Influence of grinding on the structure and colour properties of talc, bentonite and calcite white fillers

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ABSTRACT: The influence of grinding on colour and particle-size properties of talc and smectite from a white bentonite were studied and compared with a fine-grained calcite from a chalk. Grinding decreased the grain size of all three minerals. The crystallite size and structure of smectite was not affected but the crystallite size of talc decreased. The Si–O–Mg and Mg–O bonds of talc were disrupted and cation exchange capacity increased with increasing grinding. Delamination of talc crystallites was observed in the initial stages of grinding, whereas with more intense treatment, amorphous material was formed. Comminution improved the colour properties of all three minerals, namely brightness, L^* (lightness) and ΔE^*ab (deviation from perfect white diffuser). Grinding time exerts greater influence on the reflectance from calcite surfaces than from clay minerals. This difference is attributed to continuous formation of progressively smaller diffuse reflection units forming a smoother calcite surface. Decrease of grain size does not form considerably smaller diffuse reflection units in clay minerals unless delamination takes place. With prolonged grinding, amorphization forms additional diffuse reflection units and a smoother surface due to comminution.

KEYWORDS: talc, bentonite, calcite, grinding, crystallite size, diffuse reflection unit.

Extenders and fillers are inexpensive minerals, used almost entirely to reduce cost and add solids to paints, paper, plastics, rubber and sealants (Carr *et al*., 1994; Naydowski *et al*., 2001). Included in this broad category are most clay minerals (kaolinite, talc, smectite, pyrophyllite, mica, asbestiform serpentine) along with non-clay minerals such as natural and precipitated calcium carbonate (GCC and PCC respectively), wollastonite, feldspars, nepheline syenite, baryte, diatomite and silica among others. The performance of industrial fillers results both from the inherent characteristics of the minerals themselves and the characteristics imparted by processing, e.g. beneficiation, grinding, classification, calcination, slurring, surface treatment. Important properties of fillers include hard-

ness, particle size and shape, colour, refractive index and chemical properties. Colour and particle size and shape properties of mineral fillers are of particular importance because they affect the properties of the end products (Adams, 1993). Particle size and size distribution affect colour; the colour of white minerals produced by grinding becomes whiter as particle size deceases (Scott, 1990). Grinding is also known to affect the structure and properties of various minerals used as industrial fillers such as kaolinite (Gregg, 1968; Kristoff *et al*., 1993; Suraj *et al*., 1997; Stepkowska *et al*., 2001), talc (Mukherjee & Roy, 1973; Liao & Senna, 1992; Sanchez-Soto *et al*., 1997), pyrophyllite (Perez-Rodriquez & Sanchez-Soto, 1991; Wiewióra *et al*., 1993; Uhlík *et al*., 2000), and smectite (Mingelgrin *et al*., 1978; Čičel & Kranz, 1981; Volzone *et al*., 1987). Grinding causes delamination in the initial stages followed by

destruction of the structure and subsequent amorphization, associated with reaggregation (cold welding according to Gregg, 1968) of the mineral grains (Sanchez-Soto *et al*., 1997 and Stepkowska *et al*., 2001, among many others). Reynolds & Bish (2002) showed that progressive grinding of kaolinite produces increased amounts of disordered kaolinite, coexisting with relatively unaffected material.

Colour properties are important parameters investigated during assessment of clay minerals as mineral fillers. Nevertheless, with a few exceptions (e.g. Christidis & Scott, 1997), the factors affecting the colour of white clays has not been studied in detail. In this contribution we (1) examine the influence of grinding on colour and particle size properties of talc and of smectite from a white bentonite and compare them with calcite, a non-clay industrial mineral used as a filler; and (2) examine the role of the mineral structure and texture in these properties.

MATERIALS AND METHODS

The talc samples come from the ultramafic sequence (mantle unit) in the southern part of the of the Troodos ophiolitic Complex, Cyprus. Talc is the predominant mineral in the deposit associated with trace amounts of Mg-rich chlorite (clinochlore). The smectite studied comes from the Fanara deposit, in the southern part of Kimolos Island, Greece (Christidis, 1998). It is a low-quality bentonite with high-quality white bentonite lenses. The samples used were collected from these bentonite lenses. The material consists principally of Ca-Mg Chambers-type montmorillonite (~90%) with trace amounts of K-feldspars and opal-CT. It has a cation exchange capacity (CEC) of 0.90 mEq g^{-1} and a swelling index of 230 ml of gel/10 g of clay (Christidis, 1998). The calcite comes from a fine-grained unbedded chalk of Eocene-Oligocene age at the SW part of Kefalonia Island in Western Greece belonging to the Paxos Geotectonic Unit (Bergmann, 1964). The chalk has a limited outcrop and is usually fractured and strongly karstified in the higher stratigraphic horizons. It is remarkably rich in calcite (>99.4 wt.%) (Triantafyllou *et al*., 2003).

The materials were crushed using a fly press to pass a 1.18 mm sieve and were subsequently ground in an agate ball mill (Fritsch) for 1−90 min under dry conditions. The talc- and smectite-rich materials were also dispersed in an ultrasonic probe for 20 s and dried at 60ºC prior to ball-mill grinding. The particle size of the ground clay samples was studied by X-ray diffraction (XRD) (Siemens D-500 Cu-*K*α radiation, graphite monochromator, 35 kV and 35 mA) using oriented specimens and by laser diffraction (Malvern© particle size analyser). Each clay-mineral filler grain consists of an unknown number of clay mineral crystallites. Therefore, XRD was used to determine the thicknesses of smectite and talc crystallites whereas laser diffraction was used to measure the mean size of smectite or talc grains. The mean grain size (d_v), measured by laser diffraction, corresponds to a sphere having the same volume as the grain (Allen, 1990). Oriented specimens were prepared by separation of clay fraction via sedimentation onto glass slides (3 mg/cm^2). The smectite samples were solvated with ethylene glycol at 60ºC for 24 h. The crystal size of ground calcite crystals was measured by SEM (JEOL 5400 JSM) using gold-coated glass slides.

