Comparison of Dry Grinding Effect on Commercial Quartz-Free and Tunisian Quartz-Rich Kaolin Clays milled using a Grinding Aid

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(Received: 14 June 2017, accepted: 28 August 2017)

Abstract: The activation effect generated by the dry grinding of a commercial quartz-free kaolin and a natural Tunisian quartz-rich kaolin was studied. The Tunisian kaolin has a similar chemical composition to that of pyrophyllite. The grinding operation was conducted using a laboratory planetary ball mill, while adding triethanolamine as a grinding aid. The textural analyses show that the grinding does not seem to follow the three steps conventionally observed when minerals are ground without the use of a grinding aid. The latter seems to prevent the particles agglomeration when minerals are milled for a long time. Regardless of the presence of quartz, a rapid and significant alteration of the kaolinite structure during the first 30 min of grinding was observed. Beyond those 30 min, alteration attenuates clearly. The distortion of the quartz structure follows a different evolution. Thermal events show classical evolution of the kaolinite dehydroxylation peak. However, the presence of quartz seems to affect the mullite crystallization peak: for the quartz-free sample, this peak widens but for the quartz-rich sample, it refines and its intensity increases when prolonging grinding. It is likely that Si-O-Al bonds are formed during grinding, where Si is derived from quartz and Al from kaolinite.

Keywords: Kaolinite, quartz, grinding, grinding aid, mullite.

Kaolinite is the main constituent of kaolin, and is formed by rock weathering, namely by the decomposition of potassium feldspars, aluminium silicates and granite [2]. Kaolinite has very important uses in industries. It is used extensively in the industries of ceramics, paint, plastics, papermaking and also for the production of synthetic zeolites. Since these industrial processes may include a grinding step, kaolinite has long been the object of studies that elucidate the transformations it incurs when it undergoes wet and dry grindings [3,4]. Both wet and dry grindings have been known for affecting solid materials resulting in the fragmentation of their particles, a change in their specific surface area, and a modification of their pore size distribution. These effects give rise to structural changes as polymorphic transformations like the amorphization of the material. Physicochemical changes are mostly observed when the grinding of materials is ensured by impact and friction forces, as vibratory, oscillating, and planetary mills [5,6]. In literature, the dry grinding of kaolin has been first ensured by a mechanical mortar that effectively ensured a change in the clay’s structure leading to a completely amorphous substance [7,8]. Later, ball-milling process has been used for the grinding of kaolin, and it has been proved that dry conditions were more effective to induce more

