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Evolution of pyrophyllite particle sizes during dry grinding

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ABSTRACT: The Bertaut-Warren-Averbach (BWA) technique and high-resolution transmission electron microscopy (HRTEM) were used to characterize the products of dry-ground pyrophyllite. Mean crystallite thickness and crystallite thickness distributions were measured for each sample using the BWA technique. Mean crystallite thickness decreases during the treatment with respect to grinding time and energy applied per unit mass. The BWA data were checked by HRTEM measurements and good fits were obtained for samples having small mean particle thicknesses. Samples with thicker particles could not be measured properly by HRTEM because the number of particles counted from images is statistically insufficient. The shape of the crystallite and the particle-size distribution were used to determine the mechanism of pyrophyllite particle degradation. Particles initially having a lognormal size distribution are first delaminated randomly, then some are delaminated preferentially, thereby producing polymodal thickness distributions. Finally all particles undergo delamination yielding a lognormal thickness distribution.

KEYWORDS: Bertaut-Warren-Averbach technique, grinding, pyrophyllite crystallite, HRTEM.

The properties and behaviour of pyrophyllite have been studied by many authors in order to find new technological approaches for processing pyrophyllite materials. The most frequently studied treatments are dry grinding (Pérez-Rodriguez & Sánchez-Soto, 1991; Sánchez-Soto *et al.*, 1992; 1994; Wiewiora *et al.*, 1993), thermal treatment (Sánchez-Soto & Pérez-Rodriguez, 1989; Sánchez-Soto *et al.*, 1997a) and chemical treatment (Pérez-Rodriguez *et al.*, 1995). The effect of grinding on kaolinite-pyrophyllite-illite natural mixtures has been also studied (Sánchez-Soto & Pérez-Rodriguez, 1994).

Grinding (dry and/or wet) degrades the crystal structure of phyllosilicates. Some minerals disappear completely when intensive grinding is applied (smectite – Čičel & Kranz, 1981; kaolinite – Kristof *et al.*, 1993; Suraj *et al.*, 1997), whereas other minerals change their original properties (kaolinite – Miller & Oulton, 1970; Kristof *et al.*, 1993; Suraj *et al.*, 1997; talc – Sánchez-Soto & Pérez-Rodriguez, 1994). Wet grinding of basalts leads to the formation of smectite (Kühnel & Van der Gaast, 1989) from volcanic glass.

In this study, pyrophyllite from a recently-described accumulation in Slovakia was dry ground. It was analysed subsequently by two methods. First, the Bertaut-Warren-Averbach (BWA) technique was used for crystallite size (X-ray scattering domain size) measurements based on X-ray diffraction (XRD) patterns (Drits *et al.*, 1998). This method has previously been used for crystallite size measurements of different clays (Eberl *et al.*, 1998b; Kotarba & Środoń, 2000; Šucha *et al.*, 1999; Mystkowski *et al.*, 2000). The second is HRTEM of ultrathin sections. The main objective is to describe the evolution of pyrophyllite

