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Crystallite size distribution of kaolin minerals

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ABSTRACT. — The new BWA (Bertaut-Warren-Averbach) technique for measurement of mean crystallite thickness and thickness distributions of phyllosilicates was applied to a set of kaolin minerals. We analyzed 39 kaolins from the western Carpathians and from other main world deposits, which are of residual, sedimentary, or hydrothermal origin. We show that the BWA technique can be successfully applied to both kaolinites and halloysites. Three different shape types of thickness distribution were found – longnormal, asymptotic and polymodal – among the studied set of samples. Mean thickness data were compared with kaolinite crystallinity indices (Stoch index and Hughes and Brown index) and good correlations were found only for unimodal distributions. These crystallinity indices are not suitable for characterisation of kaolin mixtures.

RIASSUNTO. — Una nuova tecnica BWA (Bertaut-Warren-Averbach) per la misurazione dello spessore medio dei cristalliti e la distribuzione dello spessore dei fillosilicati è stata applicata a un gruppo di minerali del caolino. Sono stati analizzati 39 caolini provenienti soprattutto dai Carpazi occidentali, considerati di origine residuale, sedimentaria o idrotermale. È stato dimostrato che la tecnica BWA può essere applicata con successo sia ai caolini che alle halloisiti. All'interno del gruppo dei campioni studiati, sono stati rilevati tre differenti tipi di distribuzione dello spessore: lognormale, asintotico e polimodale. I dati dello spessore medio sono stati comparati con gli indici di cristallinità della caolinite (indice di Stoch e quello di Hughes e Brown); buone correlazioni sono state trovate solo per le distribuzione unimodali. Questi indici di cristallinità non sono utilizzabili per la caratterizzazione di miscele di caolino.

KEY WORDS: *Kaolin, phyllosilicates, halloysites, BWA technique.*

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INTRODUCTION

Structural ordering of phyllosilicates often reflects conditions of the mineral origin, type of parent rock, weathering intensity, transport, pressure and temperature of the diagenetic or hydrothermal events, which is why the parameters describing structural ordering/disordering are so widely measured and used (e.g. Kisch, 1983; Frey, 1987; Eberl *et al.*, 1998b). Structural parameters of kaolin group minerals, as important constituents of soils, sediments and weathering products, have been extensively reported in the literature for many years (Hinckley, 1963; Stoch 1974;

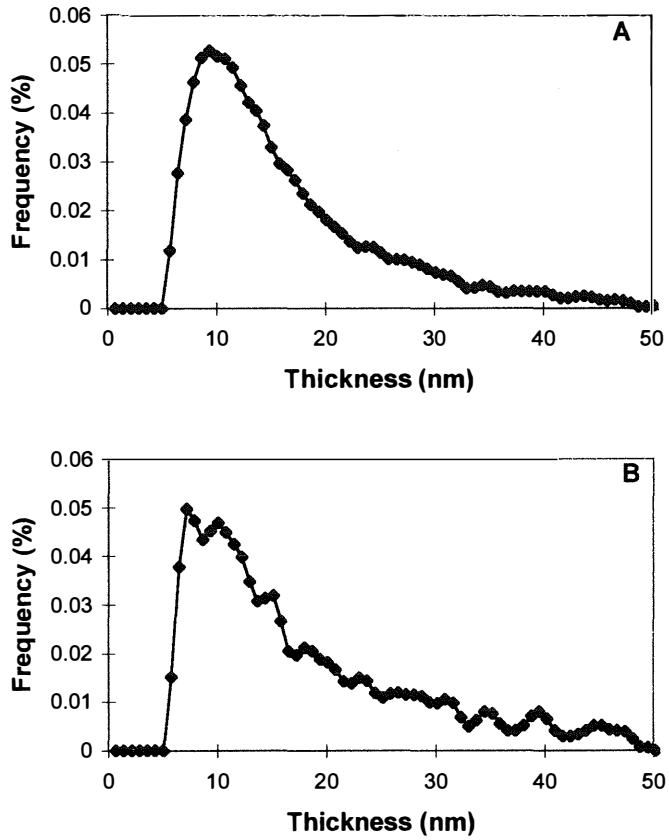

Fig. 1 – Crystallite size distribution of the GEORG5197 sample with LpG^2 correction for BWA analysis (A) and without correction (B).

Hughes and Brown, 1979; Gomes, 1987; Brindley *et al.*, 1986; Plancon and Zacharie, 1990; Galan *et al.*, 1994; Madejová *et al.*, 1997). Structural ordering of kaolinites and size parameters are important also to the kaolin industry because they play an important role in technological processes.

The main goal of this paper is to find the best approach to reproducibly measure kaolin crystallite thickness and thickness distribution by the BWA (Bertaut-Warren-Averbach) technique, measure a set of kaolins from all deposits in the western Carpathians and other world kaolin deposits and show how the data are related to those obtained by measuring other crystallinity indices.