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amorphization compared to wet conditions [5]. Among current high-energy ball mill designs, planetary ball mill is characterized by significant centrifugal forces, reaching up to 20 times the gravitational acceleration. This design involves a repeated fracturing and soldering of particles leading to the reduction of their size and changes in their shape, affected by the milling parameters such as rotation speed, ball size, ball-to-powder weight ratio and milling time [9]. A huge number of studies has been conducted construing the effect of grinding on the structure of kaolinite for a better understanding of its structural behavior change [10]. At first, the dry grinding of kaolinite was found to result in the reduction of its particle size due to the cleavage and fracturing of the kaolinite crystal [11-13]. In the late 1950s, it was thought that the grinding of kaolinite produced a zeolite-like material, and two processes were identified: A first stage, where kaolinite layers were destroyed creating a new amorphous material, attended by the disordering of the crystals and the reduction of their particle size. In a subsequent stage, the ground particles were aggregated, producing an agglomerated material [22]. Later, complementary research proved that the decrease of particle size induced by the dry grinding of kaolinite, occurred along the c-axis of the crystals first, then mainly along the b-axis, and the resulting distortion was more important along the former axis [14-16]. The dry grinding of kaolinite was proved to be an effective method for the synthesis of nanomaterial [17]. Besides, dry grinding was found to not only cause the kaolinite layers to fragment resulting in the formation of spheroidal particles, but also to remove the hydroxyl units from the kaolinite leading to the formation of surfaces with new OH groups [18,19]. Further studies have shown that the mechanochemical treatment of kaolinite resulted in the loss of the d(001) peak intensity and caused the destruction of its crystal structure by the rupture of the O–H, Al–OH, Al–O–Si, and Si–O bonds [20,21]. Since the major mineral constituents of natural kaolin are kaolinite and quartz, the effect of quartz content in the distortion of kaolinite induced by dry grinding was obvious. Being so far not well defined, some researchers found needful to study the influence of the co-presean of quartz, whether natural or added, on the grinding of kaolinite. Makò et al. [21] have studied the role of quartz (a natural sand) content in the mechanochemical amorphization of kaolinite, and found out that the more quartz was added to kaolinite the more the mechanically induced amorphization of the kaolinite structure was accelerated. Their results indicated that the added quartz particles acted as grinding bodies during the intensive dry grinding of kaolinite. Frost et al. [22] have found out in a comparative study that low defect kaolinites were more mechanically altered than high defect ones. It was then claimed that the mechanochemical treatment effectiveness depended rather on the crystallinity of the kaolinite than on the presence of quartz. Later, Carmody et al. [24] figured out that the added quartz appeared to accelerate the kaolinite dehydroxylation process that seemed to be less pronounced when equal amount of natural quartz occurred within the experienced kaolinite sample. The evolution of the kaolinite thermal behavior as a function of the grinding time has been extensively studied by DTA-TG. Besides a typical evolution of the endothermic peak relative to the clay mineral dehydroxylation, contradictory results have been reported on the evolution of the exothermic peak that appears at high temperature. This disagreement has been found to probably result from differences in starting materials and compositions [6]. This peak was attributed to the crystallization of alumina-spinel transition and/or primary mullite phases [25]. According to Okada and Otsuka [26], the lower limit of kaolinite composition for the formation of Al-Si spinel is 30 wt. % of Al₂O₃. Furthermore, an increase in the intensity of this peak as a function of the grinding time has been reported in the case of pyrophyllite. Actually, the pyrophyllite belongs to the 2:1 group clay minerals with a structure consisting of an octahedral sheet sandwiched by two tetrahedral sheets, and it contains twice more silica than kaolinite.

In this paper, the mechanochemical activation of a commercial well-crystallized kaolin, and a Tunisian high-grade natural kaolin associated to significant amounts of natural quartz, is reported. A grinding aid was used during grinding. Grinding aids are widely used in the mineral industry in general to improve the energy efficiency of
grinding operations. The purpose of their use in this work is to avoid the sticking of thin layers of powder on the surface of the grinding bowl and balls after the milling operation, making the cleaning longer and more difficult and amplifying the abrasion effects. The first aim of this work is to study the effect of the addition of a grinding aid on textural, structural and thermal properties, of both quartz-rich and quartz-free kaolin samples during the grinding. The evolution of the ancillary quartz structure was also followed. As the chemical composition of the Tunisian clay is close to that of pyrophyllite, the effect of its grinding is particularly followed and compared to that of pure kaolinite and pure pyrophyllite already reported in the literature. Many techniques have been employed to study the structural processes during mechanochemical activation. Before mechanochemical treatment, the two kaolin powders have been characterized, in order to reveal their chemical and quantitative mineralogical compositions by XRF elemental analysis, their Loss on Ignition (LOI) at 1000°C by thermal analysis, the identification of their crystalline structure and the percentage of their crystallinity represented by the Hinckley Index (HI) by XRD analysis, their particle size distribution by PSD analysis, their Specific Surface Area by N₂-physisorption at 77K, and finally their textural morphology by SEM. These same characterization techniques were used to follow the effects of grinding on kaolinite samples.

**EXPERIMENTAL**

**1. Material**

The samples used in this study are two clays, a commercial kaolin (KC) and a Tunisian kaolin (KT). The commercial kaolin powder is provided in form of chalk-shaped paste, from SIBELCO, a supplier of advanced industrial minerals based in Bristol in United Kingdom. The Tunisian kaolin is extracted from clay deposits occurring at “Sidi El Bader” site situated at about 4 km east of Tabarka in the north-west of Tunisia [27]. Chemical composition of the two minerals was determined by X-ray fluorescence. Mineralogical composition was estimated using a quantitative approach developed based on the common content of alumina in kaolinite and illite, the distribution of silica between kaolinite, quartz and illite, and finally the mobilization of potassium by illite [28] (Table I).

