EFFECT OF SONICATION ON STRUCTURE
AND PARTICLES DIVISION OF PYROPHYLLITES

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ABSTRACT
Pyrophyllites from Zalamea (Badajoz, Spain) and from Hillsboro (North Carolina USA), were subjected to treatment in ultrasonic liquid processor and studied by BET, SEM and XRD methods in an attempt to reveal changes in structure ordering and particle sizes. Original sample of pyrophyllite from Zalamea is characterized by clay size particles and well organised polytypic structure $1A_A$-II,1. During 5 hrs of sonication the structure suffered only small destruction, but further sonication for 10 hrs produced significant structure disorder marked by smearing out of all the polytypic 02*l*, 11*l* reflections. Pyrophyllite from Hillsboro is represented by lath-crystals of macroscopic size, displaying poorly ordered structure classified to subfamily A of polytypes. MDO group and polytype could not be determined and stay unknown. Changes in particle sizes in terms of specific surface area, e.s.d. and best mean thickness of the domains of coherent X-ray scattering were most rapid during first 10 hrs of sonication, similar in the both studied pyrophyllites. Limit of particle division was achieved after 20 hrs – 40 hrs sonication. Irrespective of differences in the initial morphology and structural order the samples finally divided during sonication reached similar particle sizes (e.s.d. around 30 nm), best mean thickness of the domains of coherent scattering (around 12 nm) and showed alike structural disorder.

KEYWORDS: pyrophyllite, polytypes, sonication

1. INTRODUCTION

The structure of minerals classified in the talc-pyrophyllite group is built up of 2:1 layers, characterized by three octahedral positions per four tetrahedral positions and no charge on the layer. The detailed pyrophyllite structure is known from several X-ray studies (Grüner, 1934; Rayner and Brown, 1966; Brindley and Wardle, 1970; Wardle and Brindley, 1972; Lee and Guggenheim, 1981) and from electron diffraction (Zvyagin et al., 1979; Sidorenko et al., 1981). Naturally occurring pyrophyllite is known to have one-layer triclinic, two-layer monoclinic structure and/or a mixture of these two forms.

Practical determination of pyrophyllite polytype in natural samples met with difficulties. The identification of the triclinic pyrophyllite by using X-ray powder diffraction is unquestionable. Triclinic ($1T_c$ = $1A_A$ - II,1) structure was successfully determined by the powder method (Wardle and Brindley, 1972) and fully refined by the single crystal method (Lee and Guggenheim, 1981). Using this structure data to calculate the powder diagram makes polytype identification reliable. Frequently polytypic diffractions are completely or severely blurred. Wiewióra et al. (1993) demonstrated that ground

triclinic ($1A_A$-II,1) pyrophyllite from Zalamea, Spain resembled monoclinic pyrophyllite from Honami, Japan. Possibility of the coexistence of these two forms, triclinic and monoclinic, mixed in a sample (Brindley and Wardle, 1970; Wiewióra and Hida, 1996) is possible, too.

Identification of pyrophyllite occurring in natural multiphase samples, its purification and behaviour on dry and wet grinding as well as the effects of chemical treatment in acid solutions have been studied in previous works by means of several methods, such as X-ray diffraction, scanning electron microscopy and chemical and thermal analyses (Pérez-Rodríguez et al., 1985, 1988; Pérez-Rodríguez and Sánchez-Soto, 1991; Maqueda et al., 1986, 1987; Sánchez-Soto et al., 1992; Wiewióra et al., 1993). The knowledge of the mineralogical and chemical composition of natural pyrophyllite material, and several observations recently made on the ground material (X-ray characteristics, surface area and dehydroxylation temperatures) have now made it easier to approach the structural alteration with a new look from a point of view of polytypism. In natural samples of clay minerals of the talc-pyrophyllite group one finds significant structure disorder (Wiewióra et al., 1993;

Wiewióra and Hida, 1996). These minerals are extremely fragile and susceptible to mechanical treatment; even weak shear forces affect crystallinity and produce degradation in particle sizes (Wiewióra at al., 1996, 1997; Sanchez-Soto et al., 1997).

For pyrophyllite, different grinding procedures are used in industry: dry grinding and wet grinding. It is well known that grinding produces not only particle size reduction but also various effects on structure and properties of laminar silicates, such as amorphization, aggregation or modification of the surface properties (Grim, 1968), that are in general undesirable for the most applications of pyrophyllite. Very recently, the use of sonication for processing laminar silicates has been proposed: for vermiculites (Pérez-Maqueda et al., 2001; Pérez-Rodríguez et al., 2002) and for micas (Pérez-Rodríguez et al., 2004).

Study of the effect of sonication on pyrophyllite structure requires recognition of structural properties. It appears that the results of structure determination and its ordering is dependent on the used technique. Important condition was to apply the most effective technique for the study of such samples, namely the transmission focusing diffractometry and position sensitive detector, enabling recording the diffractogram in the interval of 120° 2θ, at once. In this paper this technique was used to determine subfamily and MDO (maximum degree of order - see Weiss and Durovič, 1984) group and thus polytypic structure of the studied samples of pyrophyllite, and quite unexpectedly the superstructure in the pyrophyllite crystals from Hillsboro, similar to this first determined by Wiewióra and Hida (1996) in the pyrophyllite samples from Japan.

The aim of this paper is to do the comparative study of the sonication effect on two pyrophyllites different in their morphology and structure ordering. The sonicated materials are characterized in terms of structure modification, specific surface area and particle size distribution.

2. EXPERIMENTAL DETAILS
2.1. MATERIALS

Raw pyrophyllite from Zalamea (Badajoz, Spain) and from Hillsboro (North Carolina, USA) were used for this study. The natural sample of pyrophyllite from Zalamea has admixtures of kaolinite, mixed layer illite-smectite, illite, rutile and quartz (Pérez-Rodríguez et al., 1985) The raw pyrophyllite was purified by the procedure described by Maqueda et al. (1987). As a result of this chemical purification, all the extraneous phases were eliminated except for a small admixture of rutile (Wiewióra et al., 1993).