Particle thickness and *ab* surface area of smectite and talc crystallites were determined using the MudMaster program (Eberl *et al*., 1996), which calculates crystallite size (in this case thickness) distribution and strain from the shapes of XRD peaks, according to the Bertaut-Warren-Averbach (BWA) method (Drits *et al*., 1998). The XRD analysis of the talc and smectite clay fractions (air dried for talc and ethylene glycol solvated for smectite) was performed on the 001 peak in the ranges 4−10 and 3−7º2θ, respectively, at a step size of 0.02º2θ with 5 s count time per step. The *ab* specific surface area was used to calculate the equivalent spherical crystallite diameter, according to the formula: $d_{v'} = 6/\rho S_w$ where $d_{v'}$ is the spherical crystallite diameter (μm), ρ is the density of talc or smectite and S_w is the *ab* specific surface area of the crystallite. The *ab* specific surface area is considered an adequate approximation of the real crystallite specific surface area because the area of the crystallite edges is minimal compared to that of the planar surfaces. The number of crystallites per grain was determined from the ratio $d_v/d_{v'}$ where d_v is the equivalent spherical diameter of mineral grain determined by laser diffraction. In the case of calcite, $d_{v'}$ was measured on SEM microphotographs. A minimum of 250 calcite grains was measured per sample.

The effect of grinding on clay mineral structure was studied further by infrared (IR) spectroscopy

(Perkin Elmer 1000 FTIR spectrometer) in the range $400-4000$ cm^{-1}. Each spectrum was the average of 100 scans collected at 2 cm^{-1} resolution. $1.5-2$ mg of the talc and smectite clay fractions was diluted in 200 mg KBr. The CEC of the original and selected ground smectite and talc samples was measured with ammonium saturation (1 N ammonium acetate at pH 7), Kjeldahl distillation and titration of the evolved ammonia with 0.05 N H_2SO_4.

The colour properties of the ground minerals were measured according to the CIELAB system using a Diffusion Systems reflectance spectro-photometer with a 45º/90º geometry and illuminant "A" source. The spectrophotometer was calibrated against the perfect white diffuser by means of a ceramic plate standardized by British Ceramic Research Ltd. The colour parameters determined are brightness (Y filter), $L*$, $a*$ and $b*$. $L*$, $a*$ and $b*$, which are calculated from the X, Y and Z tristimulus values which represent lightness on a scale of zero (black) to 100 (white), redness (positive value) $-$ greenness (negative value) and yellowness (positive value) $-$ blueness (negative value), respectively (Billmeyer & Saltzman, 1981). Another useful parameter used to describe colour is $\Delta E*ab$, which determines the colour difference between the sample and perfect white.

RESULTS

Evolution of crystallite size with grinding

X-ray diffraction traces of the 001 peak of smectite and talc for different grinding times are shown in Fig. 1. The two minerals follow different
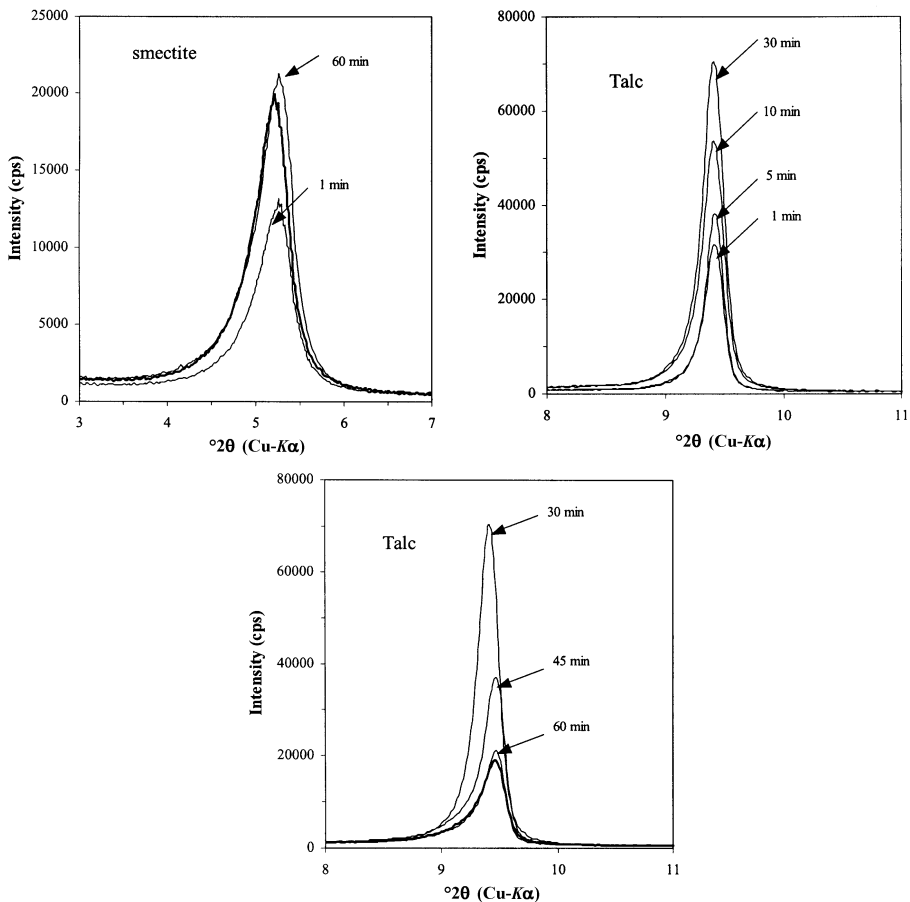

FIG. 1. Evolution of the 001 reflection of smectite and talc with increasing grinding time. The bold traces correspond to 90 min of grinding.

trends in the evolution of the 001 peak. In smectite the intensity of the 001 peak increases continuously reaching a maximum after 15 min of grinding and remains virtually unchangeable thereafter. In talc, the intensity increases continuously reaching a maximum after 30 min grinding time, decreasing drastically at greater grinding times. Continuous grinding is well known to cause delamination of crystallites of various clay minerals as has been observed in smectite (Mingelgrin *et al.*, 1978; Čičel & Kranz, 1981), kaolinite and pyrophyllite (Uhlík *et al.*, 2000; Stepkowska *et al.*, 2001). Delamination can be considered in the case of talc, due to the decrease of crystallite thickness, but not in the case of smectite. To the authors' knowledge, delamination with progressive grinding has not been reported in talc. For example, Sanchez-Soto *et al.* (1997) observed continuous destruction of talc structure, eventually leading to amorphization. This difference may be attributed to different sample preparation methods used in the two studies (oriented *vs.* quasi-randomly oriented samples).

Mean crystallite thicknesses and *ab* specific surface areas calculated from MudMaster and equivalent spherical diameter of crystallites and number of layers per crystallite of smectite and talc with grinding time are listed in Table 1. The two minerals display different crystallite thickness evolution with increasing grinding time: the coherent scattering domain (CSD) of talc decreases continuously whereas the CSD of smectite remains essentially unchanged (Table 1). Also, the number of layers per CSD decreases gradually whereas *ab*

specific surface area increases in talc. By contrast, in smectite these parameters remain virtually constant for up to 90 min of grinding time. Therefore the observed increase in the intensity of the 001 reflection of smectite with increasing grinding time (Fig. 1) is attributed to better orientation.