<table>
<thead>
<tr>
<th>Sample</th>
<th>KC</th>
<th>KT</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>48.0</td>
<td>60.3</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>36.3</td>
<td>27.0</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.8</td>
<td>3.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.3</td>
<td>2.9</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.02</td>
<td>2.9</td>
</tr>
<tr>
<td>MgO</td>
<td>0.39</td>
<td>1.4</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>CaO</td>
<td>0.05</td>
<td>0.4</td>
</tr>
<tr>
<td>Cl</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>11.7</td>
<td>8.7</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>75</td>
<td>57</td>
</tr>
<tr>
<td>Illite</td>
<td>20</td>
<td>9</td>
</tr>
<tr>
<td>Quartz</td>
<td>-</td>
<td>32</td>
</tr>
<tr>
<td>Other minerals</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>(Mica, Feldspar)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hinckley Index</td>
<td>1.2</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Before characterization, selected Tunisian Kaolin rocks (KT) were prewashed, left to completely dry under sun, and crushed manually in an agate mortar till obtaining a homogeneous greyish powder. The Commercial Kaolin (KC) powder, provided in form of chalk-shaped paste, was also crushed manually in an agate mortar till obtaining a powder.

**2. Milling procedure**

A laboratory planetary ball mill (Pulverisette 7-type, Fritsch, Germany), equipped with a pair of agate grinding bowls of 80 cm³ inner volume, and ten (46.8 g in total) agate grinding balls (15 mm diameter), was used for the dry grinding of 11.7 g of kaolinite powder in each bowl. A constant 4:1 ball-to-powder weight ratio was fixed for all grinding sets. Powder samples were ground under atmospheric conditions, for desired milling times from 10 to 240 min, at a rotation speed of 600 rpm. The grinding series were performed, such as successive ten-minute milling cycles were each spaced by ten-minute ventilation break cycles, to ensure the cooling-down of the ball-mill and to prevent excessive heat build-up inside the grinding bowls. Preliminary grinding series were first performed without the addition of a grinding aid,
but a very hard and thick layer of powder sticked on the balls and bowls was observed once grinding was finished. These conditions would never be enticing for an industrialist applying minerals ball milling since extensive cleaning of the balls and bowls is needed. For this reason, triethanolamine (0.7 g) was used as a grinding aid to prevent the balls and bowls coating [29]. Both kaolin powders KC and KT were ground under precisely the same conditions. All samples are denoted KCt and KTt for the commercial kaolin and the Tunisian kaolin, respectively where t is the grinding time in minutes.