Pyrophyllite from Hillsboro (NC, USA) was obtained from Ward's N. S. Establishment (Rochester, N. Y.). It is crystallized in a shape of the flattened needles of various length of the order of several millimetres up till over 1 cm. The needles are composed in rosettes of the greyish-white colour with addition of scattered pinkish pigmentation. Rosettes are densely packed. Before sonication the pyrophyllite samples were crushed and subjected to short time action in the isogranulometric knife-mill (Retsch ZSM-1) and sieved under 2 mm. Subsequently they were sonicated during 2, 5, 10, 20, 40 and 60 hours.

2.2. SONICATION

The sonication procedure was performed with a high-intensity ultrasonic horn (Misonix inc.), which consists of a solid titanium rod connected to a piezoelectric ceramic, and a 20 KHz, 750 W power supply was used. 3 g of original sample were mixed with 100 cm^3 of freshly deionised water. The temperature of the reactor was kept constant at 20 ºC during the entire treatment by means of a cooling recirculator. The dispersion was sonicated for periods ranging between 10 and 60 hrs in cycles of 10 hours each.

2.3. BET MEASUREMENTS

The specific surface areas (S_{BET}) of the samples were determined using an automatic system (Micromeritics 2200, Norcross, GA) with the help of the BET method, performed at liquid nitrogen temperature. Nitrogen gas was used as the adsorbate. The equivalent spherical diameter (e.s.d. in μm) was calculated from the S_{BET} by means of the expression: e.s.d. $= 6/\rho S$, where, ρ is the density of the material (2.8 g/cm^3), and S is the S_{BET} (m^2/g) determined by BET.

2.4. SEM MICROGRAPHS

A direct examination of the particles was carried out using an electron scanning microscope (SEM, model of Jeol). The acceleration of 20 kV was applied.

2.5. XRD MEASUREMENTS

X-ray diffraction (XRD) powder patterns were recorded, using Co tube, on a transmission focusing diffractometer with a position sensitive detector (PSD-120 of Inel, France). The curved quartz crystal monochromator placed between the source of radiation and the sample was adjusted to strictly monochromatic Kα_1 radiation focused on the recording edge of the multi-channel detector (4096 channels per 120º 2θ). In effect, diffraction maxima are free of convolution broadening, so much characteristic for the standard type of reflection and transmission coupled θ, 2θ diffractometers, equipped with the mobile detectors. X-ray transmission patterns of randomly oriented particles were recorded from capillary and monolithic samples.

Monolithic samples were used to demonstrate a superstructure in the Hillsboro pyrophyllite. The structure refinement data of Lee and Guggenheim (1981), end-member structural formulas and unit cell

Table 1 Unit cell parameters of pyrophyllites

Polytype	Space group	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	Locality
$1A_A$-II,1	C $\bar{1}$	5.160	8.966	9.347	91.18	100.46	89.64	Zalamea
		5.166	8.952	18.687	90.0	99.82	90.0	Hillsboro

parameters refined from diffraction patterns of original (non treated) samples of the studied pyrophyllites (Table 1) were used as input data for modelling the diffraction patterns. The DIFK program (Weiss and Ďurovič, 1984; Wiewióra et al., 1985; Smrčok and Weiss, 1993) was used to calculate the diffraction patterns with or without the effect of texture on intensities. The simulated X-ray powder diffraction patterns, based on structural data, were used to compare diffractions or to index reflections in the experimental diffractograms.

Particle sizes were estimated from 002 reflection by the use of MudMaster software developed by Eberl et al. (2000). X-ray methods are fast and statistically justified, as X-ray diffraction peaks average diffraction effects from billions of individual clay size particles. Besides, XRD measured sizes are never related to agglomerates, but directly to domains of coherent scattering. This method applies to crystallite sizes less than 100 nm (Eberl et al., 2000), similar to Scherrer's broadening. The MudMaster takes into account distribution of different particle sizes. Therefore, it was preferred over the Scherrer's method, which calculates rather maximum sizes than the mean ones.