Representative crystallite thickness distribution curves for smectite and talc minerals obtained from MudMaster are shown in Fig. 2. Smectite displays lognormal distribution both in the original state and after grinding. This is typical of several clays (Eberl *et al.*, 1998). The lognormal distribution is characterized by parameters α (mean of the logarithms of the observations; thickness in this case) and β^2 (variance of the logarithms) (Koch & Link, 1971). Talc (Fig. 2d−f) displays a multimodal size distribution, which is attributed to the complex geological evolution of the material. Furthermore, the size distribution curves of talc migrate to smaller-mode thickness values with increasing grinding time. By contrast, the size distribution curves of smectite (Fig. 2a,b) remain essentially unchanged with increasing grinding time.

The evolution of the mean crystal size of calcite for different grinding times, measured by SEM, is listed in Table 1. Only grains consisting of one calcite crystal were measured. After 5 min of grinding, the crystal size of calcite is increased slightly compared to the original material, it remains essentially constant for up to 15 min of grinding time and decreases after longer grinding times. The original increase in crystal size is within

TABLE 1. Evolution of crystallite thickness, specific surface area (SSA, m² g⁻¹) and number of layers per CSD of talc and smectite, and the crystal size (μm) of calcite with grinding time.

Grinding time (min)	Talc				Smectite				Calcite
	Thickness of CSD (nm)	SSA (*ab*)	No. of layers per CSD	Crystallite size (μm)	Thickness of CSD (nm)	SSA (*ab*)	No. of layers per CSD	Crystallite size (μm)	Crystal size (SEM)
Initial	22.5	35	24	0.068	10.3	72	6.05	0.030	4.2
1	21.9	34	24	0.065	10.2	73	6	0.03	−
3	20.2	37	22	0.06	10.2	73	6	0.03	−
5	19.5	38	21	0.058	10.7	69	6.3	0.031	4.77
10	19	40	20	0.055	10.2	73	6	0.03	−
15	18.2	41	20	0.054	10.6	70	6.2	0.032	4.58
30	16.7	45	18	0.049	10.7	69	6.3	0.032	−
45	15.1	49	16	0.045	10.4	71	6.1	0.031	3.45
60	13.9	53	15	0.042	10.3	72	6.05	0.031	−
90	12.9	58	14	0.038	10.5	71	6.2	0.031	−

experimental error and is not considered statistically significant. In general, calcite crystals display multimodal, lognormal CSD, which is considerably narrower compared to both talc and smectite. Crystal-size distribution of calcite crystals after 7 min of grinding is shown in Fig. 2c.

Evolution of grain size with grinding

The evolution of grain sizes of all materials determined by laser diffraction is listed in Table 2.

The grain size of smectite and talc is two to three orders of magnitude greater than the crystallite size of these minerals determined from MudMaster. Considering that each grain of talc and smectite contains a certain number of crystallites, we determined the number of crystallites per grain. With increasing grinding time, the number of crystallites per grain decreases for both minerals (Fig. 3). This decrease is more rapid for talc than for smectite. Moreover, the number of crystallites of talc per grain reaches a plateau after 15 min of grinding
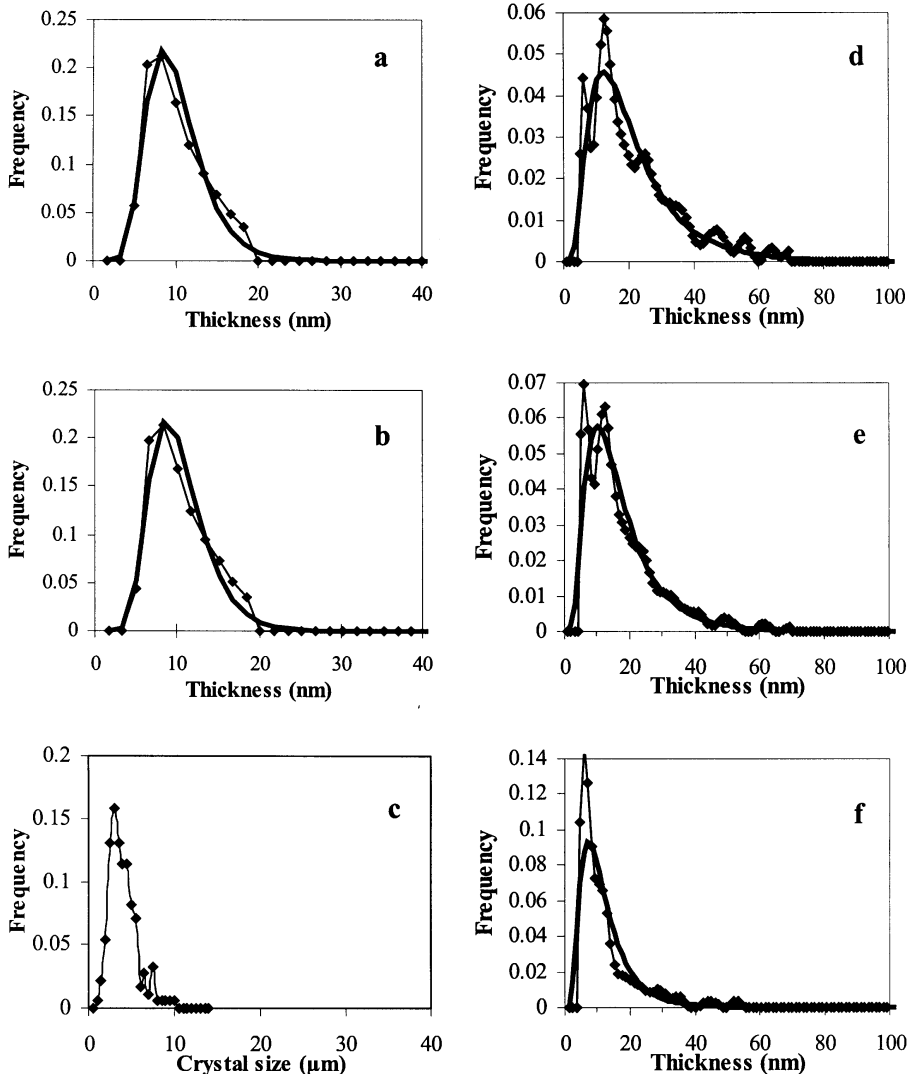

FIG. 2. Crystallite size of smectite (a−b), calcite (c) and talc (d−f). a and d = grinding for 1 min, b and f grinding for 60 min, c = grinding for 7 min, and e grinding for 15 min.