3. Characterization techniques
Elemental analysis was conducted in order to disclose the chemical composition of starting kaolin samples, using X-Ray Fluorescence spectroscopy performed with an S2 Ranger Energy Dispersive X-ray Fluorescence (EDXRF) analyzer from Bruker, operating with the Flash Technology. Once calibrated with the copper disc, and set to the Equa Powder mode, the sample was placed on a 2.5 μm Milar film inside the sample holder, and the analysis was conducted. The X-ray diffraction analyses of the samples were conducted with a 2-circle PANalytical XPert Pro Multipurpose Diffractometer (MPD) instrument, powered by a Philips PW3040/60 X-ray generator and fitted with an X'Celerator detector. Powder samples were exposed to Cu-Kα monochromatized X-ray radiation, which has a characteristic wavelength of 1.5418 Å. The data were collected over a 20 range of 5-50° with a scan rate of 0.02°/s. All measurements were made on disoriented powder samples. The quantitative mineralogical composition was estimated using a quantitative approach developed by Bich [28], based on the mineral chemical composition. The crystallinity index calculated by the Hinckley (1963) method, [30] called the “Hinckley crystallinity index”, was determined based on the intensities of the peaks revealed on the samples’ X-Ray diffractograms and was obtained by measuring the heights of the 110 and 111 kaolinite peaks in the region between 19 and 25° (20). Besides, the “Scherrer Equation” was used to estimate the size of the crystallite in studied solids. The value of the shape factor was taken equal to 0.9. The Fourier-transform infrared (FTIR) spectra were recorded using a Perkin-Elmer 882 IR spectrometer. Measurements were conducted in the wavenumber range 4000-400 cm⁻¹, on KBr sample-pellets. Particle Size Distribution (PSD) was measured using a Mastersizer 2000E laser diffraction particle size analyzer (Malvern Instruments Ltd., UK), covering the particle size range of 0.1-1000 μm, equipped with a Hydro 2000 SM Small-Volume Dispersion Unit. 50 mg of the samples were dispersed into 20 mL of deionized water, into where 1 drop of commercial ammonia solution was added, and the whole was ultrasonicated during 2 min. To maintain the analyzer software’s obscuration rate in range (5-10%), few drops (~ 5 mL) of the sample were added to the Small-Volume Dispersion Unit containing approximately 100 mL of distilled water with a stirring rate of 1500 rpm. Each result was the average of four successive measurements. Thermal analyses, namely Differential Thermal Analysis (DTA) and Thermo-Gravimetric Analysis (TGA), were carried out on a Labsys EVO instrument from Setaram, by placing around 40 mg of kaolinite sample in a 100 μL platinum crucible, and operating with a dynamic air stream as a carrier gas, and a heating rate of 10°C/min. Data acquisition was set with Labsys EVO software, and results processing and exploring were ensured with Calisto Processing software. The Specific Surface Area (SSA) of the samples was determined by the BET method. The N₂ adsorption isotherms were obtained at 77 K with an automatic system (Model No. ASAP 2020, Micromeritics Instrument Corp., Norcross, GA). Samples have been previously out-gassed to a vacuum between 10 and 5 Torr, at 120°C. Surface Areas (SBET) were calculated by applying the BET method to the linear section of the isotherms over 0.05-0.30 p/p°. Morphological characteristics of kaolinite samples were examined in a Zeiss Supra 40 Scanning Electron Microscope (SEM), equipped with a Back-Scattered Electron detector (BSE) and an Oxford INCA Energy Dispersive X-Ray Spectrometer (EDS), operating from 0.02 to 30kV. The samples were metallized with platinum and the images were taken at 15,000× magnification.

RESULTS AND DISCUSSION
1. Textural characterization
The specific surface area value recorded for KT sample (36 m² g⁻¹) is higher than that of KC sample (13 m² g⁻¹). This can be ascribed to the low crystallinity of the Tunisian mineral. Actually, the lower the crystallinity, the lower the number of sheets per primary particle and the greater the external surface [31]. Figure 1 displays the specific
surface area values evolution as a function of grinding time for KC and KT samples in presence of grinding aid. This figure evidences that during the first 60 min of dry grinding, the recorded specific surface area values are almost proportional to the grinding time, but with a more marked increase slope for KC. The slope decreases, for both KC and KT, for longer grinding times. After 4 hours of grinding, the two minerals converge to about the same specific surface area value (53 m$^2$ g$^{-1}$ for KC240 and 51 m$^2$ g$^{-1}$ for KT240) which seems to be the final reached surface. The changes in the surface areas of the minerals, characterized by different behaviors depending on the milling time, were often used to identify the different steps or sections of the grinding process. For kaolinite, three steps were reported in the literature: i) The cleavage section (Rittinger section) characterized by an increase in the surface areas caused by the fracture and disintegration of primary particles of the original material, ii) The aggregation section with a slight decrease in the surface areas and the formation of stable aggregates by material compaction, and iii) The agglomeration section when the surface area decreases dramatically [17,22]. In this work, only the first step was observed, while the aggregation and agglomeration steps were not clearly evidenced in figure 1.

The particles size distribution (PSD) of the commercial Kaolin and Tunisian Kaolin samples ground during 0, 30, 60 and 240 min, is displayed in figure 2. The particle size distribution is defined, by reference to a unit volume of suspension, as the average number of particles within a given size class of width. Because the particle shape is usually unknown, curves report the particle size as a volume equivalent sphere diameter [32]. The KC sample exhibits a bimodal distribution (Fig. 2-A-a) with two peaks centered at 0.7 μm and 7 μm respectively. These two peaks might correspond to two discrete kaolinite particle groups: 0.7 μm primary particles and 7μm flocculi [33]. Flocculi consist of strongly bound primary clay particles with a face-to-edge association. The KT sample exhibits a trimodal distribution (Fig. 2-B-a). In addition to the two peaks corresponding to the 0.7-μm primary particles and the 7-μm flocculi, a third peak appears at 2 μm. The latter would most probably correspond to the quartz. For both minerals, grinding does not seem to affect the size of the primary particles, but brings their quantity to slightly change.