MATERIAL AND METHODS

Samples of 35 kaolinites and 4 halloysites from kaolins of three different geological environments were used for the study. Geological environments are represented by residual kaolins (originated by weathering), sedimentary kaolins (originated in weathering crust and transported into sedimentary basins) and hydrothermal kaolins (originated by hydrothermal fluids). The geological origin of each sample is indicated in Table 1. Analysed samples represent a complete collection of kaolins from all deposits in the western Carpathians (Slovakia; Kraus, 1989) and from several main world deposits.

Prior to analyses, <2μm fractions were separated from the bulk kaolin samples by sedimentation. Separated fine fractions were used for two types of X-ray diffraction (XRD) specimens – oriented and randomly oriented. Oriented specimens were prepared by two different approaches. Most of them were prepared by sedimentation of the clay suspension onto glass or silicon slides (2 × 4 cm polished Si metal wafer cut perpendicular to (100) plane and glued on glass slide). A few oriented specimens were prepared by fast vacuum filtration of clay suspension through Millipore filters. The effect of sample amount on the mean particle thickness measurement was tested using different sample weights (between 4 and 100 mg) mounted on Si slides. A Si-substrate is particularly important when very low sample weights are used because it produces low-background XRD intensities (Eberl *et al.*, 1998a).

All specimens were analysed by XRD on diffractometers Philips PW 1710 and Siemens D500 equipped with Cu radiation with Ni filter and graphite monochromator, respectively. The step size was 0.02° 2θ and counting times were 1s for randomly oriented specimens and 5s for oriented specimens.

Resulting basal reflections of kaolinite registered at longer counting time were used for determination of mean crystallite thickness (crystallite = X-ray scattering domain) and thickness distribution using the BWA techniques (Drits *et al.*, 1998) and the MudMaster program (Eberl *et al.*, 1996). First basal reflection of all samples was subjected to BWA analysis in the two theta interval between 6 and 13°. A longer XRD exposition time (5s) was used to get the smooth XRD pattern for analysis. The BWA technique is a new approach for calculating mean crystallite thickness, thickness distribution and crystal strain from the interference function for phyllosilicates. The interference function is extracted from XRD intensities by dividing the intensities by the Lorentz-polarization (Lp) and layer structure factors (G^2) (Drits *et al.*, 1998). Finally, the interference function is treated with Fourier analysis. If XRD intensities are not corrected for LpG^2, the resulting distribution is distorted and the mean is significantly affected (fig. 1). LpG^2 of kaolinites is modulated and

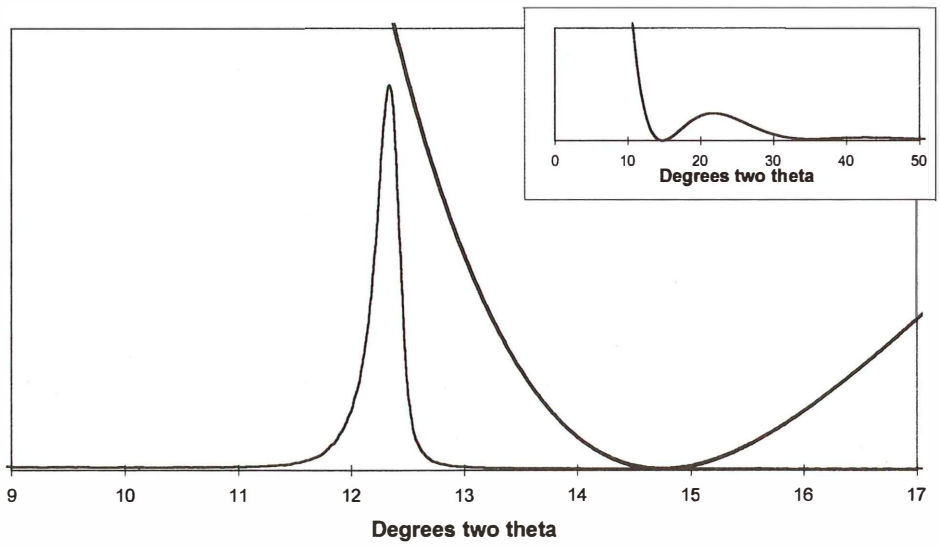

Fig. 2– XRD pattern of 001 reflection of the sample GEORG5197 and kaolinite LpG^2 (thicker line and minimized pattern in upper right corner).

has approximately zero values at several 2 theta angles (fig. 2). The interference function produced by division of the experimental XRD intensities by LpG^2 are deformed near such angles and produce distortion of the interference function (fig. 1). Drits *et al.*, (1998) developed a technique that relies on the fact that the interference function peaks are strictly symmetric so they suggested to flip the undistorted half of the interference function