TABLE 2. Evolution of grain size of talc, smectite and calcite with increasing grinding time, measured with laser diffraction.

Grinding time (min)	Talc grain size (μm)	Smectite grain size (μm)	Calcite grain size (μm)
Initial	27.74	15.8	8.59
1	25.97	15.48	7.05
3	22.3	15	6.81
5	20.22	14.62	5.2
10	18.71	13.46	5.13
15	16.65	13.04	5.18
30	15.09	12.29	5.08
45	14.09	11.26	3.62
60	13.55	10.74	–
90	11.81	9.73	–

whereas in the case of smectite the decrease in the number of crystallites continues until the end of the experiment, but at a slower rate (Fig. 3).

The decrease in the grain size of calcite is gradual for grinding times up to 5 min. For grinding time up to 15 min the grain size remains essentially constant, decreasing slightly thereafter until the end of the experiment. Each calcite grain consists of 1−2 crystals even for very short grinding times (compare Tables 1 and 2). This is an important characteristic of this fine-grained calcite, which affects the evolution of colour properties with grinding (see below).
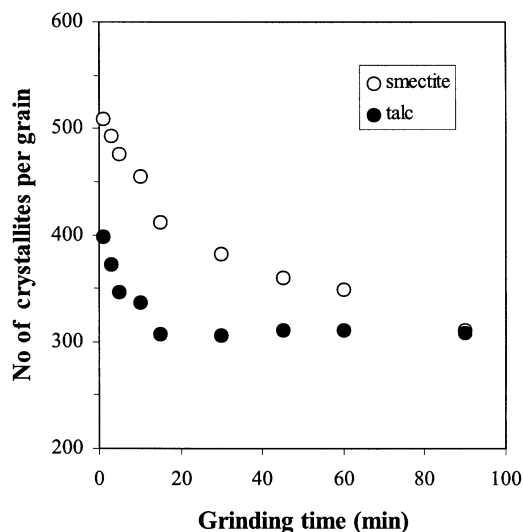

FIG. 3. Evolution of the number of crystallites per grain of smectite and talc with grinding time. See text for discussion.

FTIR and CEC results

Representative Fourier transform infrared (FTIR) spectra of smectite and talc are shown in Fig. 4. The grinding process did not affect the structure of smectite. By contrast, the FTIR spectra of talc (assignment of the bands follows Farmer, 1974) display significant modifications with increased grinding time. This can be observed better in the $400-1600$ cm^{-1} region where lattice vibrations are present. More specifically, the intensity of the bands at 451 cm^{-1} (Si–O–Mg), 466 cm^{-1} (Mg−O and/or translational OH-vibration) and 532 cm^{-1} (Mg−O) decreases, while the intensity of the bands at 1041 cm^{-1} (Si−O stretching) and 425 and 441 cm^{-1} (Si−O bending) increases with increasing grinding time, and so does the intensity of the band at 796 cm^{-1}, which is associated with amorphous SiO$_2$. By contrast, the band at 669 cm^{-1} (librational OH vibration) is not affected by grinding. Similarly, the OH-stretching region (not shown here) remains unaffected by grinding throughout the whole time range used.

The CEC of smectite does not change with increasing grinding time. By contrast, talc subject to grinding displays a CEC, which, after 90 min, reaches 6 mEq/100 g (Table 3). Since the original material has negligible CEC it follows that the CEC resulted from structural modifications during grinding. Talc is virtually free of octahedral or tetrahedral substitutions; therefore the CEC is attributed to broken bonds, which resulted from grinding.
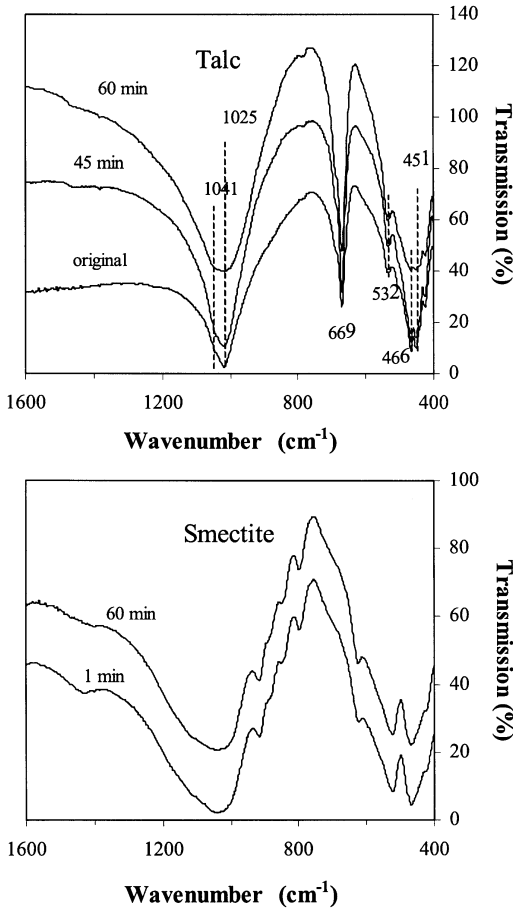
TABLE 3. CEC of smectite and talc after different grinding times.

Grinding time (min)	Cation exchange capacity (mEq/100 g)	
	Talc	Smectite
Initial	Bd	90.0
7	2.5	91.0
15	3.0	89.7
60	4.5	90.8
90	6.0	90.2

Bd: below detection limit

FIG. 4. FTIR spectra of talc and smectite for different grinding times.

Colour properties of the ground materials

Comminution affected the colour properties of the three minerals (Table 4). In general, grinding improves most of the colour properties. Thus *Y* (brightness) and *L** increase and ΔE^*ab decreases with grinding time and thus with decreasing grain size (Table 4, Fig. 5). Talc has a low brightness even after prolonged grinding. The increase of *L** with decreasing grain size is due to the formation of a smoother surface. It should be noted that light is not reflected by a mirror surface but by a powdered sample with irregularities (i.e. roughness) causing diffuse reflection (cf. Billmeyer & Salzman 1981). Therefore, with prolonged grinding, the mean height of irregularities (*h*) decreases approaching the Rayleigh value. For a powdered surface to act

as a mirror, *h* should be <0.1 μm for the visible spectrum (Cervelle & Moëlo, 1990). Calcite has superior colour properties to the clay minerals studied, due to its high purity and thus compositional homogeneity. In smectite and calcite *a** (redness value) and *b** (yellowness value) display an overall tendency to decrease with increasing grinding time. The same is observed with parameter *b** in talc. However parameter *a** in talc does not display a clear pattern with increasing grinding time due to the presence of chlorite, which imparts a green hue, and thus the negative values of *a** can be explained. The existence of positive *a** values in several ground talc samples (Table 4) is attributed to sample heterogeneity.