a

b
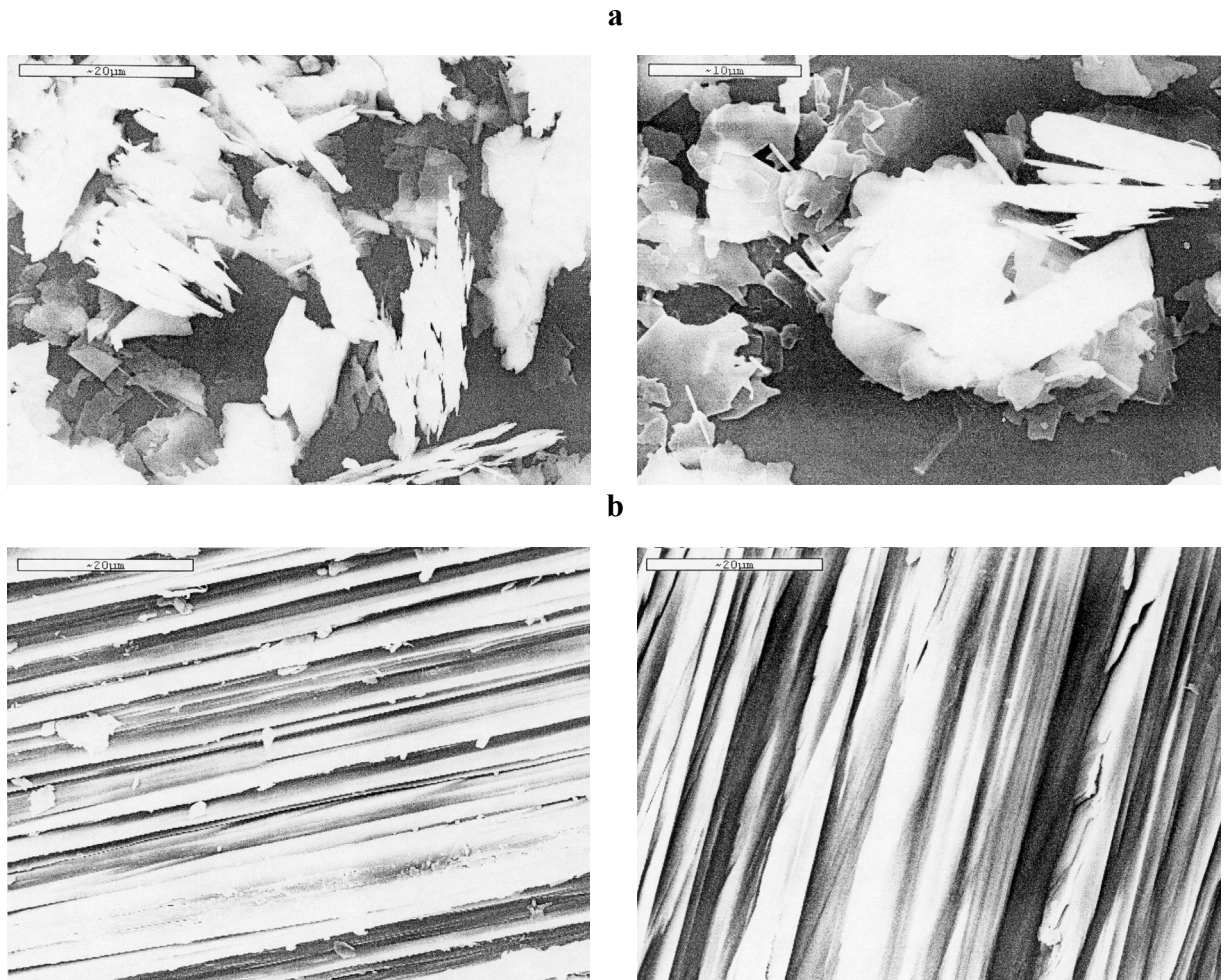
Fig. 1 SEM micrographs of raw pyrophyllites from Zalamea (a) and Hillsboro (b).

3. RESULTS

3.1. ORIGINAL SAMPLES

SEM micrographs are shown for Zalamea pyrophyllite at Fig. 1a and for Hillsboro at Fig. 1b. In the both cases the same magnification was kept. Direct comparison of the micrographs proved different morphology. Zalamea pyrophyllite displays aggregates of the thickness about 0.2 μm and average diameter of about 10 μm. Morphology of Hillsboro very strongly deviates from the habit typical for clay minerals. Fig. 1b shows very thin but very long laths displayed parally with respect to each other. They form quite a massive structure.

XRD tracings of the studied raw samples of both pyrophyllites are compared to the calculated powder diffractogram for the triclinic pyrophyllite (Fig. 2). They permitted to identify the triclinic structure of pyrophyllite from Zalamea, belonging to subfamily A (based on 20l, 13l reflections) and to the II,1 MDO group (based on 02l, 11l reflections). Pyrophyllite from Hillsboro no doubt belongs to the same polytype subfamily A but identification of MDO group was not possible because all 0kl, 11l reflections are smeared out. There appeared only the broad band at 4.15 Å. In consequence, identification of the polytypic structure (1T$_C$ or 2M) was impossible.

X-ray diffractogram from natural non-ground Hillsboro pyrophyllite sample in a form of a lath, picked up directly from the rock-body is presented in Fig. 3 The most surprising is the appearance of the reflections forming series with $d_{(00l)}$ x l = 18.4 Å (double of $d_{(001)}$ = 9.2 Å, common for the most known pyrophyllites). Similar width of all, odd and even basal orders proves that the observed reflections are due to the superstructure, as proved by simulated diffraction pattern. The simulation was done using two-layer structural model based on the published structure refinements by Lee and Guggenheim (1981). To obtain the effect of superstructure, there were assumed the differences in the electron densities of the structural sheets, in octahedra of the every second layer. In the experimental diffractograms two or three orders of basal reflections of kaolinite admixture were also revealed (Fig. 3).

3.2. SONICATED SAMPLES

Diffractograms of original and sonicated samples of pyrophyllite from Zalamea are presented in Fig. 4. After 5 hrs sonication the reflections 02l, 11l ($\bar{1}\bar{1}1$, $0\bar{2}1$, $\bar{1}11$, $\bar{1}12$, 022, 112) are present yet (b), although their intensities are visibly diminished in comparison with the intensities of the original sample (a). After sonication for 10 hrs all the 02l, 11l reflections disappeared, and there appeared a broad band at about 4.16 Å attributed to disordered (initially triclinic) structure (c). Increase in sonication time to 20 hrs and 40 hrs (d and e, respectively) resulted in broadening of practically all reflections, including basal 00l ones. It should be noticed that the subfamily reflections, 13l, 20l, namely 130, $\bar{1}\bar{3}1$, 200, $\bar{1}31$, 131 were not affected by sonication, besides a negligible widening and thus their worse resolution.

Diffraction patterns of pyrophyllite from Hillsboro are presented in Figure 5. Diffractogram of a knife milled, original sample (a) shows 001 and 002 basal reflections stronger than 110 reflection at 4.429 Å due to texture of the sample. In diffractograms of all sonicated samples the intensity ratio of these reflections changes sharply after 10 hrs sonication (b), and step by step for 20 hrs (c) and 40hrs (d) sonication. From 20l, 13l reflections the subfamily A is recognized, similar to Zalamea pyrophyllite. The MDO group and thus the polytype can not be determined because 02l, 11l reflections are smeared out in all diffractograms. The broad band at 4.169 Å proves the structure disordered in a way similar to the disorder produced by sonication of Zalamea pyrophyllite for 10 hrs and more than that.