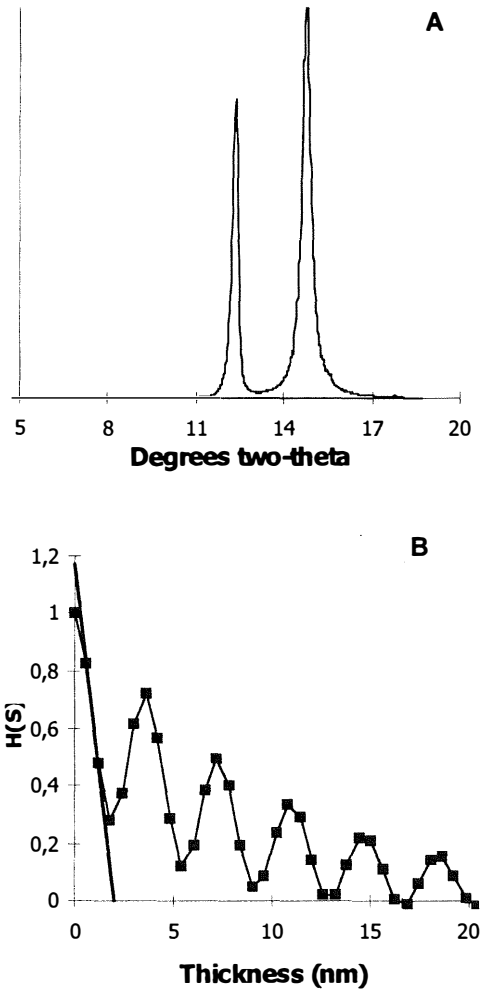

Fig. 3 – Interference function obtained from BWA analysis for the sample GEORG5197 without flip (A) and subsequently calculated Fourier coefficients, H(S), plotted against crystallite thickness.

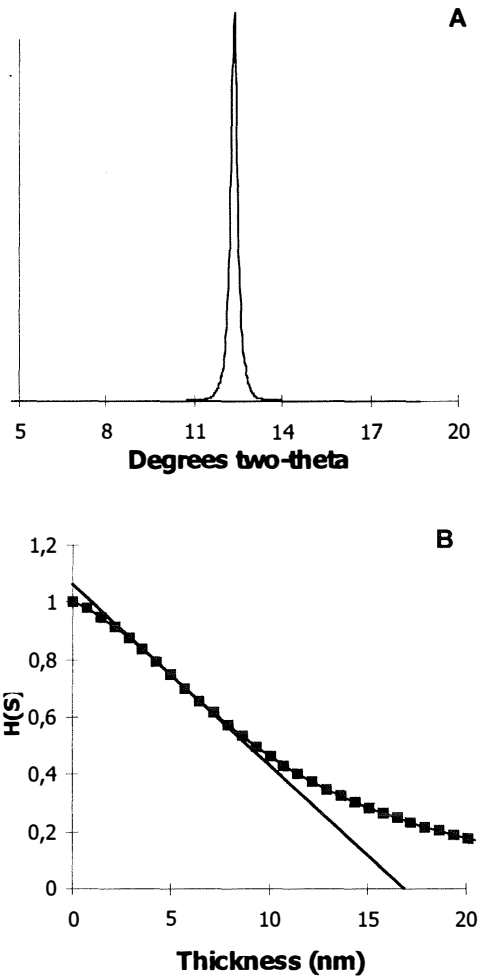

Fig. 4 – Interference function obtained from BWA analysis of the sample GEORG5197 with flip from low to high two theta (A) and subsequently calculated Fourier coefficient, H(S), plotted against crystallite thickness.

peak over a vertical plane passing through the peak maximum. For the kaolinite 001 peak used for BWA analyses, the flip was applied from low to high two theta values (figs. 3, 4). Drits *et al.* (1998) showed by treating calculated XRD patterns and applying a mineral standard that for crystallite thicknesses less than 20 nm there is no effect of machine broadening and $K\alpha_1$ and $K\alpha_2$ doublet used for

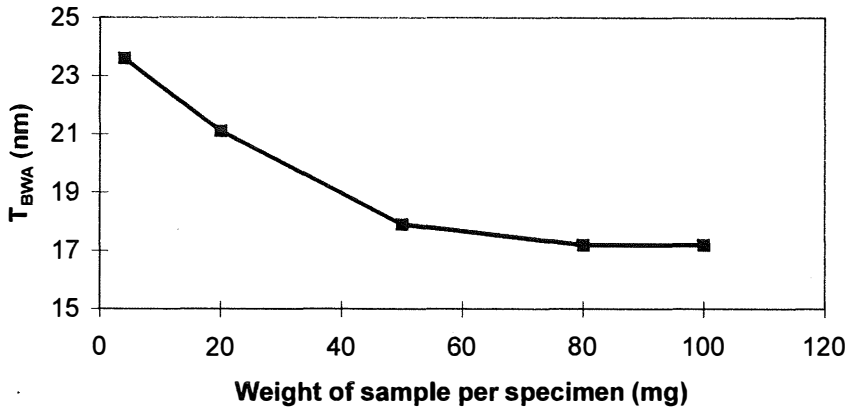

Fig. 5 – Relation between the weight of kaolin sample mounted on XRD slide and mean crystallite thickness measured by BWA tecnique.