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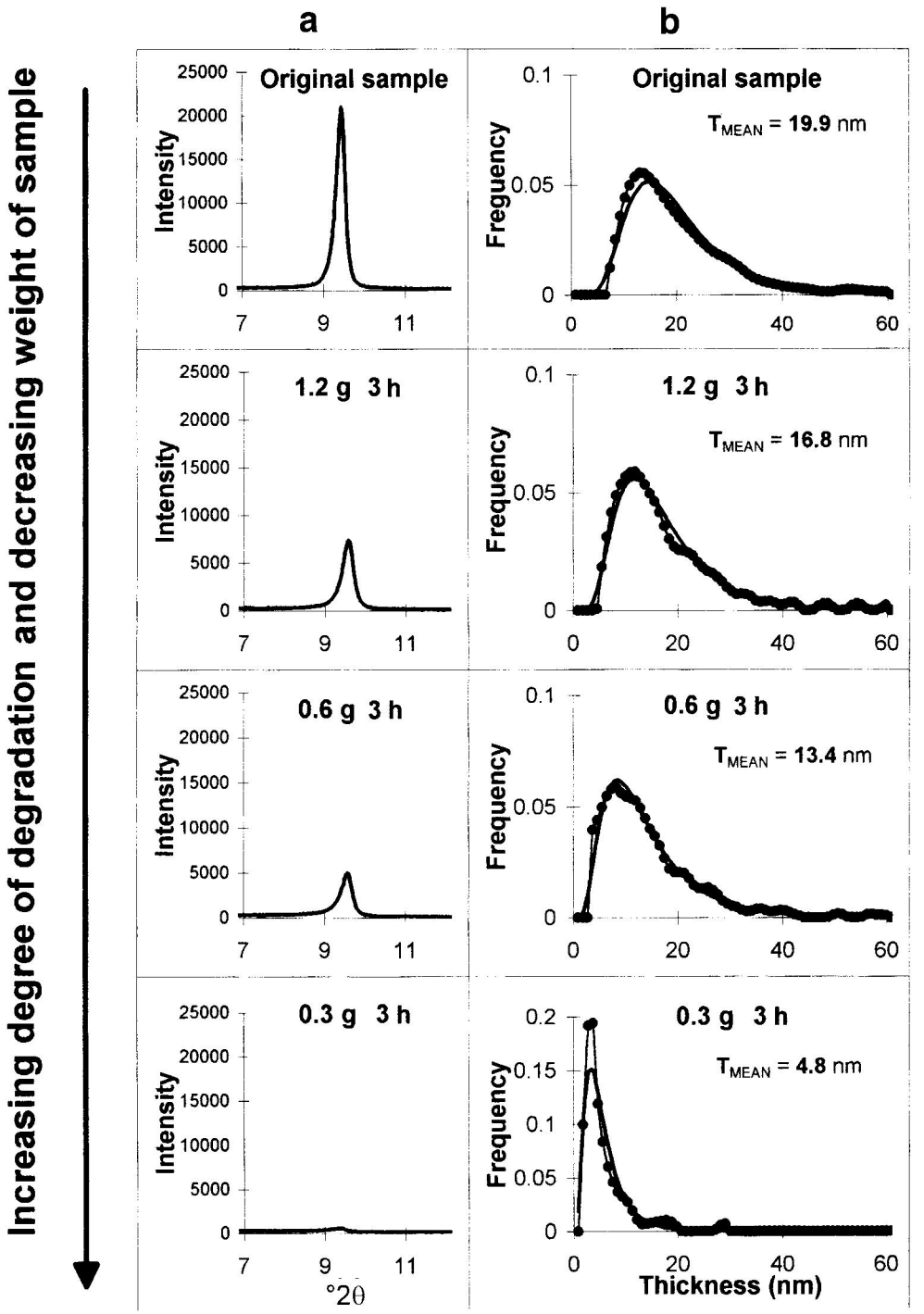


FIG. 1. XRD pattern of 001 reflections of original and treated samples VH3 (a) Distributions of crystallite sizes (black spots) calculated using MudMaster© (b) g = amount of ground samples in grams; h = time of grinding in hours; T_{MEAN} = mean thickness calculated using MudMaster, solid line = theoretical lognormal distribution).

particle-size distributions with increasing intensity of grinding, and to deduce the mechanism of pyrophyllite degradation.

GEOLOGICAL SETTING AND MATERIALS

The pyrophyllite used comes from the Vígl'ašská Huta deposit, which is related to the stratovolcanic structure of the Javorie Mts. and is of Miocene age. The stratovolcanic structure is situated in the internal part of the Western Carpathian arc (Central Slovakia).

The deposit was formed by hydrothermal alterations of andesitic tuffs, breccias and andesites by highly sulphidic, hydrothermal fluids related to intrusions of granodiorites and diorites (Štohl *et al.*, 1994), which led to the formation of quartzite bodies surrounded by argillic zones. The central zone, close to the quartzite body, contains mainly pyrophyllite, pyrite and alunite. An external zone has a slightly different mineralogical association dominated by pyrophyllite, illite, pyrite and alunite accompanied by kaolinite, zunyite and andalusite (Galko, 1998).

Pyrophyllite (VH3) from the Vígl'ašská Huta deposit has the following crystallochemical composition: $(Si_{8.13})(Al_{3.76}Fe_{0.04})(Ca_{0.02}Na_{0.02})O_{20}(OH)_4$. It belongs to the *1Tc* polytype group (Uhlík & Šucha, 1997).