Fig. 6 shows the variation of specific surface area (Table 2) for pyrophyllite from Hillsboro and Zalamea as a function of sonication time. The graph shows that sonication produces a considerable increase in the specific surface area with a treatment time between 0 and 40 hrs. The specific surface area of Hillsboro pyrophyllite increased from 4.2 to 60.81 m^2/g and for Zalamea pyrophyllite from 3.95 to 51.56 m^2/g after 10 hrs of treatment. This change of surface area value is associated with particle size reduction.

Table 2 Specific surface, equivalent spherical diameter (e.s.d) and best mean values.

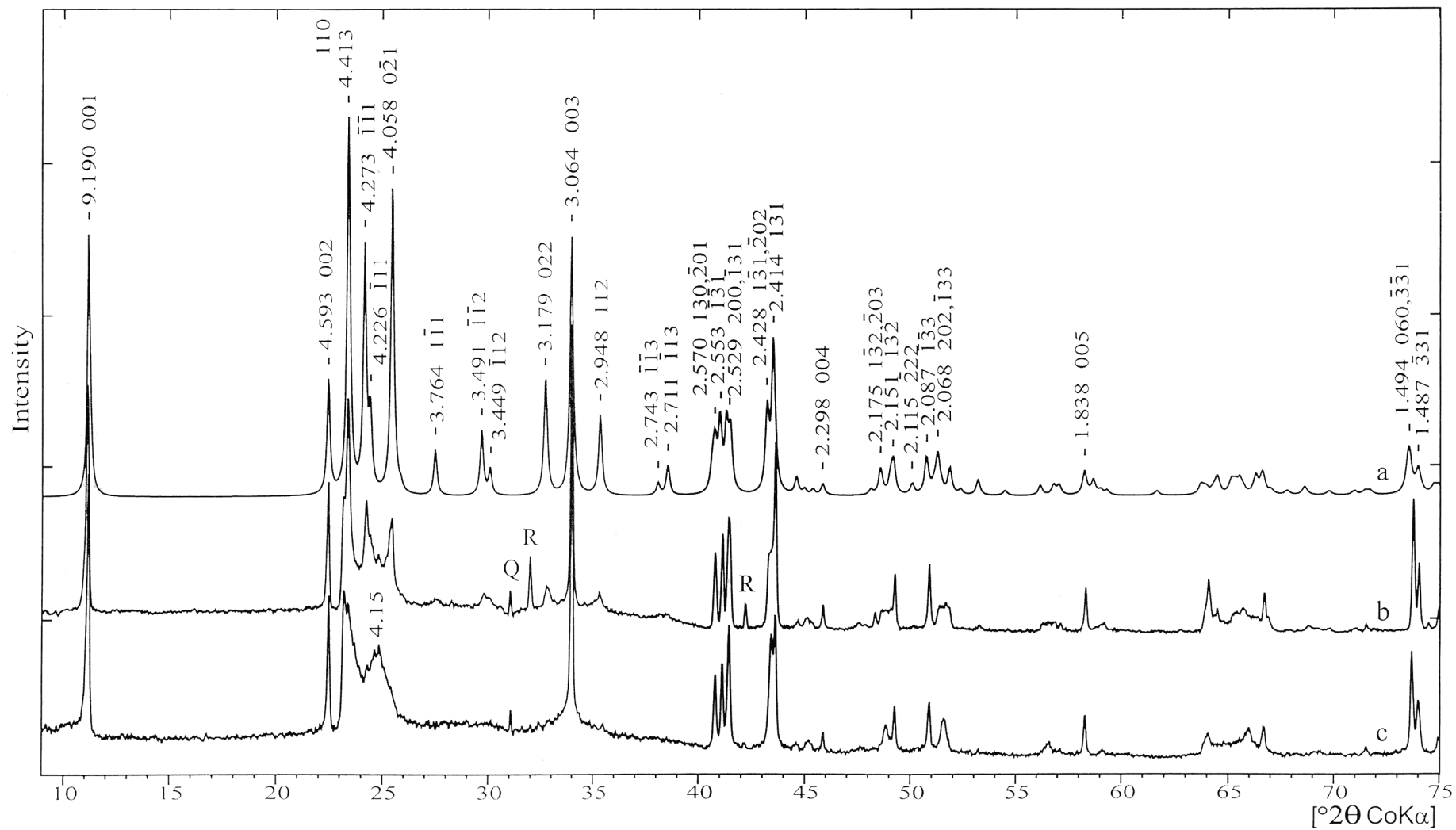| Time of treatment (hrs)	Hillsboro			Zalamea		
	S_{BET} (m^2/g)	e.s.d. (nm)	Best mean for 001 (nm)	S_{BET} (m^2/g)	e.s.d. (nm)	Best mean for 001 (nm)
0	4.2	510	40.1	3.95	543	38.5
10	60.81	41.2	16.8	51.96	35	22.5
20	80.26	30.2	13.9	70.89	27	13.2
40	80.19	30.2	12.2	70.65	26.7	11.7