XRD analysis. To thest the potential machine broadening effect two XRD machines as described above were used for our set of samples. BWA data obtained using XRD patterns collected from both machines were exactly the same within the error of ± 0,1 nm.

All of the steps are built into the MudMaster program (Eberl *et al.*, 1996, the program is available from D.D. Eberl, USGS, Boulder, Colorado, USA on CD free of charge). The program works with Microsoft Execel and is applicable to all clay minerals.

XRD patterns of randomly oriented specimens were used to calculate two kaolinite «crystallinity» indices: the Stoch index (S; Stoch, 1974) and the Hughes and Brown index (H&B; Hughes and Brown, 1979).

Scanning electron images were taken from fresh rock chips coated with gold on Jeol JXA 840 scanning electron microscope (SEM).

Experimental results and interpretations

BWA measurements

The most important aspect of particle size data interpretation is reliability and reproducibility of measurements. In the first part of the study the effect of sample mass and the effect of particle segregation during drying of the specimen were evaluated.

Specimens with different sample weights were analysed by XRD and mean crystallite thicknesses (T_{BWA}) were calculated by the BWA technique (MudMaster program) for each specimen. A relationship between the amount of sample and the mean thickness is observed where the mean thickness increases with decreasing amount of sample. The most dramatic change is observed for the smallest sample amounts (< 50 mg per specimen, fig. 5). Identical crystallite thicknesses, not affected by the sample mass, were obtained when > 80 mg of clay was mounted on the XRD specimen (> 80 mg/cm^2). The same behaviour was observed and the same results were obtained for each of the two XRD machines used in this study. The effect could be explained either by preferred orientation of larger particles or by segregation during the preparation of the specimen.

Possible size segregation effect of particles during sedimentation on the XRD slide was tested for larger sample weights by running the same sample prepared by vacuum filtration and regular sedimentation. No differences in mean thickness between both specimen preparation techniques were found. Small sample weights were not tested due to technical problems with filtration and handling of such small samples.

TABLE 1

List of samples used for analyses and data obtained by BWA technique (T_{BWA}), Hughes and Brown index (H&B index) and Stoch index (S index) with indicated type of kaolin deposit, country of origin and type of crystallite size distribution.

Sample	Kaolin type	T_{BWA}	Type of distribution	H&B index	S index	Country
WESTERN CARPATHIAN DEPOSITS						
HP5183	Residual	5.6	Lognormal	20.7	1.52	Slovakia
HP5207	Residual	4.6	Polymodal	11.5	N	Slovakia
HP5202	Residual	4.8	Polymodal	10.5	N	Slovakia
VSL4783	Residual	5.3	Lognormal	13.2	1.29	Slovakia
VSL4790	Residual	5.9	Lognormal	18.35	1.5	Slovakia
VSL4789	Residual	4.9	Lognormal	12	1.8	Slovakia
VAL4776	Sedimentary	4.7	Lognormal	11.4	N	Slovakia
VAL4766	Sedimentary	4.5	Polymodal	10.1	N	Slovakia
HA5211	Sedimentary	4.8	Polymodal	11.1	N	Slovakia
TOC5212	Sedimentary	3.1	Asymptotic	10.9	N	Slovakia
VP5188	Sedimentary	7.9	Lognormal	N	N	Slovakia
RU5215	Sedimentary	5	Polymodal	11.6	1.38	Slovakia
PI2154	Sedimentary	3.4	Asymptotic	8.4	N	Slovakia
HN1096	Sedimentary	4.1	Asymptotic	7.3	N	Slovakia
HN1	Sedimentary	3.9	Asymptotic	7.2	N	Slovakia
RU2042	Sedimentary	6.7	Polymodal	38	0.7	Slovakia
RA5214	Hydrothermal	8.2	Polymodal	65	0.54	Slovakia
HO5201	Hydrothermal	15.7	Polymodal	58	0.61	Slovakia
CIC	Hydrothermal	13.3	Polymodal	N	N	Slovakia
OTHER DEPOSITS						
SEDLEC1	Residual	13.4	Lognormal	33.8	0.94	Czech Rep.
SEDLEC2	Residual	10.5	Lognormal	37	0.98	Czech Rep.
MONTECAST	Residual	17	Polymodal	15.4	0.64	Spain
ALVÃRES	Residual	11.1	Lognormal	23.2	0.92	Portugal
BUSTELO	Residual	11.4	Lognormal	17.4	0.9	Portugal
UKR5016	Residual	15	Polymodal	81	0.8	Ukraina
HB5208	Sedimentary	10	Polymodal	35	0.87	Czech Rep.
GEORG5206	Sedimentary	10.9	Polymodal	20.4	N	USA
GEORG5196	Sedimentary	13.5	Polymodal	47.2	1.22	USA
GEORG5197	Sedimentary	16.8	Lognormal	82.8	0.63	USA
GEORG5200	Sedimentary	14.6	Polymodal	54	0.62	USA
GEORG	Sedimentary	17.5	Polymodal	44.4	1.09	USA
POVEDA	Sedimentary	17	Lognormal	19.3	0.83	Spain
LA GUARDIA	Sedimentary	10.3	Lognormal	15	1.37	Spain
KIRALY HEGY	Hydrothermal	14.9	Polymodal	46.3	0.69	Hungary
ST AUSTEL	Hydrothermal	15.7	Lognormal	30.9	0.76	UK
HALLOYSITES						
MI1905	Residual	3.9	Asymptotic	8.8	N	Slovakia
RA5213	Hydrothermal	3.5	Asymptotic	8.5	N	Slovakia
KAL474	Residual	3.6	Asymptotic	8.5	N	Slovakia
ZVS403	Residual	3	Asymptotic	5.5	N	Slovakia