METHODS

The <2 μm fraction, separated by sedimentation from bulk rocks, was used in all experiments. Pyrophyllite was ground using a Fritsch 601 agate ball mill for times ranging from 1 to 6 h. Three series of samples with variable weights, 0.3, 0.6 and 1.2 g, respectively, were exposed to grinding.

Oriented specimens were prepared by sedimentation of clay suspension onto glass slides (10 mg/cm^2). The XRD analysis was carried out using a Philips X-ray diffractometer model 1710 equipped with a Cu tube and a Ni filter at 20 mA and 40 kV. The step size for all analyses was 0.02°2θ, with counting times of 1 and 5 s/step. Patterns with the longer counting time were used for analysis by the MudMaster© computer program (Eberl *et al.* 1996).

MudMaster© (MM) is a program for calculating crystallite size distribution and strain from the shapes of XRD peaks, according to the Bertaut-Warren-Averbach (BWA) method (Drits *et al.*, 1998). It is based on the observation that XRD peaks are broadened regularly as a function of decreasing crystallite size. Mean crystallite size and distribution are calculated from the interference function. Before the interference function is submitted to Fourier analysis, the program corrects for the Lorentz polarization function, structure factor and background. Pyrophyllite 001 peaks

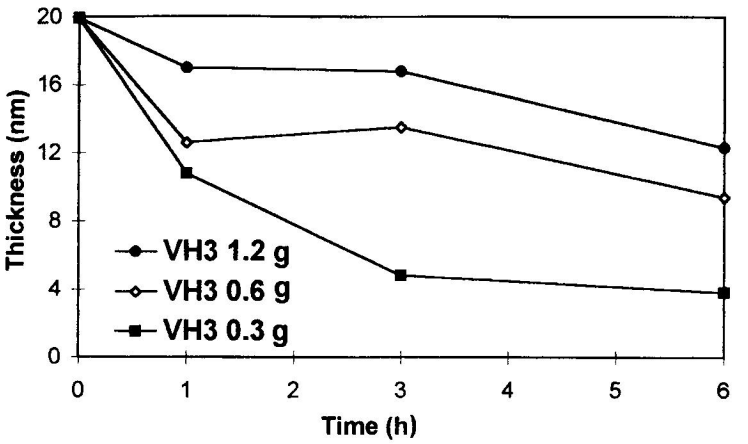


FIG. 2. Mean thickness data of sample VH3 determined using the BWA technique *vs.* the time of grinding and amount of sample treated.