Fig. 2 XRD transmission patterns of pyrophyllite: a - calculated pattern, b – Zalamea, c – Hillsboro. Q - quartz, R -rutile admixtures. CoKα₁ radiation.
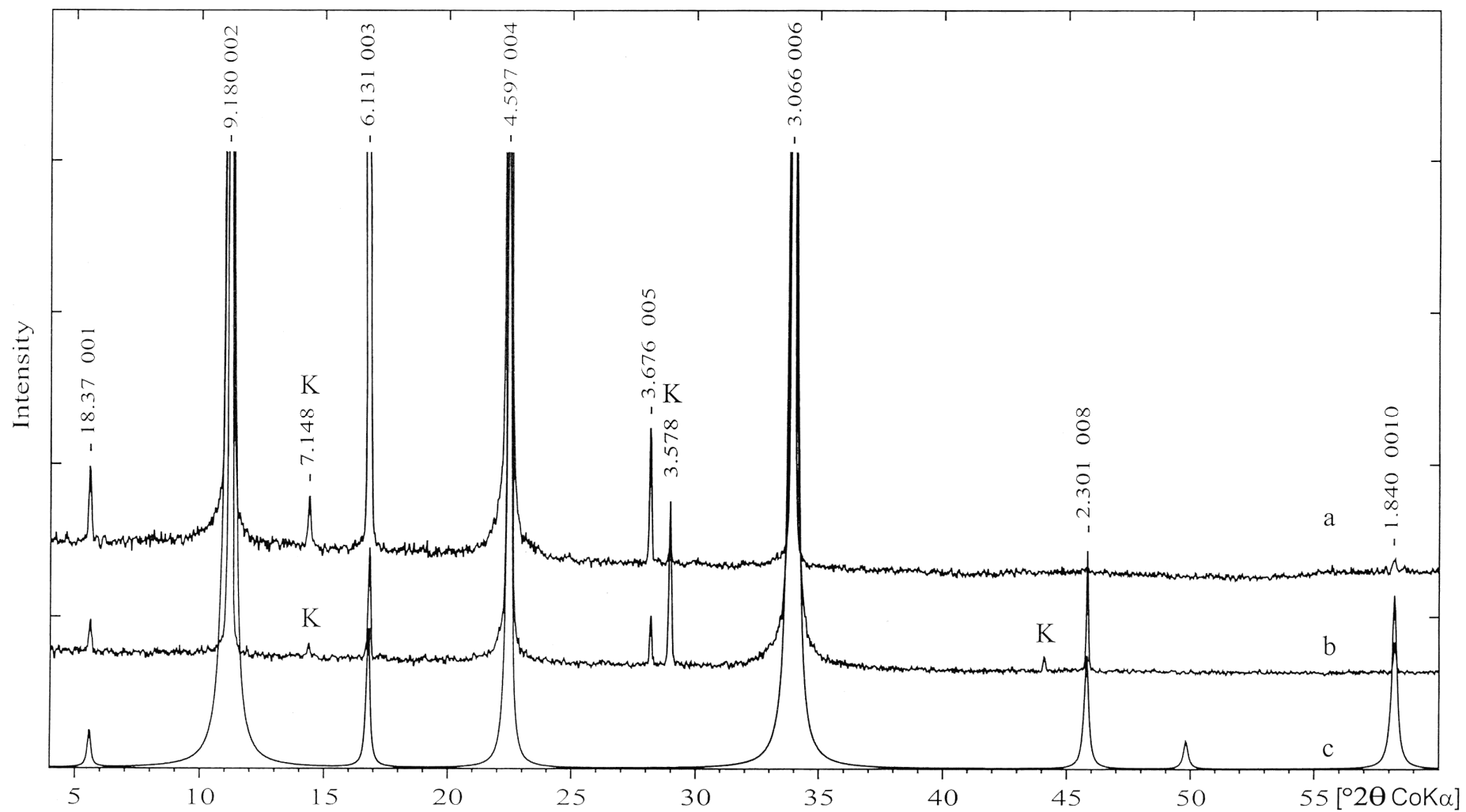
Fig. 3 XRD transmission patterns showing a superstructure: a and b – patterns from a lath of Hillsboro pyrophyllite, c – calculated pattern with coefficient of texture g = 50. K – kaolinite (admixture). CoKα₁ radiation.
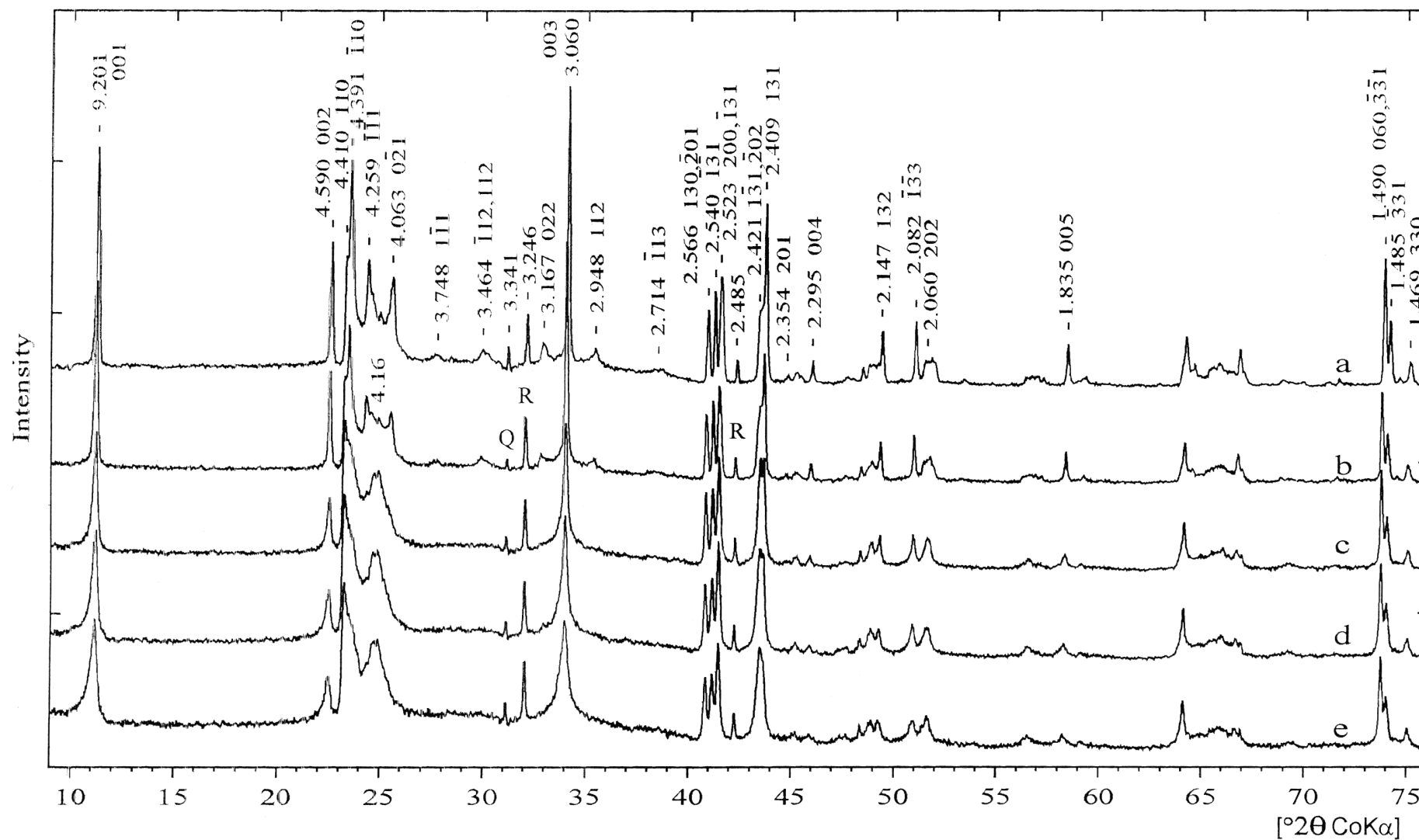
Fig. 4 XRD transmission patterns of pyrophyllite Zalamea: a – untreated; b, c, d, e – sonicated