Nevertheless, the shape of the peaks relative to the larger sized particles evolves considerably with the grinding time. During short grinding time, the intense 7-μm flocculi peak refines and decreases in intensity, to split into a new, not negligible, smaller-sized (3 μm), and a new bigger-sized (10.7 μm) flocculi populations. This move is basically...
accompanied by the increase of the specific surface area, proportional to the grinding time (Fig. 1). It would actually correspond to the disintegration of the original 7-µm floculi that break down and evolve towards finer particles (3 µm) generating more available surfaces. For longer grinding time (60 min), the peaks relative to primary particles and small floculi (3 µm) increase slightly in intensity, and those relative to the large floculi (7 and 10.7 µm) decrease gently in intensity. The disintegration process still continues and an increase in surfaces is still recorded. For KT, the shortly ground sample reveals a particles size distribution with an almost unchanged shape, but with a considerable drop in primary particles quantity, a slight increase in the original floculi quantity and the rise of a new bigger-sized (10.7 µm) floculi peak. For longer grinding time, the intensity of the peaks relative to both floculi decreases slightly, with a parallel increase in primary particles quantity. The effect of these two processes is manifested by the minor increase in the mean particle size (from 5.5 to 13 µm). However for KT, the very petty microflocs peak seen at 100 µm does not even affect the mean particle size that seems to remain almost unchanged for milling times up to 60 min (~6 µm). Similar results were previously disclosed as a decrease in particle diameters below 30 min of grinding, and higher particle diameters for 60 and 120 min were observed by Aglietti et al. [34] and Sanchez-Soto et al. [6]. The agglomeration phenomenon was also seen by Dellisanti and Valdre [35], who have reported that significant modification in particle size distribution was result in a significant increase in the mean particle size (from 5.5 to 13 µm). However for KT, the very petty microflocs peak seen at 100 µm does not even affect the mean particle size that seems to remain almost unchanged for milling times up to 60 min (~6 µm). Similar results were previously disclosed as a decrease in particle diameters below 30 min of grinding, and higher particle diameters for 60 and 120 min were observed by Aglietti et al. [34] and Sanchez-Soto et al. [6]. The agglomeration phenomenon was also seen by Dellisanti and Valdre [35], who have reported that significant modification in particle size distribution was

**Fig. 3.** Mean Particle Size (d50) evolution of KC (a) and KT (b) samples as a function of grinding time.

**Fig. 4.** Scanning Electron Micrographs of the Commercial Kaolin non-ground sample (a), and those ground for 30 min (b), 60 min (c), and 240 min (d).

**Fig. 5.** Scanning Electron Micrographs of the Tunisian Kaolin non-ground sample (a), and those ground for 30 min (b), 60 min (c), and 240 min (d).
observed after 5 h of milling, consisting of a bimodal distribution with two maxima centered at about 5 µm and 50 µm, which shifted to larger classes above 75 µm for very large milling durations indicating that agglomeration follows size reduction. The morphological changes that occurred during dry grinding were revealed by Scanning Electron Microscopy (Figs. 4 and 5). The micrograph of the non-ground well-ordered KC (Fig. 4-a) clearly displays kaolinite “books” characterized by hexagonal platelets shaped particles (~7µm long), and some thin individual plates all around, that would most probably correspond to primary particles. Basically, the same morphology is also revealed in KT0 micrograph, but much more covered by compiled layers of fine flat particles, with a majority of rounded corners particles, that most probably correspond to quartz particles (Fig. 5-a). After 30 min of dry grinding, a polydispersed powder of irregularly shaped particles, some unevenly round, and others hexagonal with rounded apices probably arising from a non-total mild alteration of the unground kaolinite, is formed (Figs. 4-b and 5-b). These fine crystallites are produced by disintegration, cleavage and fracturing of the kaolinite floccule [8]. When prolonging grinding to 60 min, we observe particles of different shapes and sizes (Figs. 4-c and 5-c) and original layered shape is lost. After 240 min of grinding, finer particles are observed but the great disparity in particles size persists (Figs. 4-d and 5-d). Literature results on the morphological studies on ground samples of kaolinite report that grinding causes its disintegration, aggregation and agglomeration subjecting kaolinite layers to fragment and results in the formation of spheroidal particles [5, 17, 18]. Such spheroidal particles are not observed in intensively ground samples of KC and KT probably due to the stabilization of the surface energy by triethanolamine.