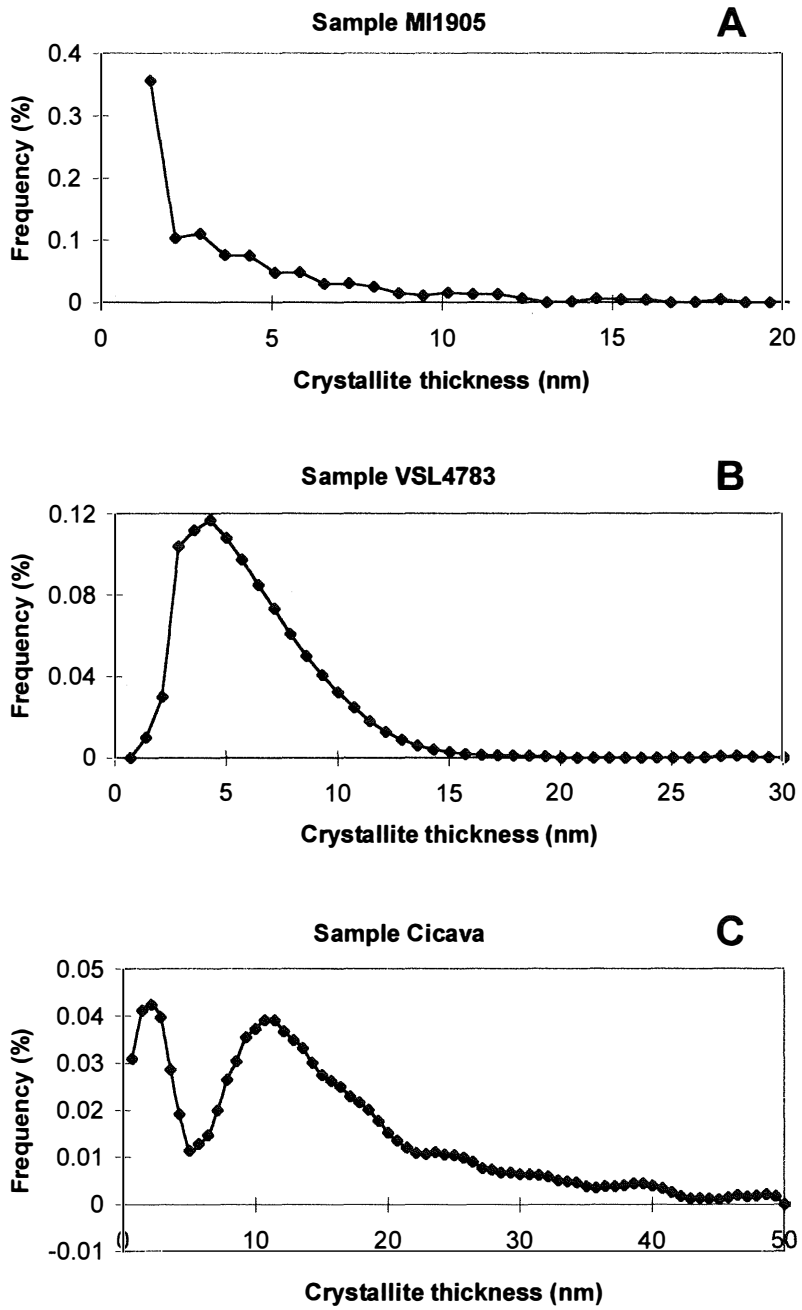

Fig. 6 – Examples of three types of crystallite size distributions obtained by the BWA technique. A - asymptotic distribution of sample MI1905, B - lognormal distribution of sample VSL4783, C - polymodal distribution of sample Cicava.

Kaolin crystallite thickness and thickness distribution

Both mean crystallite thickness (T_{BWA}) and thickness distributions were calculated for kaolinite and halloysite samples. All obtained results are listed in Table 1. Mean crystallite thicknesses range between 3 and 17.5 nm. Generally, the values of kaolins of hydrothermal origin have the largest mean thickness.