It was shown that continuous grinding of talc and smectite yields grains with progressively smaller number of crystallites (Table 1). Since the grain size affects colour properties (Table 4), it is expected that the latter may be related to the number of crystallites per grain. This indeed is shown in Fig. 6 for *L** and ΔE^*ab in talc and smectite, which display different trends, however. In smectite, the relationship between colour properties and the number of crystallites per grain is linear. In talc, the colour properties change towards that of a perfect white diffuser with a decreasing number of crystallites per grain up to a limit, beyond which they remain virtually constant. This difference is attributed to the different nature of the two minerals (see below). In calcite there is no relationship between the number of crystallites per grain and colour properties due to the small, nearly constant number of crystallites per grain.

Complete spectrophotometric curves, which display the percentage of reflectance of light from the surface of ground talc and calcite over the

TABLE 4. Evolution of colour parameters of talc, smectite and calcite with grinding time.

Grinding time (min)	Talc							Smectite							Calcite						
	X	Y	Z	L^*	a^*	b^*	ΔE^*ab	X	Y	Z	L^*	a^*	b^*	ΔE^*ab	X	Y	Z	L^*	a^*	b^*	ΔE^*ab
1	80.4	73.1	23.8	88.5	0.21	5.2	12.63	86.15	77.7	25.25	90.64	1.45	5.42	10.91	100.4	90.5	30.9	96.2	1.57	2.65	4.89
3	81.3	73.5	24	88.69	1.07	5.04	12.43	87.05	78.15	25.25	90.85	2.17	5.78	11.04	100.4	90.9	30.9	96.36	1.02	2.91	4.99
5	81.2	74.1	24.5	88.97	0.4	4.32	11.85	87	78.45	25.4	90.98	1.49	5.66	10.75	100.8	91.2	31.1	96.48	1.14	2.65	4.55
10	81.2	74.4	24.7	88.97	−0.53	5.06	11.69	87.9	79.25	25.9	91.35	1.52	5.12	10.51	101.7	91.9	31.3	96.78	1.28	2.76	4.43
15	82.1	75.6	24.7	89.67	−1.71	5.06	11.62	89.55	80.8	26.5	91.63	1.41	4.94	10.39	102	92.8	31.9	97.13	0.18	2.22	3.63
30	82.5	76	24.5	89.79	0.23	5.05	11.75	91.2	81.2	26.2	92.22	3.49	5.93	9.47	–	–	–	–	–	–	–
45	83.5	76.4	25.4	90.04	−0.75	4.04	10.77	91.1	82.5	27.2	92.4	0.84	4.65	9.35	104.8	95	32.9	98.03	0.78	1.71	2.72
60	85.2	77.5	25.6	90.55	0.15	4.44	10.44	89.5	81	26.4	92.43	0.94	5.32	9.24	–	–	–	–	–	–	–
90	85.3	77.9	25.8	90.73	−0.46	4.29	10.22	90.4	81.85	26.9	92.51	0.87	4.83	8.96	–	–	–	–	–	–	–
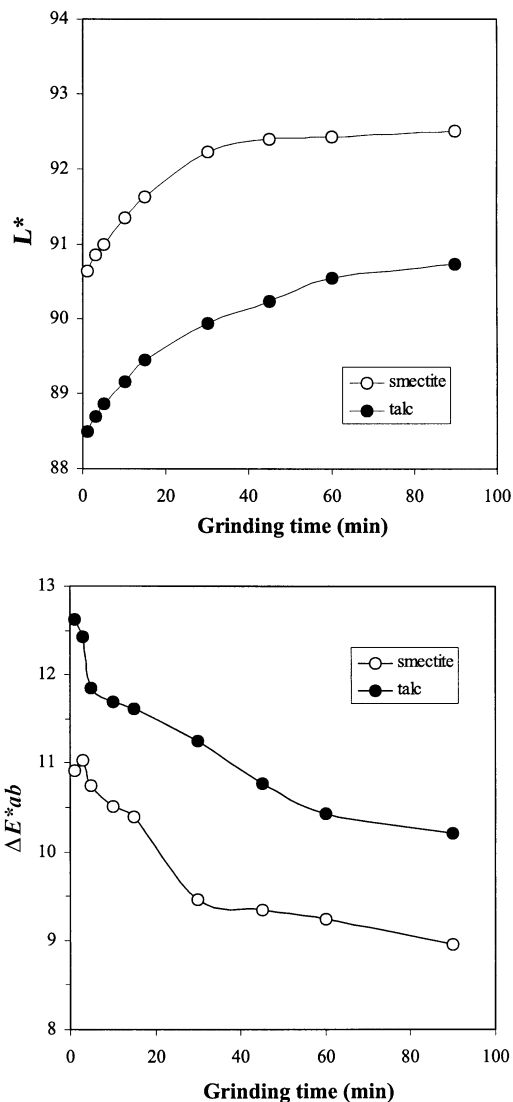
FIG. 5. Evolution of L^* and ΔE^*ab of smectite and talc with grinding time.

wavelength range 4260–6840 nm (visible spectrum), are shown in Fig. 7. All curves shift to higher reflectance values with increasing grinding time, although for grinding times up to 30 min, the increase in reflectance is minimal. The spectrophotometric curve of smectite (not shown) shows a slight increase in reflectance throughout the whole grinding cycle. A very similar trend was also observed in the spectophotometric curves of halloysite from Maungaparerua, New Zealand (Makri, 2002). However, the response of calcite to
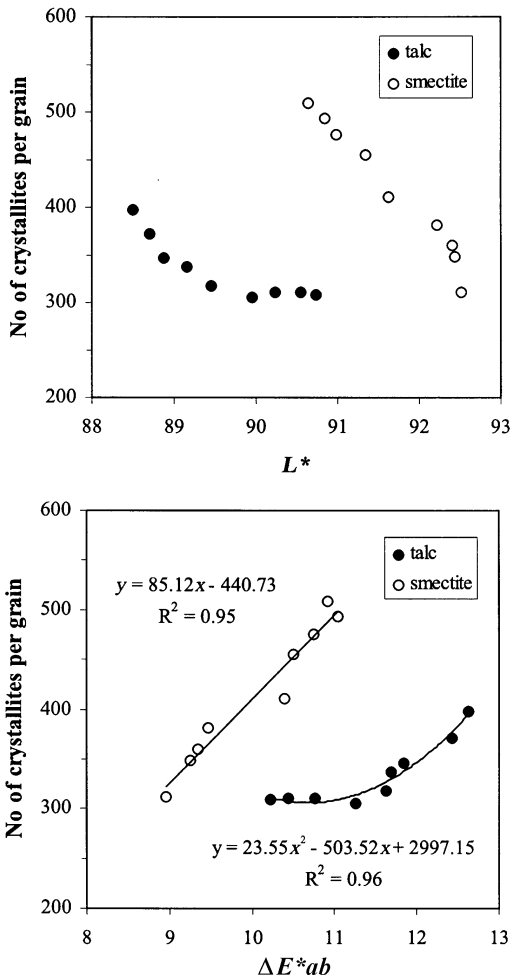
FIG. 6. Variation of of *L** and Δ*E*ab* of smectite and talc with number of crystallites per grain.