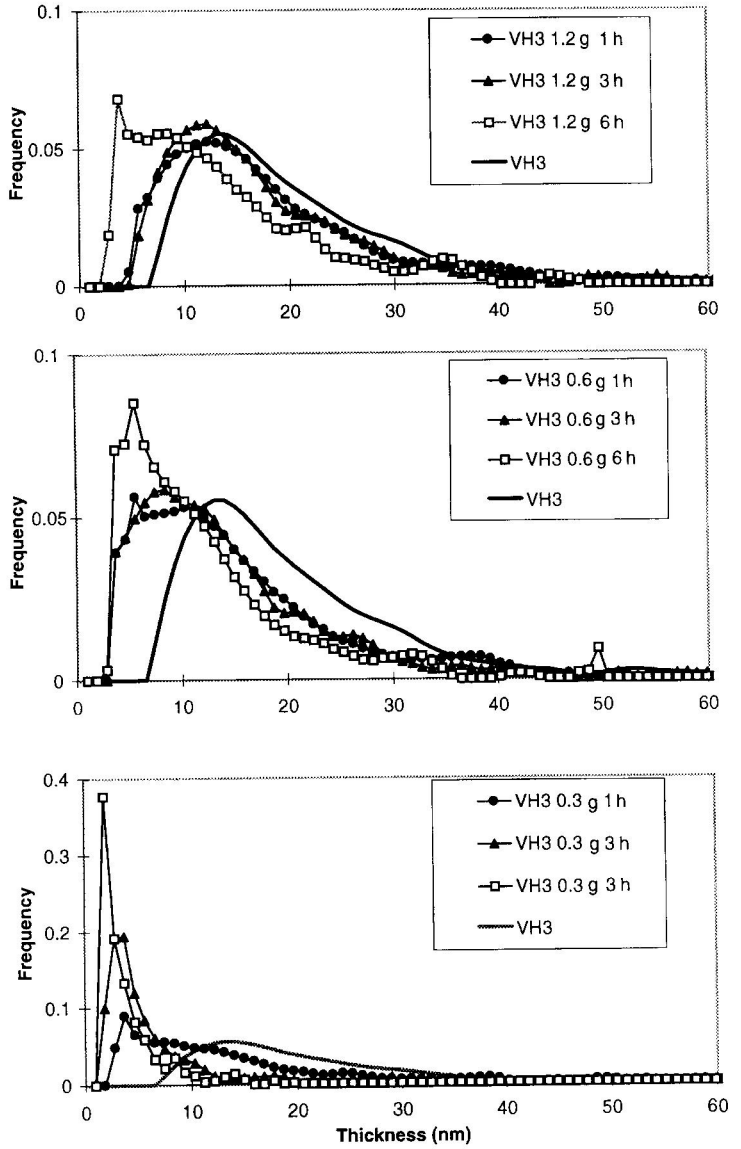


FIG. 3. Thickness distributions of original and treated samples determined using the BWA technique. g = amount of ground samples in grams; h = time of grinding in hours.

were used for analysis as suggested by Eberl *et al.* (1996), because low-angle reflections are not affected significantly by strain broadening.

A small portion of natural and treated samples were coated with agar before applying the embedding procedure described by Tessier (1984). Agar-coated samples were saturated first with water. Samples were subsequently saturated by methanol and propylene oxide to expel all water and then impregnated with Spurr resin. Ultrathin sections, 70 nm thick, were cut using a Reichert Ultracut microtome with a diamond knife. The HRTEM measurements were performed using a JEOL JEM-2000 FX electron microscope at 160 kV, magnification 60,000× and at under-focused conditions using an objective aperture of

50 μm. High-resolution images were observed using binocular with 10–40× magnification.

RESULTS AND INTERPRETATION

XRD of dry-ground samples

Significant broadening and decrease of 00l peak intensities were observed (Fig. 1a) with increasing grinding time. This observation supports previous works (Čičel & Kranz, 1981; Sánchez-Soto *et al.*, 1992, 1994; Wiewiora *et al.*, 1993). Differences in degradation intensity were observed for different weights of samples. The less the amount of sample, the more intense was the degradation observed, indicating that the same energy applied to a smaller mass of sample causes more intensive degradation (Fig. 1a).

Particle size distribution

BWA method. Mean crystallite thicknesses calculated from XRD patterns using the BWA method are very consistent with visual evaluation of the XRD basal reflections. Crystallite thicknesses decrease with grinding time and inversely with sample mass (Figs. 1b, 2). The original mean crystallite thickness of the Vígl'ašská Huta sample is ~20 nm. The mean thickness of the largest mass (1.2 g) of this sample exposed to 1, 3 and 6 h treatment, changed to 17.5, 17.0 and 13.0 nm, respectively, whereas the 0.6 g sample reached mean thicknesses of 13.0, 13.2 and 10.3 nm after the same treatment. The most dramatic decrease was observed for the smallest sample. The mean thickness at first dropped to 11 nm and subsequently to 5 nm. After the 6 h treatment the sample was strongly degraded and almost no XRD peaks could be detected. The BWA technique gave a mean thickness of 3.8 nm.

Crystallite thickness distributions for the original, untreated pyrophyllite (Fig. 1b uppermost) have the lognormal shape that is characteristic of many clays (Eberl *et al.*, 1990; 1998a,b). The lognormal distribution can be characterized by two parameters, α and β^2. α is a function of the mean size, and β^2 is a function of the shape or uniformity of the distribution (Eberl *et al.*, 1998a).