samples for 5hrs, 10hrs, 20hrs, 40hrs, respectively. Q – quartz, R – rutile admixtures. CoKα_1 radiation.
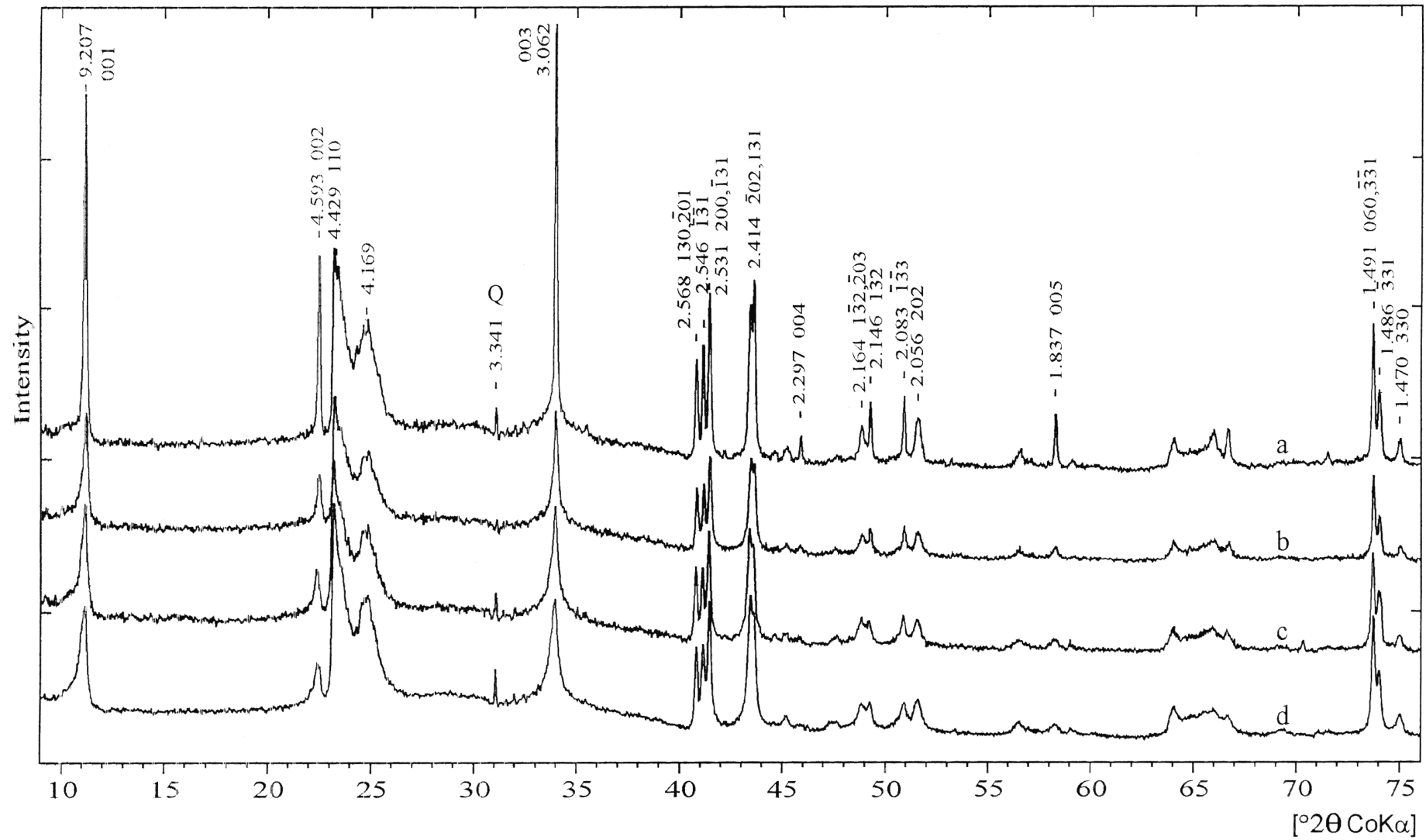
Fig. 5 XRD transmission diffractograms of sonicated Hillsboro pyrophyllite: a – untreated; b, c, d – sonicated for 10hrs, 20hrs, 40hrs, respectively. Q – quartz admixture. CoKα_1 radiation.
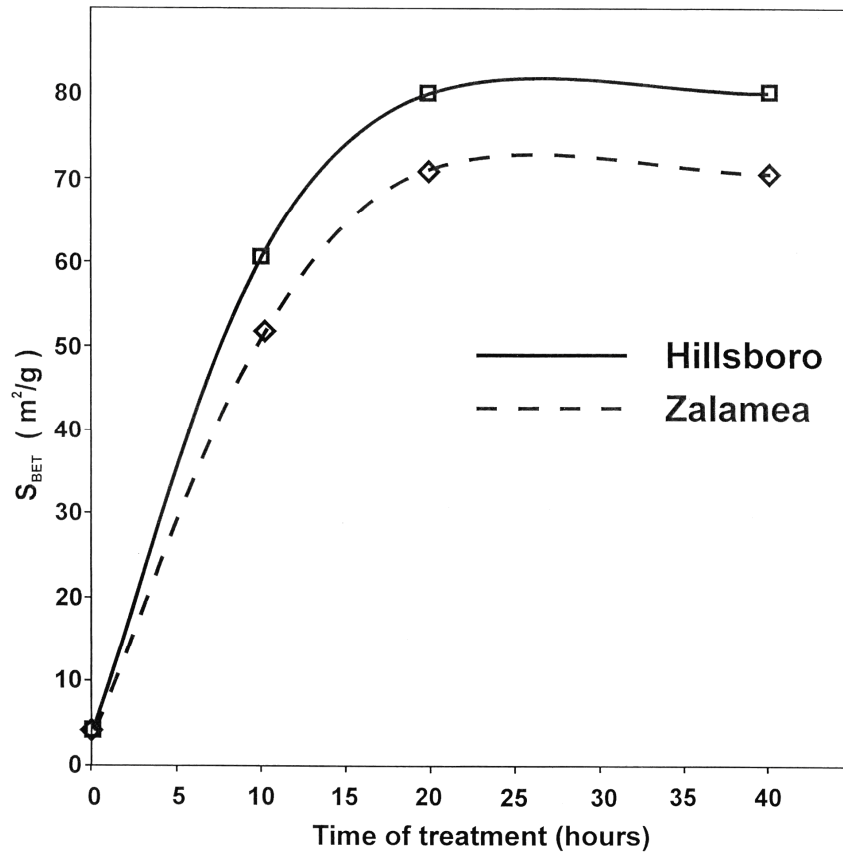
Fig. 6 Specific surface area vs. time of treatment. Dashed line - pyrophyllite from Zalamea, solid line - pyrophyllite from Hillsboro.
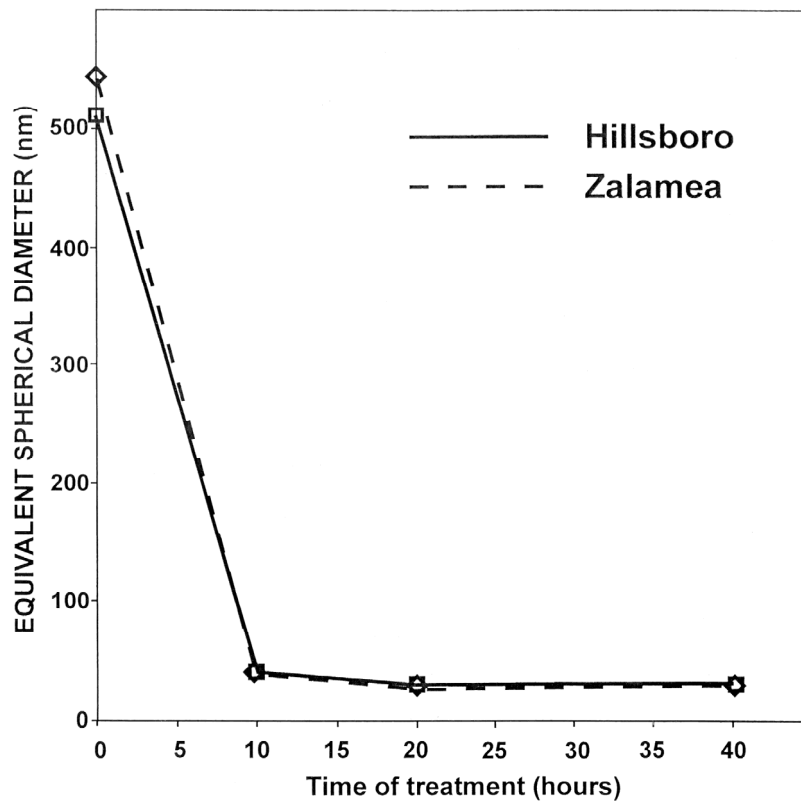