FIG. 7. Spectrophotometric curves of talc and calcite for different grinding times. See text for discussion.

comminution is considerably greater compared to talc and smectite, because the increase of reflectance from its surface is more pronounced over the whole wavelength range. Therefore, the surfaces of clay minerals respond to a different degree than calcite to the incident light beam over a large range of wavelengths.

DISCUSSION

Modifications of talc and smectite crystallites during grinding

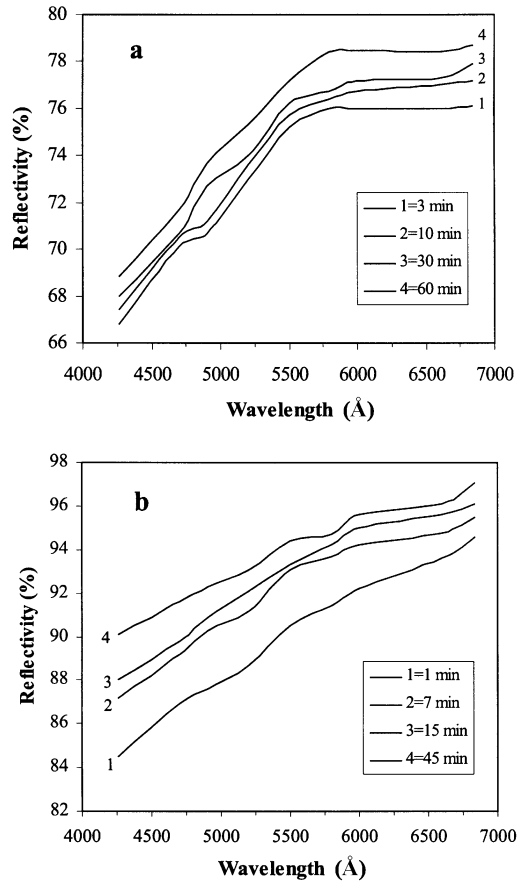Grinding affected talc and smectite crystallites to a different degree. Smectite crystallites, as measured by XRD, remained essentially unaffected during comminution (Figs 1, 4) although smectite grain size, as measured by laser scattering, decreased gradually (Table 1). The increase in intensity of the 001 reflection of ethylene glycol-solvated smectite with increasing grinding time (Fig. 1) is attributed either to better orientation of smectite particles or to an increase of coherent scattering domain (CSD) of smectite crystallites. The latter alternative is not plausible because particle thickness remained essentially unchanged or even slightly increased at prolonged grinding time (Table 1). A better orientation of smectite crystallites is expected to have taken place due to disaggregation of minor clay size (1−2 μm) opal-CT crystals during comminution. These crystals are intimately associated with smectite crystallites in the Fanara bentonite (Christidis, 1998) and thus are

expected to affect particle orientation. Also, it is interesting that although prolonged grinding has been reported to cause gradual amorphization of smectite (Mingelgrin *et al.*, 1978; Čičel and Kranz, 1981; Volzone *et al.*, 1987), the formation of amorphous material has not been substantiated in this study. This is attributed to the different sample preparation protocols used. For example, Mingelgrin *et al.* (1978) used material prepared under conditions which they did not describe in their paper, possibly pre-ground to an unspecified grain size. Volzone *et al.* (1987) disaggregated smectite by grinding with a ball mill so as to pass from a 200 mesh (75 μm) sieve, while the main grinding cycle was carried out with an oscillatory mill. Finally Čičel and Kranz (1981) used an oscillatory mill, which is considerably more effective than ball mills (e.g. Suraj *et al.*, 1997). Any pretreatment involving grinding increases the time the smectite structure is subjected to stress, facilitating formation of amorphous material.

In the case of talc, the initial delamination was followed by destruction of talc crystallites. Both crystallite and grain size decreased with increasing grinding time. The FTIR spectroscopy (Fig. 4) yielded significant insights into the structural modifications in talc. The increase in intensity of the Si−O bands coupled with a decrease of the Mg−O and Si−O−Mg bands, especially after prolonged grinding, suggest that comminution leads to disruption of the Mg−O and Si−O−Mg bonds, which link the tetrahedral and octahedral sheets (Perdikatsis & Burzlaff, 1981); thus they indicate that the coherence of the talc layer has decreased with increasing grinding time. These changes are expected to be associated with incipient amorphization of the talc structure for grinding time >30 min as observed in other studies (Sanchez-Soto *et al.*, 1997), and as is indicated by the increase in the intensity of the band at 796 cm^{-1}. Disruption of the Si−O−Mg bond may create additional Si−O linkages and amorphous SiO_2 thus contributing to the increase of the bands at 1041 cm^{-1} and 796 cm^{-1}, respectively. Also, the disruption of Mg−O and Si−O−Mg bonds is linked with the CEC for talc (Table 3). The fact that CEC is observed after 7 min of grinding indicates that initial delamination is associated with partial disruption of the talc crystallites.