Distributions of crystallite thicknesses were determined for all of the ground samples from Vígl'ašská Huta (Fig. 3). When they are compared to the original distribution of the untreated sample, some differences in the shape and/or in the position of distribution maxima can be observed. A convenient way to compare shapes of distributions is by using reduced axes. This normalization removes the effects of mean size and maximum frequency, so that distributions having the same shapes will coincide. Thickness divided by mean thickness is plotted on the x-axis, and frequency divided by maximum frequency on the y-axis. The thickness distributions evolve with respect to the time of grinding and the mass of the sample (Fig. 4a,b,c). The reduced profile depicted in Fig. 4d coincides with the original lognormal distribution of starting sample, which indicates that the shape of the distribution did not change during treatment, even though the mean particle thickness decreases (Figs. 1,2). Such behaviour, observed in two of nine samples, indicates random delamination of the particles without regard to size. This mechanism is analogous to random ripening, but is opposite in direction. Random ripening, according to Eberl *et al.* (1998a) is a crystal growth mechanism during which some crystals dissolve, and others grow longer, at the expense of the dissolving crystals. Unlike Ostwald ripening, in random ripening a factor other than size determines particle stability, and during this process the shape of the profile is preserved. In the case of grinding of the sample, depicted in Fig. 4d, breaking of particles is random, probably controlled by strain in crystals, stacking faults or other imperfections in particles. The important point is that the particles undergo this process randomly, and no particle is delaminated completely. This process preserves the original, lognormal shape of the initial distribution.

When further grinding is applied, or a smaller amount of the sample is used, different distribution shapes are observed (in five of nine samples). A bimodal or polymodal distribution is obtained, with a maximum at small thicknesses (Fig. 4b) which is significantly different from the original distribution of untreated VH3 (Fig. 4e). This change in shape indicates that particles are not destroyed (or delaminated) at the same rate, but that some particles are delaminated faster than others. This process could be related to some structural and/or crystallochemical properties of pyrophyllite particles. The maximum of the reduced profile in Fig. 4e is shifted to the left towards a smaller thickness/mean thickness ratio even though the mean remains large because a large number of thick particles still remain in the system.