The BWA technique has already been applied to measurements of illite, smectite and pyrophyllite crystals (Šucha *et al.*, 1997; Eberl *et al.*, 1998b; Uhlik *et al.*, in press). These studies also demonstrated good agreement between mean crystallite size (T_{BWA}) and real particle thicknesses determined by high resolution transmission electron microscopy (HRTEM). The range of statistical reliability of HRTEM is at least up to a mean thickness of 10 nm (the relation between the number of measured particles and the reliability of calculated mean thickness is discussed by Środoń *et al.*, 1992). We believe that mean crystallite thickness obtained for kaolinites could be extrapolated to real mean crystal thickness for samples in the interval from 3 to approximately 10 nm.

Three shapes of crystallite size distributions were found among the analysed kaolins: lognormal, asymptotic, and polymodal (fig. 6). A lognormal distribution was found to be the most frequent for phyllosilicates (Eberl *et al.*, 1990; Šucha *et al.*, 1993, 1996; Eberl *et al.*, 1998a,b). An asymptotic distribution shape was first reported by Eberl *et al.* (1998a) for illites. It also was observed for some kaolinites and for all halloysites of our set. Asymptotic distributions are typical for sampels with small mean crystallite thickness, and could be characteristic of early stages of kaolin origin (Eberl *et al.*, 1998a). A large number of samples have bimodal or polymodal size distributions, which means that the sample contains two or more generations of crystals with different thickness. Different generations of crystals might be expected in sedimentary (overgrowths after deposition of minerals) and in hydrothermal environments. The type of distribution indicated in Table 1 supports this assumption, as 4 of the 5 analysed hydrothermal samples and 10 of the 18 sedimentary kaolins have polymodal shape of distribution. SEM analyses were performed on the hydrothermal sample from Cicava which has a polymodal distribution based on our BWA measurements. Different crystal generations could be easily distinguished in the SEM images, confirming the sample's polymodal distribution (fig. 7).

Crystallite sizes of kaolins from the western Carpathians

Sudied samples of the western Carpathians represent all kaolin deposits of the area so our results can be used for general interpretation. Mean crystallite thicknesses (T_{BWA}) vary between 3 nm and 7.9 nm for both residual and sedimentary kaolins. The arithmetic mean of the obtained T_{BWA} values from residual and sedimentary kaolins is 4.6 nm, significantly less than data of other world kaolins (see Table 1). Considerably lower thickness values of the western Carpathian kaolins fit well to published interpretations assuming that the weathering conditions during geological history of the western Carpathians (Kraus, 1989) did not lead to the origin of well developed kaolin weathering crusts. Mean crystallite thickness of hydrothermal kaolins depends strongly on local conditions and it is difficult to compare them with other localities.

BWA and crystallinity index

Mean crystallite thickness measured by the BWA technique was compared to Stoch and H&B crystallinity indices. When values of either index is plotted versus all BWA data (fig. 8) no correlation is observed. However, when samples with polymodal distributions are excluded and only samples with unimodal distributions (lognormal and asymptotic) are considered, a much better relation is observed, particularly with the S index (fig. 9A). A good correlation between T_{BWA} and H&B indices was obtained only for small mean size data (fig. 9B). This supports the observation of Galan *et*