2. Spectroscopic characterization

Figure 6 illustrates the FTIR spectra of KC and KT samples, non-ground, and ground during 240 min, in the wavenumbers ranges of 3750-3550 cm\(^{-1}\) and 1200-400 cm\(^{-1}\). The first wavenumbers window in figure 6 reveals bands assigned to “inner surface” and “inner” hydroxyls stretching vibrations, that appear respectively at 3691 cm\(^{-1}\), 3651 cm\(^{-1}\) and at 3617 cm\(^{-1}\) for KC; and at 3694 cm\(^{-1}\), 3648 cm\(^{-1}\) and at 3617 cm\(^{-1}\) for KT. Whereas the second wavenumbers window reveals bands assigned to Si-O, Si-O-Si and Si-O-Al bending vibrations. For KC, the absorption bands ascribed to Si-O stretching vibration are observed at 1104 and 438 cm\(^{-1}\). The bands observed at 1033, 1008, 695 and 465 cm\(^{-1}\) are attributed to Si-O-Si elongation and stretching vibrations. Those seen at 796, 754 and 542 cm\(^{-1}\) are attributed to Si-O-Al compounded vibrations. The two bands at 932 and 912 cm\(^{-1}\) are assigned to Al-OH hydroxyls bending vibrations. For this same area, besides the bands attributed to Al-OH, Si-O-Al and Si-O-Si vibrations, KT spectrum reveals another band at 780 cm\(^{-1}\) ascribed to Si-O quartz [36-39]. In accordance with previous reports [23,40,41], figure 6 shows that the bands assigned to OH stretching vibrations are highly altered and dissipated after intensive grinding, which indicates the loss of hydroxyl units throughout grinding. The band attributed to the adsorbed surface water at 3695 cm\(^{-1}\) persists during the grinding. Figure 6 evidences that intensive grinding of KC induced the vanishing of the Si-O bands attesting the breakdown of Si-O bonds and the destruction of the tetrahedral sheets. Likewise, Al-OH bands almost disappear which indicates the damage of the octahedral sheets. Si-O-Si and Si-O-Al bands are almost all gone indicating the breakdown of the Si-O-Al bonds and the destruction of the linkages between the octahedral and the tetrahedral sheets. However, for KT, interesting changes in the spectra features are visible, besides the slight decrease in intensity of

![Image](image_url)
Al-OH, Si-O-Si and Si-O-Al bands that are still present. Firstly, the 1110-990 cm\(^{-1}\) originally flat region attributed to the presence of quartz, seems to gain in resolution after grinding. Moreover, in the 600-400 cm\(^{-1}\) region, the resolution of the 472 cm\(^{-1}\) Si-O-Si and the 437 cm\(^{-1}\) Si-O bands is improved after grinding. In previous studies, it was found that associated quartz particles contribute to the deceleration of the amorphization of pyrophyllite [42]. In relation with these studies, we can suggest that the high content of quartz in KT sample is the reason why aluminosilicates characteristic bands are still visible even when it is intensively ground. Prolonged grinding of KT seems to create a better order at short distance and even a better resolution of bands corresponding to Si-O-Al newly formed bonds, where Si might come from quartz and Al from kaolin. Meanwhile, the bands corresponding to quartz are still observed.