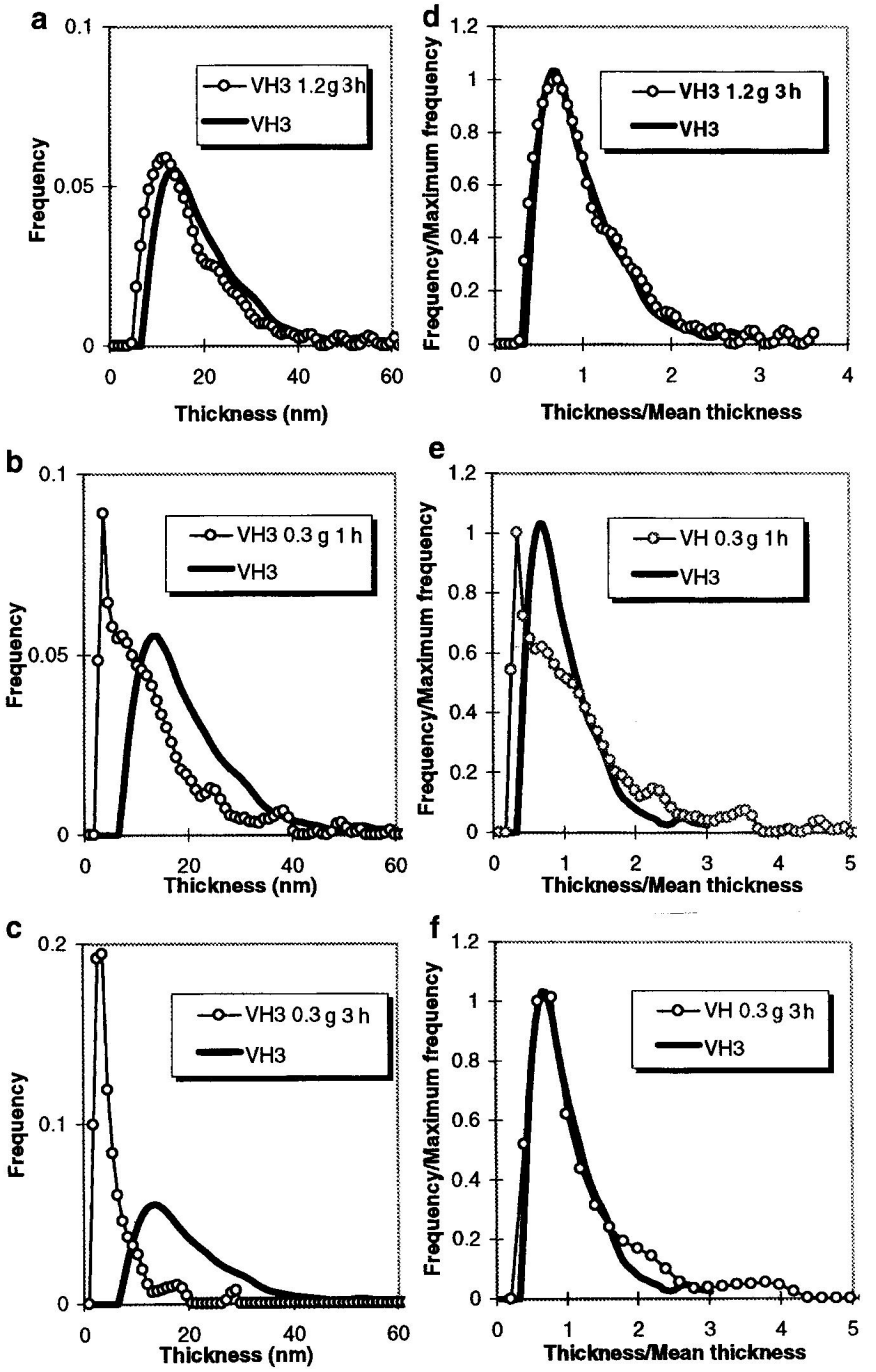


FIG. 4. Thickness distributions (a, b, c) and reduced plot (d, e, f) of natural and ground samples. Similar shapes of reduced profiles for natural and treated samples (steady-state plots in d and f) indicate the same rate of degradation for all particles. Different shapes for reduced curves (e) indicate that some particles are delaminated more quickly than others.

Finally, for two the most degraded samples (Fig. 4f), the maximum is shifted in the opposite direction, towards larger values, because the mean is significantly smaller. Reduced profiles of the most degraded samples are again close to the original lognormal shape. This means that finally, all particles are affected by delamination. According to the theory of breakage (Aitchison & Brown, 1957), a lognormal distribution may be expected to be produced by grinding, but it is interesting that the final distribution (Fig. 4f) seems to have a very similar shape of reduced profile to that of the initial distribution.

HRTEM method. High-resolution images were used for measuring the thicknesses of pyrophyllite crystals and subsequent calculation of mean particle thickness and thickness distribution. The results in Fig. 5a,b indicate a good fit between distributions obtained by the BWA technique and by the HRTEM images for samples with small mean thicknesses. The fit indicates that measurements obtained using the BWA technique from the MudMaster program are reliable for pyrophyllite (the reliability has been documented previously for illite by Eberl *et al.*, 1998b). It means that the mean crystallite thickness is equivalent to pyrophyllite crystal thickness for measured samples. Significant differences between the BWA data and the HRTEM measurements were determined for thicker samples (Fig. 5c,d). The smaller mean thicknesses for the HRTEM data may be due to a statistically insufficient number of measured particles for the HRTEM technique because the samples with higher mean thickness contain particles with more variable thicknesses than the samples with lower mean thickness.

HRTEM images

Images of ultrathin sections taken at low and high magnifications were used to document morphological changes during the treatment.