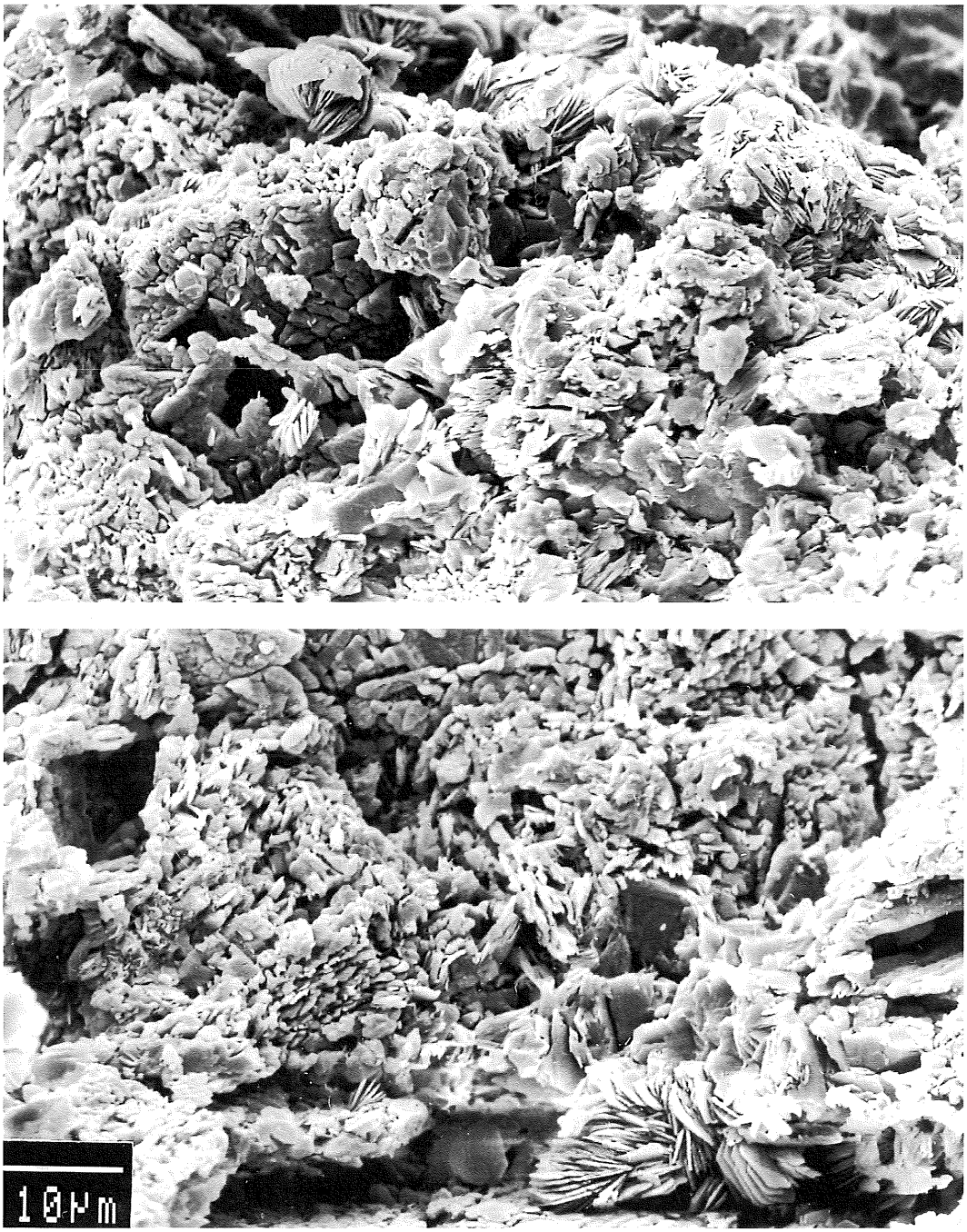

Fig. 7 – SEM images of hydrothermal kaolin from Cicava documenting different particle generations in the sample.

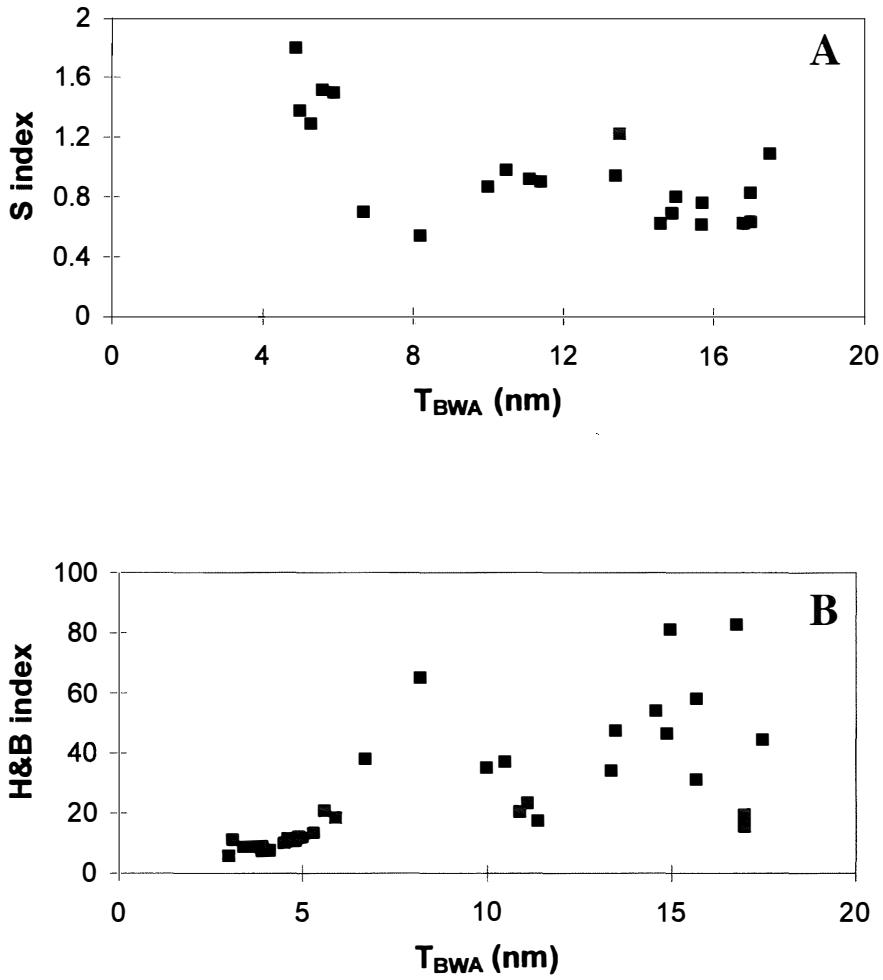

Fig. 8 – Relation between mean crystallite size of all analysed kaolins by BWA technique (T_{BWA}) and Stoch index (A) and Hughes & Brown index (B).

al. (1994) that H&B index can be applied only to poorly ordered kaolins. Crystallinity indices based on selected hkl reflections and/or XRD background could underestimate (H&B index) or overestimate (S index) the structural ordering of mixtures enhancing XRD traces of smaller or larger crystallites. BWA analysis takes into account all particles, gives real mean size and distinguishes different generations.