3. Structural characterization
Figures 7 and 8 illustrate XRD patterns recorded for different times of grinding of KC and KT, respectively. Figure 7 infers that the original non-ground commercial kaolin sample is a highly crystalline kaolinite, accompanied by some illite (20 %). However, XRD pattern of the Tunisian Kaolin sample reveals a less well crystalline kaolinite which contains an important amount of quartz (32 %). From figure 7, it can be noticed that while increasing grinding time from 10 to 240 min, the diffraction peaks of the identified kaolinite and illite minerals broaden and flatten intensely, and their intensity decreases substantially. From figure 8, we do also observe a broadening and a vanishing of the diffraction peaks related to kaolinite, and an important decrease of their intensities, while ground from 10 to 240 min. However, the most intense peaks related to quartz do not seem to be sensible to dry grinding and their intensity remains unchanged at a first sight. Despite the fact that the Hinckley crystallinity index is not widely used because it is influenced by the presence of quartz, feldspar, iron oxides and other clay minerals, it remains an empirical estimate of the kaolinite degree of crystallinity [43]. Estimating the crystallite size using the (001) reflection peak of kaolinite in a function of milling time, would allow us to notice the cleavage and reduction of crystallite size all along the grinding process. The diffraction peaks representing the 240-min grinding are so altered that they are not useable for the determination of the Hinckley indexes and crystallites sizes. The crystallinity of both kaolins decreases rapidly for short grinding times (Fig. 9-A). The fall slopes are almost similar for both solids, which infers that quartz does not have any direct effect on the amorphization of the Tunisian kaolin. The loss of crystallinity becomes much slower after about 30 min of grinding. Uysal et al. [44] have found similar results, reporting a decrease in the amorphization degree of kaolinite samples ground beyond 60 min, explained as the result of insufficient impact of balls to the powder mass in the mill bowl.
We observe the same behavior for the reduction of the crystallites size (Fig. 9-A), from where it is inferred that the presence of quartz does not seem to favor a greater fragmentation of the kaolinite primary particles. Frost et al. [22] have also denied the enhancing effect of quartz, whether natural or added, on the delamination of kaolinite. On the other hand, Uysal et al. [44] have reported that quartz reaches at least 40% of amorphization when ground during 50 min and its XRD peaks are still observed even after 90 min of milling. For some authors, the reason why quartz particles resists longer and harder to the grinding’s amorphization than kaolinite is that quartz is classified as a harder material with a higher Moh’s scale hardness (7 for quartz against 2-2.5 for kaolinite) [29]. In order to assess the grinding effects on the crystallinity of the quartz, the FWHM values of its (101) reflection are plotted vs. the grinding time for KT sample (Figure 9-B). This figure shows that the FWHM values of the (101) diffraction peak decrease which shows that quartz does not remain indifferent to the grinding process. Remember that the PSD study has shown that the peak relative to quartz decreases in intensity for short grinding time then remains practically unchanged. So, the grinding seems to first break quartz particles and then create some dislocation in its crystals. The

![Diagram](image_url)

**Fig. 9.** Evolutions in a function of milling times of (A) Hinckley Indexes (★) and particles crystallite sizes (●) of KC (a) and KT (b) and (B) Quartz (101) diffraction peak FWHMs in KT.

![Diagram](image_url)

**Fig. 10.** DTA (A) and TGA (B) curves of KC (a) and KT (b) heated at 10°C/min.
breaking of Si-O bonds in the quartz probably generates more reactive Si-OH groups. These later can react with Al-OH groups generated from the destruction of the linkages between the octahedral and the tetrahedral sheets in the kaolinite layers. This speculated reasoning is emerged from the FTIR results.