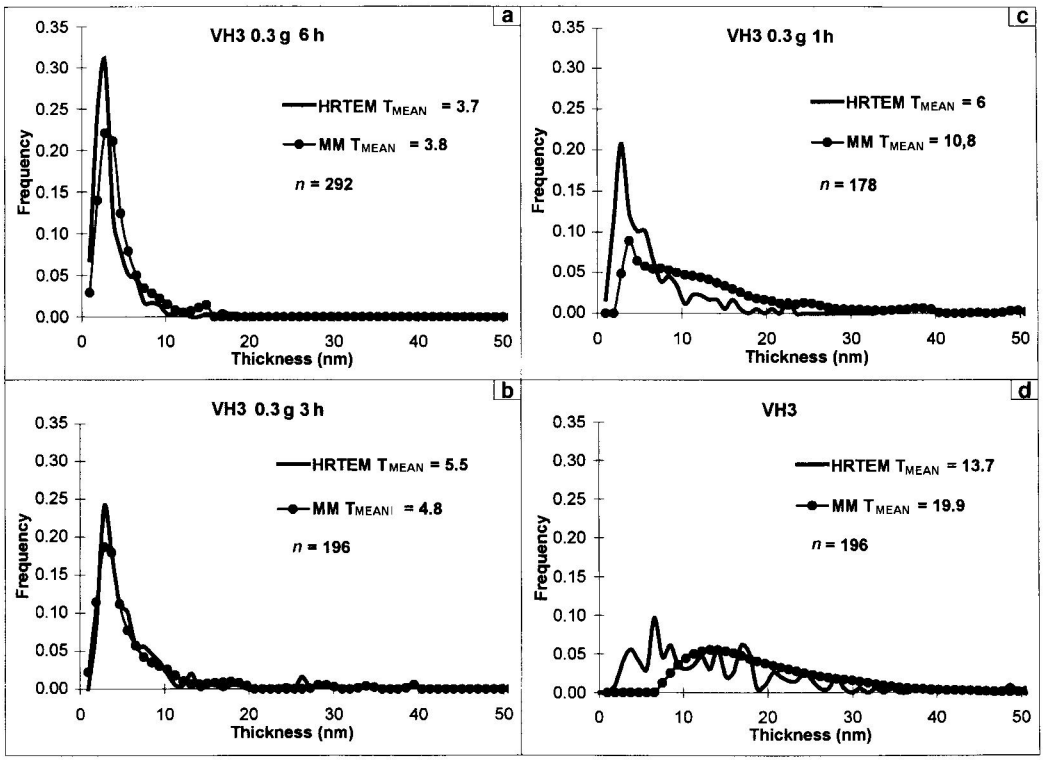


FIG. 5. Thickness distributions of four selected samples obtained using the BWA technique and HRTEM. T_{MEAN} = mean thickness in nm; n = number of measured particles on the HRTEM images.

