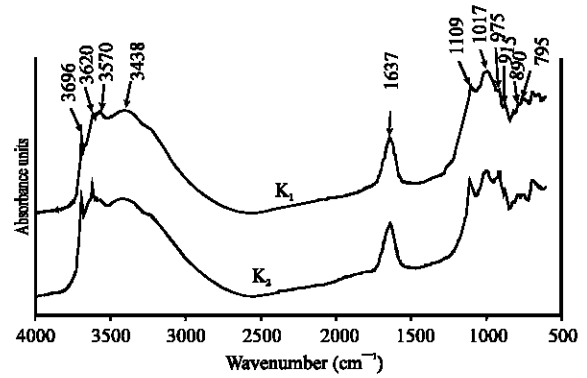


Fig. 3: Infrared spectrograms of K<sub>1</sub> and K<sub>2</sub> obtained with diffuse reflection

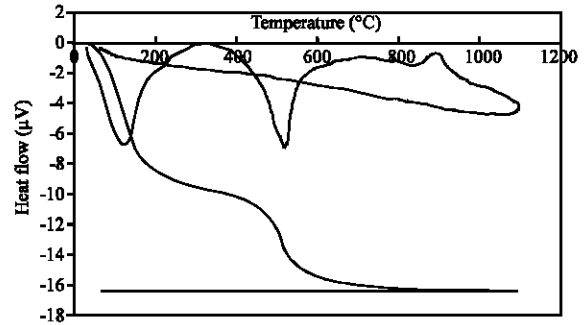


Fig. 4: Differential thermal analysis of K<sub>1</sub>

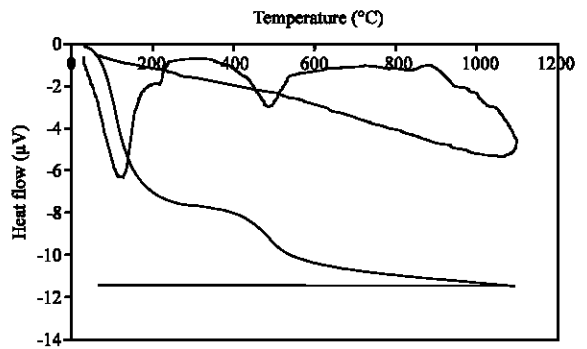


Fig. 5: Differential thermal analysis of K<sub>2</sub>

the heating of the phyllosilicates 2:1 dioctahedrals (Poinsignon, 1977; Emmerich *et al.*, 1999). In the case of the samples studied, the experimental peaks are probably cis-vacant montmorillonite clay, agreeing with the x-rays diffraction analysis (Emmerich *et al.*, 1999; Vantelon, 2001).

**Quantitative mineralogy:** It is noted that the samples of the deposits of Katiola are primarily made of inflating

Table 2: Relative quantification of argillaceous minerals present in K<sub>1</sub> and K<sub>2</sub>

Samples	Geographical coordinates	Kaolinite	Illite	Montmorillonite (%)	Interstratified	Total
K <sub>1</sub>	N: 08° 14.709° W : 005°06.505°	7.00	5.4	74.5	13.1	100
K <sub>2</sub>	N : 08°08.945° W : 005°05.959°	23.50	3.1	73.4	-	100

clays contrary to various deposits formerly highlighted through Côte d'Ivoire (Dorthe, 1984; Andji *et al.*, 2001; Konan *et al.*, 2001).

Indeed, the results show:

- For K<sub>1</sub>: 74.5% montmorillonite, with an inter-stratified clay (13.5), kaolinite (7%) and illite (5,4%).
- For K<sub>2</sub>: 73.4% montmorillonite, kaolinite (23.5%) and a trace of illite (3.1%).

These compositions could explain the difficulties experienced by Mangoro's cooperative. The results of quantitative mineralogy are consigned in Table 2.

Due to their high capacity of water absorb to inflate; montmorillonite clays induces strong withdrawals during the drying of the potters manufactured products (Delineau, 1994).

Taking into account their composition, K<sub>1</sub> and K<sub>2</sub> clays lets predict large perspectives in the clayey materials valorisation in Côte d'Ivoire. These materials can be used in environment protection, for heavy metals immobilization (Nir *et al.*, 1986; Carretero, 2002), in health science, cosmetic products and in all applications that use the properties of montmorillonites.

**CONCLUSION**

The experimental technique used for this study has shown that the studied sample K<sub>1</sub> is composed of montmorillonite (74.5%) associated with inter-stratified clay (13.5%), kaolinite (7%) and illite (5.4%). The sample K<sub>2</sub> is composed of 73.4% of montmorillonite 23.5% of kaolinite and 3.1% of illite.

The composition of the clay raw materiel explains the high rate of loss during the drying of potters products. Nevertheless, this raw materiel may be used in the cosmetic industry, in the environment protection and health science.

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