4. Thermal Analysis

DTA and TGA curves of non-ground KC and KT powders, presented in figure 10, are found to be typical of kaolinite thermal recordings [18]. The first petty endothermic peak below 100°C is ascribed to the departure of adsorbed water. The second prominent endothermic peak, sharp and intense, corresponds to the dehydroxylation of kaolinite and its transformation to metakaolinite. Thirdly, the exothermic peak, sharp for KC, broad and petty for KT, corresponds to the crystallization of spinel and/or primary mullite phases [25]. For both clay minerals, the dehydroxylation peak broadens (results not shown) and shifts to lower temperature (Fig. 11-B) as grinding time increases. These transformations affecting the endothermic thermal effect, are accompanied by a decrease in the mass loss relative to the departure of structural water in the clay minerals (Fig. 11-C), and an increase in the amount of physisorbed water (Fig. 11-D). This phenomena suggests that the kaolinite structural hydroxyls change into more loosely bonded hydroxyls and adsorbed water. Same results were already reported in previous works [5, 18, 45], associated to a decrease of bonding energy of the OH groups [34], and explained as the result of the breaking of the hydrogen bonds between the adjacent kaolinite layers and the generation of lattice defects [46] inducing the gradual and complete disintegration of the kaolinite structure [8]. Also, as the grinding process is prolonged, the exothermic peak broadens, decreases in intensity and area, and shifts to lower temperatures for KC (Figs. 12-A and 11-A). However for KT, the peak sharpens, increases in intensity and height, and still shifts to lower temperatures (Figs. 12-B and 11-A).

For kaolinite, some different results on the evolution of this peak with the grinding time were reported [5, 6, 19]. The temperature of mullite formation was found to depend on the type of raw material used for mullite synthesis. Furthermore, for the same raw material, such as kaolin, some discrepancies were reported. These divergences were attributed to the different chemical composition or particle size distribution of the different raw material sources. The evolution of the exothermic peak area as a function of grinding time seems to be related to the evolution of the kaolinite crystallinity and its crystallite size. Even if the evolution is not in the same direction, we observe for both samples, a rapid evolution during

![Fig. 11. The evolution of heat effects temperatures (A, B) and mass losses amounts (C, D), as a function of grinding times, for KC (a) and KT (b) clays.](image-url)
short grinding times followed by a slower evolution when ground longer than 60 min. For KC, which is quartz-free, the formation of low-particle-sized metakaolin seems to inhibit the formation of mullite. It seems that the breaking of the Si-O-Al linkage in KC is not in favor of the formation of mullite [26]. However, for the quartz-rich sample, the probable existence of Si\text{Quartz}-O-Al\text{Kaolin} bonds is in favor of the mullite formation (Fig. 12-B). Previous studies reported that non-ground pyrophyllite does not exhibit any exothermic peak related to the mullite formation [25]. For the same mineral, this peak appears, and increases in intensity, as long as it is ground. As already mentioned, KT clay has a chemical composition close to that of pyrophyllite, and a similar behavior in the peak area and intensity evolution was observed (Fig. 12-B).

The grinding/heating combined effect on the mullite formation seems to be more in relation to the chemical composition of the starting clay than its mineralogical nature.

CONCLUSION
The adding of a grinding aid prevents the decrease of the active surfaces of the intensively ground kaolinites and limits the agglomeration phase as it reduces the microflocs population and causes the discretion of their spheroidal compact shape. The presence of quartz does not seem to particularly decelerate or accelerate the textural and structural delamination of the Tunisian kaolin particles. For both clays, the grinding of kaolinite during short times results in a rapid and significant destruction of their crystallinity followed by a much slower amorphization degree beyond 30 min of grinding. Quartz structure is also altered by dry grinding. For long grinding times, the quartz amorphization is accompanied by the formation of new bonds engaging quartz-Si in a chemical bond with kaolin-Al. The newly formed bond is probably the reason why the mullite crystallization is promoted. \textsuperscript{29}Si and \textsuperscript{27}Al NMR complementary analyses must be conducted in order to confirm the interaction between quartz and kaolinite during grinding process.

Acknowledgement: This work was supported by the National Agency for the Promotion of Scientific Research (ANPR) belonging to the Ministry of Higher Education and Scientific Research of Tunisia, through a PhD MOBIDOC grant (N° 06-2013) covered by the PASRI (Support Project for the Research and Innovation System) program and funded by the European Union. The authors would like to express their thanks to Dr. Pr. Fakher Jamoussi, professor at the National Research Centre of Materials Science (CNRSM) at Borj Cedria, for having provided the Tunisian Kaolin sample. Finally, the authors are thankful to Mrs Souad Ammar, Head of
the Nanomaterials Team and Professor at Paris Diderot University - Paris 7 for having conducted the SEM analyses.

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