Fig. 7 Equivalent spherical diameter vs. time of treatment. Dashed line - pyrophyllite from Zalamea, solid line - pyrophyllite from Hillsboro.
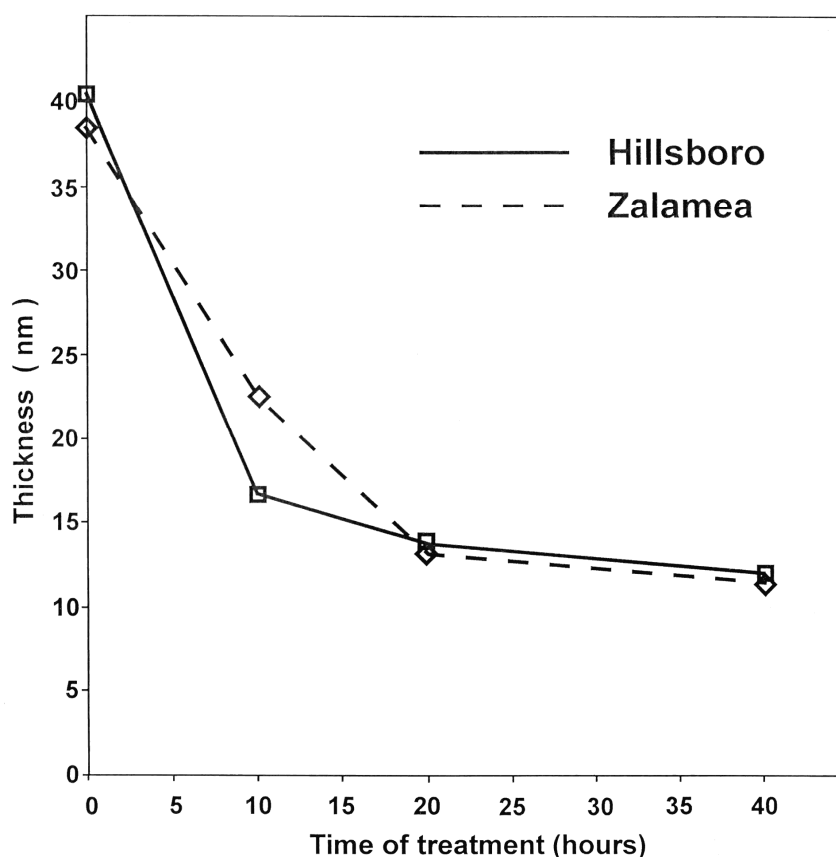
Fig. 8 Best mean thickness of coherent scattering domains vs. time of treatment.