The rate of decrease of the crystallite size of talc takes place in two steps (Fig. 8a). An initial fast step up to 10−15 min of grinding time, followed by

a slower one for longer grinding times. Note that delamination of talc crystallites continued after the completion of the first step. By contrast the decrease in the grain size of talc and smectite is a single-step process (Fig. 8b). Also, the decrease in the grain size of talc occurs twice as fast as the decrease in the grain size of smectite and at a comparable rate to the first fast step of comminution of the talc crystallites. After 15 min of grinding, the grain size of talc decreased at a considerably faster rate than the talc crystallite size.
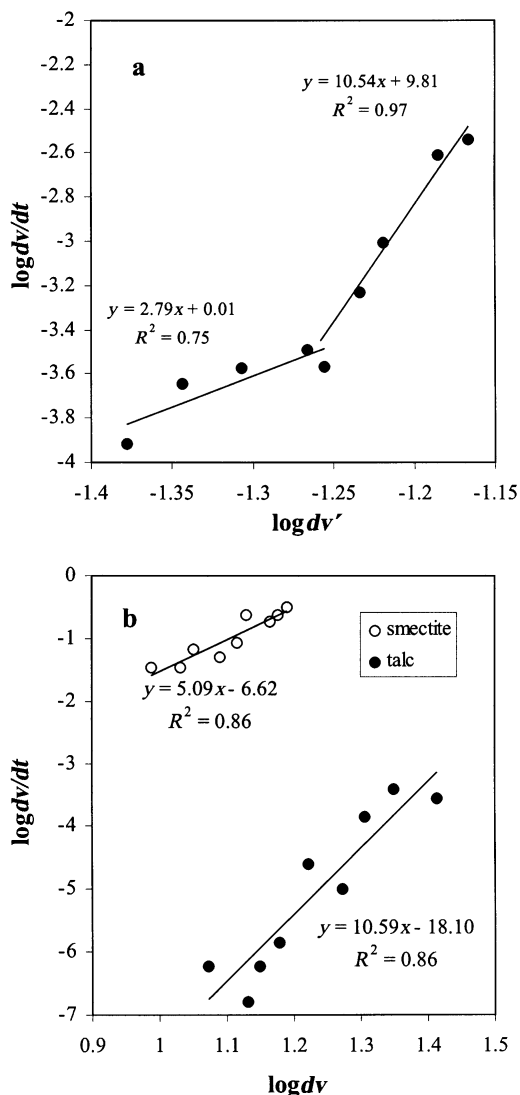

FIG. 8. Rate of decrease (a) of the crystallite size and (b) of grain size of talc and smectite.

The considerably lower rate of decrease of crystallite size of talc in the second step is attributed to precipitation of collapsed talc crystallites on fresh talc particles. These collapsed particles, which may be partly amorphous, protect the unaffected crystallites, thereby decreasing the rate of crystallite comminution. However, the deposition of collapsed particles does not cause significant agglomeration of crystallites into grains of greater size via cold sintering (Gregg 1968); hence, the grain size of talc decreases at a constant rate throughout the whole comminution cycle.

Colour properties of talc, smectite and calcite

The three minerals used displayed comparable and expected trends in the most important colour properties, i.e. brightness, L^* and ΔE^*ab with increasing grinding time. Moreover, in the complete spectrophotometric curves, the reflectance of light increased with increasing grinding time (Fig. 7). However grinding time exerts greater influence on the reflectance from the calcite than from clay minerals. This is attributed to the different texture of the clay mineral surface compared to that of calcite.

Clay mineral grains consist of crystallites of variable width, having random orientation, which are usually loosely bound together (Fig. 9a). These crystallites are the diffuse reflection units. By contrast, calcite grains from micritic limestones and chalks consist of a single crystal or a limited number of crystals with well-defined boundaries (Fig. 9b). Each calcite grain is a diffuse reflection unit. Consider that a talc grain consists of N crystallites, a fraction of which is that part of the grain surface that reflects light. During comminution the grain breaks up into smaller parts, while simultaneously, a fraction of talc crystallites display delamination at least in the incipient stages of comminution. It is delamination, not decrease of grain-size, which increases the number of diffuse reflection units because N increases. Nevertheless, delamination alone does not increase significantly reflectance from the talc surface. Thus, in Fig. 7a, grinding for up to 30 min does not increase reflectance significantly, because delamination does not reduce surface roughness. With prolonged grinding, the formation of finer, partly amorphous particles, through the destruction of talc crystallites increases considerably the number of reflection units, while simultaneously decreasing surface

roughness, thus increasing reflectance from talc surface.

A different pattern is observed during grinding of calcite crystals. In this case the number of reflecting units increases considerably with comminution, because the grains, which are the diffuse reflection units, break up continuously to smaller units creating a smoother surface thereby enhancing light reflectance. A similar behaviour is expected for other coarse-grained minerals used as fillers such as wollastonite, nepheline etc. Therefore, this study suggests that comminution modifies the colour properties of the clay-mineral fillers to a different degree than coarser minerals due to the different characteristics of the diffuse reflection unit, which affects the smoothness of the surface to a different degree. The geological history of the materials is important in this aspect because it controls the crystallite size distribution (single *vs.* multi-modal distributions) and thus delamination. These inherent characteristics are not modified by other beneficiation processes, which mainly remove other minerals affecting colour adversely, such as Fe and Ti oxides.

CONCLUSIONS

The colour properties of white mineral fillers are controlled by the inherent characteristics of the main
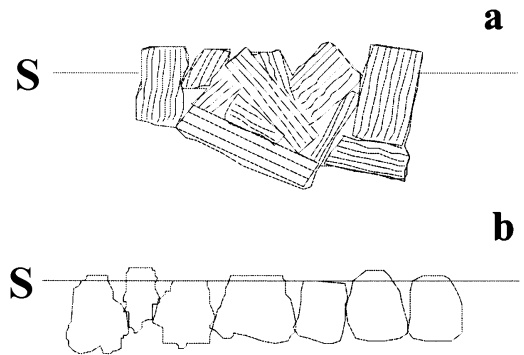

FIG. 9. Schematic sketch showing the surface roughness of clay and calcite filler. (a) In the clay filler the composite grains break up to smaller ones but the total number of diffuse reflection units (clay crystallites) remains essentially unchanged unless delamination occurs. Surface roughness does not decrease. (b) In calcite each grain is roughly a diffuse reflection unit. With comminution, roughness decreases because the smaller grains occupy the empty spaces between grains. S = sample surface.

diffuse reflection unit. Clay mineral grains consist of a large number of diffuse reflection units, the number of which increases through delamination. By contrast, coarse-grained minerals consist of a limited number or most often of a single crystal. Comminution affects reflectance of light after prolonged grinding, if it is associated with the destruction of clay mineral structure and subsequent amorphization. Delamination, which is usually observed in the incipient steps of comminution may not be observed during grinding of clay minerals such as smectite. The geological history of the material is of primary importance, because it controls crystallite size distribution, which in turn affects delamination in the case of clay minerals or reduction of grain size in the case of coarse-grained minerals. These factors control the observed difference in colour properties of talc, smectite and calcite, which were modified during comminution.