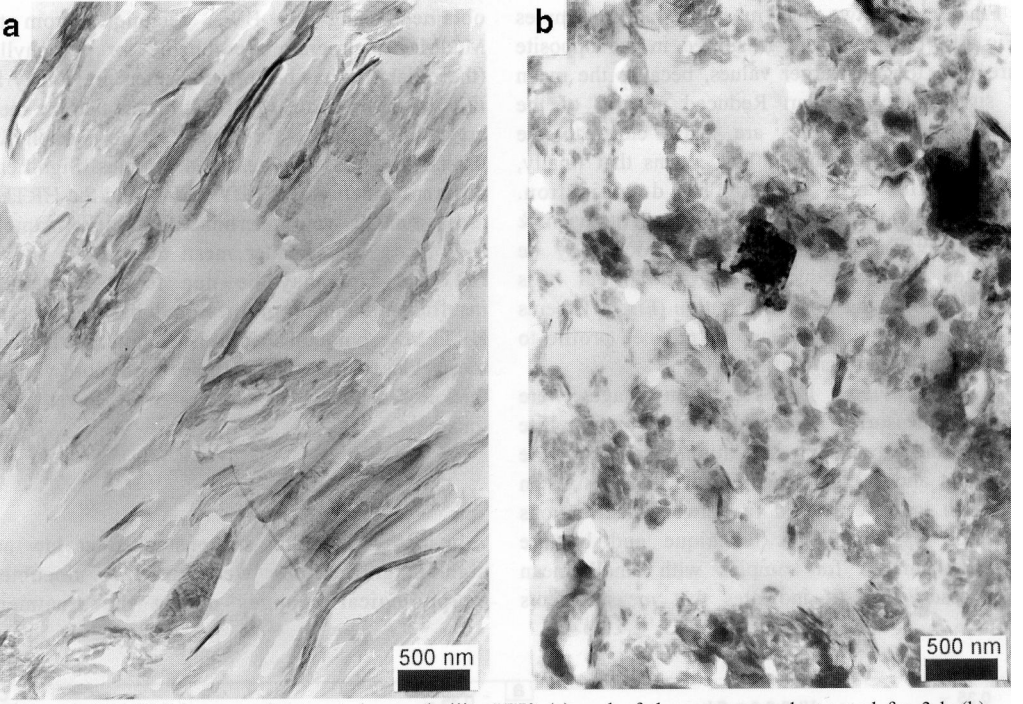
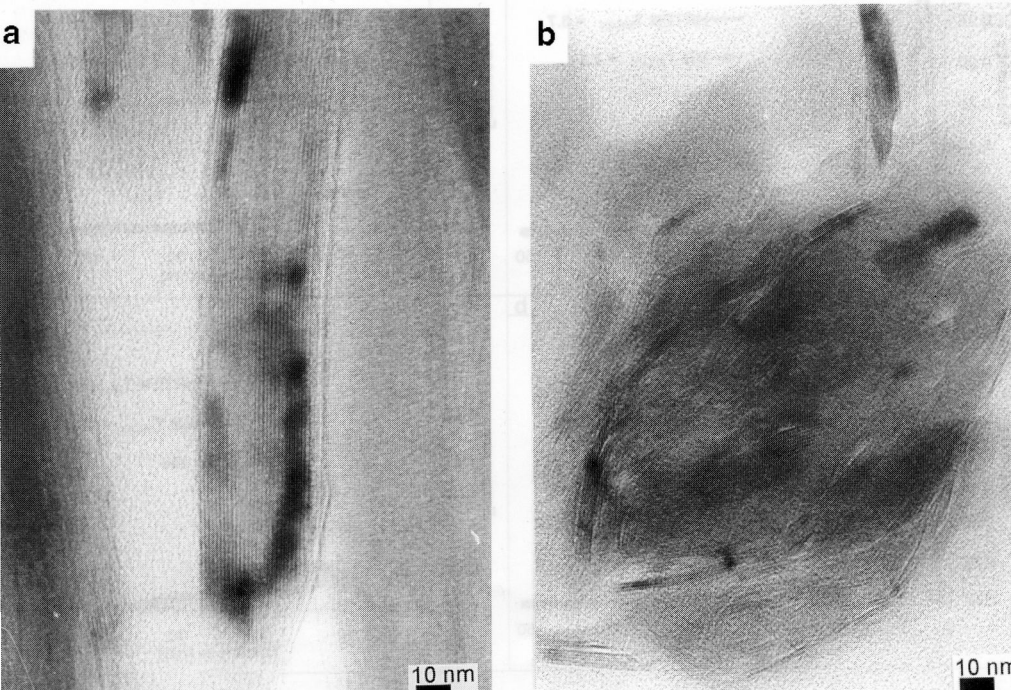


FIG. 6. HRTEM images of untreated pyrophyllite VH3 (a) and of the same sample treated for 3 h (b).



Untreated pyrophyllite (VH3) contains thick, long particles distributed regularly in the sample, and easily detectable on both low and high magnification images (Figs. 6a, 7a). During the treatment, particles were delaminated and partly amorphized, forming a large number of dark grey spots, without detectable layer fringes (Fig. 6b). Partly degraded samples tend to form rounded aggregates of amorphous matter and delaminated crystals (Fig. 7b). The presence of these aggregates supports previous observations (Hlavay *et al.*, 1977; Wiewióra *et al.*, 1993; Suraj *et al.*, 1997) of BET surface area changes during grinding. These authors found that surface area increases slightly at the beginning of the treatment, an increase which may be connected, according to the HRTEM images, with simple delamination of the particles. When rounded aggregates are formed, the surface area drops because N_2 molecules used for BET measurements can not penetrate the inside of the aggregates.

CONCLUSIONS

Dry grinding leads to a decrease of mean particle thickness which can be detected both by HRTEM images and by the BWA technique. The BWA technique gives reliable data for mean particle thicknesses and for particle thickness distributions at least for thin samples, as is confirmed by HRTEM. The level of pyrophyllite degradation is related to grinding time and to the energy applied per unit mass. Particle thickness distributions during dry grinding of pyrophyllite preserve their original shape at the beginning of the treatment. More intensive treatment leads to different rates of degradation.

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