CONCLUSIONS

Reproducible and reliable results of mean crystallite thickness and thickness distribution of kaolinites were obtained by the BWA technique when the amount of sample mounted on the XRD slide is greater than 80 mg/cm^2.

Lognormal and asymptotic shapes of crystallite size distribution were observed for

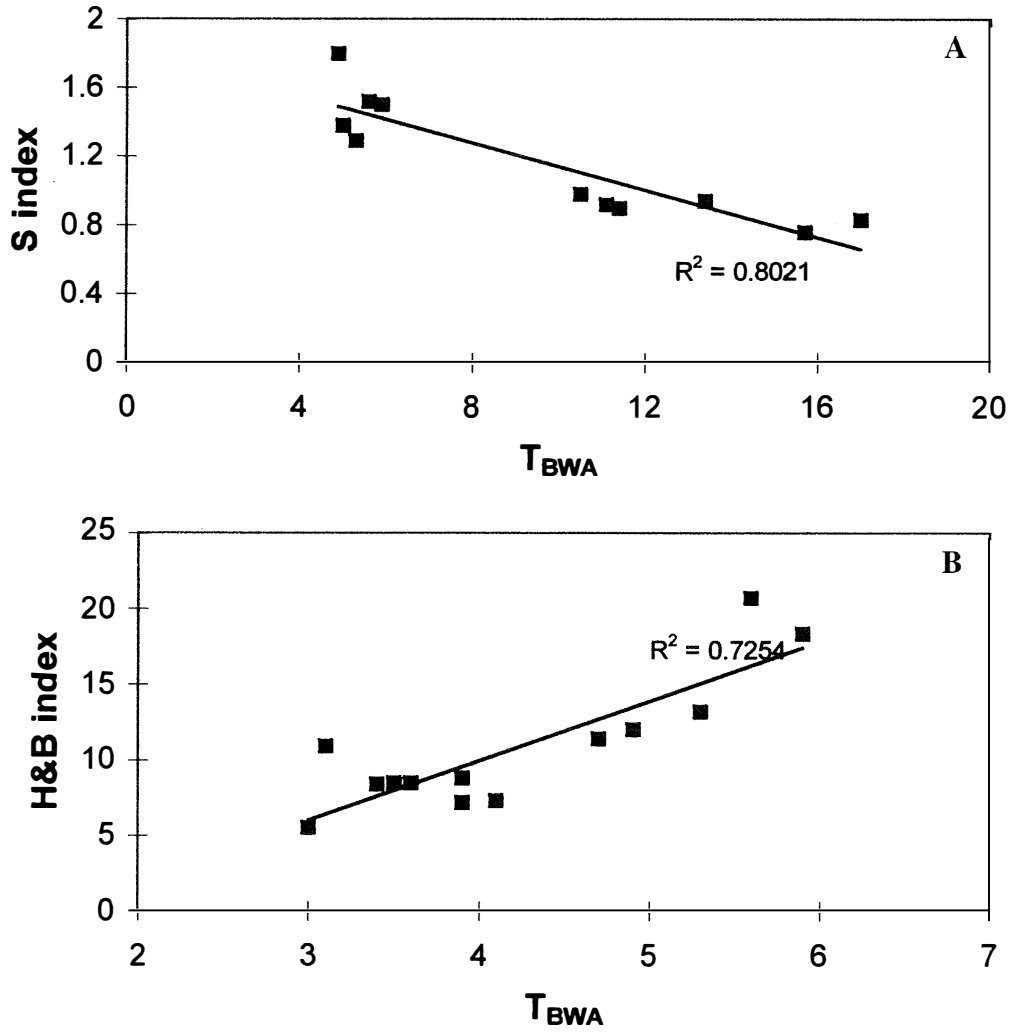

Fig. 9 – Relation between mean crystallite size of kaolins analysed by BWA technique (T_{BWA}) and Stoch index (A) and Hughes & Brown index (B) after excluding all samples with polymodal distribution from the kaolin set. Only small mean size values of Hughes and Brown index were selected for correlation according to Galan *et al.* (1994).

many samples but a significant part of the studied kaolin collection has polymodal size distributions indicating several crystallite generations.

Kaolins of the western Carpathians have a very low mean crystallite thickness, which is significantly smaller than other main world kaolin deposits. This indicates poorly developed kaolin weathering crusts.

Hughes and Brown and Stoch indices correlate well with T_{BWA} only if samples with unimodal distributions (lognormal, asymptotic) are considered. Mixture of different particle generations in kaolin samples is the main factor limiting the use of kaolin crystallinity indices for correct particle size evaluation.

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