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REFERENCES

Adams J.M. (1993) Particle size and shape effects in materials science: examples from polymer and paper systems. *Clay Minerals*, **28**, 509−530.

Allen T. (1990) *Particle Size Measurement*. Vol. 1. Pp. 44−111, Chapman & Hall, London.

Bergman H. (1964) *Geological Map of Greece, Kefalonia Sheet*. Institute of Geological and Mining Exploration, Greece.

Billmeyer F.W. & Saltzman M. (1981) *Principles of Color Technology*, 2nd edition. Pp. 1−23, Wiley Interscience, New York.

Carr D.D., Rooney L.F. & Freas R.C. (1994) Limestone and dolomite. Pp. 605−609 in: *Industrial Minerals and Rocks*. (D.D. Carr, editor). American Institute of Mining and Metallurgical Engineers.

Christidis G. (1998) Physical and chemical properties of some bentonite deposits of Kimolos Island, Greece. *Applied Clay Science*, **13**, 79−98.

Christidis G. & Scott P.W. (1997) Origin and colour properties of white bentonites: A case study from the Aegean Islands of Milos and Kimolos, Greece. *Mineralium Deposita*, **32**, 271−279.

Cervelle B. & Moëlo Y. (1990) Reflected light optics. Pp. 87−108 in: *Short Course on Advanced Microscopic Studies of Ore Minerals* (J.L. Jambor & D.J. Vaughan, editors). Mineralogical Association of Canada, Ottawa.

Čičel V. & Kranz G. (1981) Mechanism of montmorillonite structure degradation by percussive grinding. *Clay Minerals*, **16**, 151−162.

Drits V., Eberl D.D. & Środoń J. (1998) XRD measurement of mean thickness, thickness distribution and strain for illite and illite/smectite crystallites by the Bertaut-Warren-Averbach technique. *Clays and Clay Minerals*, **46**, 461−475.

Eberl D.D., Drits V., Środoń J. & Nüesch R. (1996) *MudMaster: a program for calculating crystallite size distribution and strain from the shapes of X-ray diffraction peaks.* USGS, Open File Report 96-171, Boulder, CO, USA.

Eberl D.D. Drits V. & Środoń J. (1998) Deducing growth mechanisms for minerals from the shapes of crystal size distributions. *American Journal of Science*, **298**, 499−533.

Farmer V.C. (1974) The layer silicates. Pp. 331−363 in: *The Infrared Spectra of Minerals* (V.C. Farmer, editor). Monograph **4**, Mineralogical Society, London.

Gregg S.J. (1968) Surface chemical study of comminuted and compacted solids. *Chemistry and Industry*, **11**, 611−617.

Kristoff E., Zoltan Juhasz A. & Vassanyi I. (1993) The effect of mechanical treatment on the crystal structure and thermal behavior of kaolinite. *Clays and Clay Minerals*, **41**, 608−612.

Koch Jr. G.S. & Link R.F. (1971) *Statistical Analysis of Geological Data*. Dover, New York.

Liao J. & Senna M. (1992) Thermal behavior of mechanically amorphized talc. *Thermochimica Acta*, **197**, 295−306.

Makri P. (2002) *Study of the influence of comminution on the colour properties of fillers (talc, halloysite, limestone)*. Unpublished M.Sc. thesis, Technical University of Crete, Greece.

Mingelgrin U., Kliger L., Gal M. & Saltzman S. (1978) The effect of grinding on the structure and behavior of bentonites. *Clays and Clay Minerals*, **26**, 299−307.

Mukherjee D.K. & Roy S. (1973) Effect of dry grinding on the CEC of some Indian talcs. *Industrial Ceramics*, **10**, 215−219.

Naydowski C., Hess P., Strauch D., Kuhlmann R. & Rohleder J. (2001) Calcium carbonate and its industrial applications. Pp 197−311 in: *Calcium Carbonate. From the Cretaceous Period into the 21st Century* (F.W. Tegethoff editor). Birkhäuser Verlag, Basel.

Perdikatsis V. & Burzlaff H. (1981) Structurverfeinerung am Talk Mg$_3$[(OH)$_2$Si$_4$O$_{10}$]. *Zeitschrift für Kristallographie*, **156**, 177−186.

Perez-Rodriquez J.L. & Sanchez-Soto P.J. (1991) The influence of the dry grinding on the thermal behavior of pyrophyllite. *Journal of Thermal Analysis*, **37**, 1401−1423.

Reynolds Jr. R.C. & Bish D.L. (2002) The effects of grinding on the structure of a low-defect kaolinite. *American Mineralogist*, **87**, 1626−1630.

Sanchez-Soto P.J., Wiewióra A., Aviles M.A, Justo A., Perez-Maqueda L.A., Perez-Rodriquez J.L. & Bylina P. (1997) Talc from Puebla de Lillo, Spain. II. Effect of dry grinding on particle size and shape. *Applied Clay Science*, **12**, 297−312.

Scott P.W. (1990) *Brightness and Colour Measurement*. CEC/ASEAN training course on assessment procedures for clays and ceramic raw materials. 11 pp.

Stepkowska E.T., Perez-Rodriquez J.L., Himenez de Haro M.C., Sanchez-Soto P.J. & Maqueda L.A. (2001) Effect of grinding and water vapour on the particle size of kaolinite and pyrophyllite. *Clay Minerals*, **36**, 105−114.

Suraj G., Iyer C.S.P., Rugmini S. & Lalithambika M. (1997) The effect of micronization on kaolinites and their sorption behaviour. *Applied Clay Science*, **12**, 111−130.

Triantafyllou G., Christidis G. & Markopoulos T. (2003) Influence of porosity and grain size of carbonate rocks on the reactivity of lime. Pp 931−934 in: *Mineral Exploration and Sustainable Development* (D. Eliopoulos *et al*., editors). Millpress, Rotterdam, The Netherlands.

Uhlík P., Šucha V., Eberl D.D., Puskelova L. & Čaplovičová M. (2000) Evolution of pyrophyllite particle sizes during dry grinding. *Clay Minerals*, **35**, 423−432.

Volzone C., Aglietti E.F., Scian A.N. & Porto Lopez J.M. (1987) Effect of induced structural modifications on the physicochemical behavior of bentonite. *Applied Clay Science*, **2**, 97−104.

Wiewióra A., Sanchez-Soto P.J., Aviles M.A., Justo A. & Perez-Rodriquez J.L. (1993) Effect of dry grinding and leaching on the polytypic structure of pyrophyllite. *Applied Clay Science*, **8**, 261−282.