The specific surface area was increasing with the sonication time, as shown in Fig. 6, reaching for Hillsboro pyrophyllite 80.26 m²/g and for Zalamea pyrophylite 70.89 m²/g after 20 hrs. After the applied processing no more size reduction was observed. Values of the coherent scattering domain thickness of pyrophyllite from Hillsboro and Zalamea particles are presented in Table 2 and in Fig. 9. Thickness of domains of coherent scattering for Hillsboro pyrophyllite changes from 40.1 nm for raw sample till 12.2 nm after 40 hours of treatment, and for Zalamea pyrophyllite from 38.5 nm for untreated sample till 11.7 nm after final stage of ultrasonic treatment. Calculated values of equivalent spherical diameter (Table 2 and Fig. 7) show that, the Hillsboro and Zalamea pyrophyllites are in the same range of particle size reduction. After 40 hours of sonication, the e.s.d. value of both pyrophyllites decreased suitably from 510 nm (raw sample) to 30.2 nm for Hillsboro and from 543 nm to 26.7 nm for Zalamea. For both pyrophyllites, the particle division limit was achieved after 20 hours of ultrasonic treatment.

4. CONCLUSIONS

Pyrophyllites from Zalamea and Hillsboro are different from the point of view of their morphology and structure. Clay size particles of pyrophyllite from Zalamea have very well ordered polytypic structure 1A$_A$-II,1, while macroscopic size lath-crystals of pyrophyllite from Hillsboro display significant structural disorder, which disable determination of polytype and of the number of layers per unit cell. Only subfamily A was identified. Particle division on sonication proceeded most efficiently during first 10 hours in the both pyrophyllites (Figs. 6-9 and Table 2). Lesser changes of the surface area, e.s.d. and best mean particle thickness are evidenced between 10 hrs and 20 hrs and rather negligible between 20 hrs and 40 hrs. It may be concluded that the final division limit was achieved in a cycle of 20 hrs - 40 hrs sonication. Differences observed in the relationship between e.s.d. and best mean particle thickness of pyrophyllites from Zalamea and Hillsboro disappeared after 10 hrs sonication. Irrespective of differences in the initial morphology and the structure
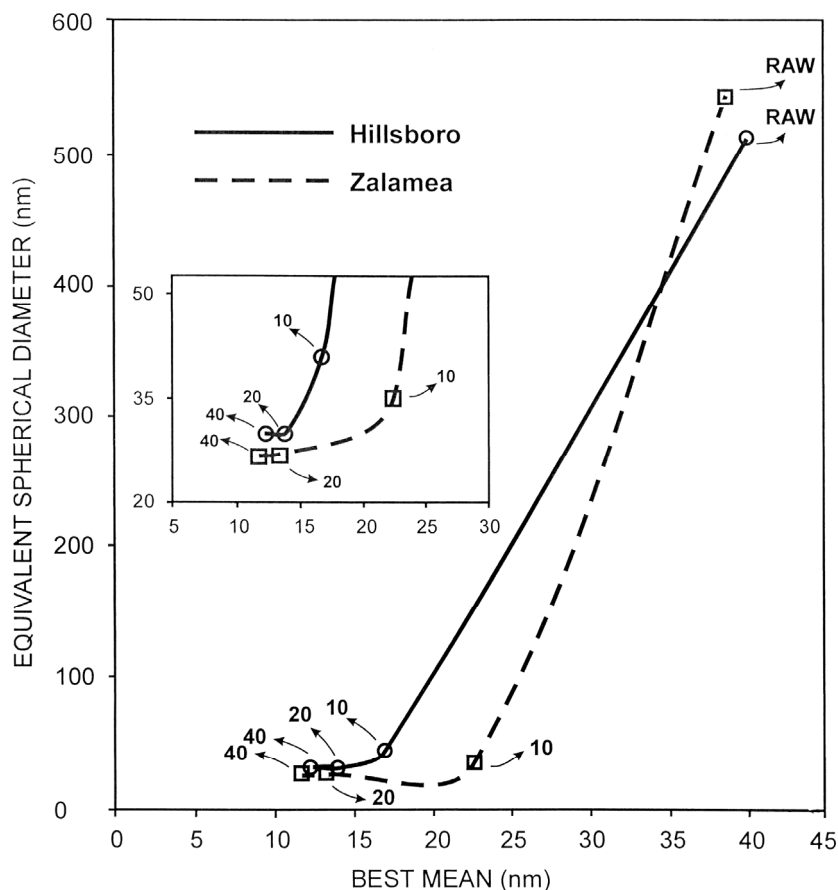
Fig. 9 Relationships between average particle size (equivalent spherical diameter) from surface area data and average thickness of domains of coherent scattering (best mean determined by the use of MudMaster). Dashed line - pyrophyllite from Zalamea, solid line - pyrophyllite from Hillsboro. Figures – time of sonication treatment.

ordering, the samples finally have similar particle sizes (see Fig. 9) and show alike diffraction patterns (Figs. 4e and 5d).

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