GEOLOGICKÝ ZBORNÍK — GEOLOGICA CARPATHICA 31, 1—2, BRATISLAVA, JUNE 1980, PP 115—124

M. HARMAN — I. HORVÁTH*

RELATIONS BETWEEN THE MORPHOLOGY OF PARTICLES IN STRUCTURALLY DIFFERENTLY ORDERED KAOLINITES AND THE KINETICS OF THEIR DEHYDROXYLATION

(Figs. 12, Tab. 2)

Abstract: Electron microscopy was used to measure particle sizes of structurally differently ordered kaolinites. Investigations on the given set of kaolinites showed that the particle thickness decreased with decreasing degree of structural ordering in kaolinites. The determined values of the activation energy of dehydroxylation were higher for kaolinites with less thick particles.

Резюме: Авторы мерили размеры частиц структурно различным образом упорядоченных каолинитов с применением метода электронной микроскопии. Из изучаемой серии каолинигов установили, что на степень упорядочения структуры не повлияла величина их частиц, а их толщина уменьшалась в направлении понижающегося упорядочения каолинитической структуры. Установленные величины активационной энергии дегидроксиляции были более высокими в каолинитах с меньшей толщиной частиц.

Introduction

Under natural conditions the kaolinites form, according to the degree of their structural order, the sequence: Kaolinite T — kaolinite pM (H. H. Murray — S. C. Lyons, 1956). The kaolinite T has a perfectly ordered structure that approaches the ideal model, while the kaolinite pM displays differences in periodical stacking of layers (G. W. Brindley — K. Robinson, 1947).

The kaolinite crystals have a plate—like form, very often with typical pseudohexagonal structure. Relations between crystal morphology of kaolinites and their structural order have not been clarified unambiguously as yet. We know of such kaolinites T whose crystals have another than pseudohexagonal symmetry — e.g. a tubular form (G. Honjo et al., 1954; P. Souza Santos et al., 1965), on the other hand well developed platy crystals of kaolinite can possess properties of a halloysite (G. W. Kunze — W. F. Bradley, 1954).

Shape, size and thickness of kaolinite crystals play an important role in their interaction with water, with organic agents and in technollogically important high—temperature reactions (e.g. dehydroxylation, formation of mullite, etc.).

In the present paper we correlate the dimensions, especially thickness and particle size, of five kaolinites whose structures possess a diverse degree of order, with some thermoanalytical data recorded in the course of their dehydroxylation.

---

* RNDr. M. Harman, CSc., Geological Institute of the Slovak Academy of Sciences, Dúbravská cesta 886 25 Bratislava; Ing. I. Horváth, CSc., Institute of Inorganic Chemistry of the Slovak Academy of Sciences, Dúbravská cesta, 809 34 Bratislava.

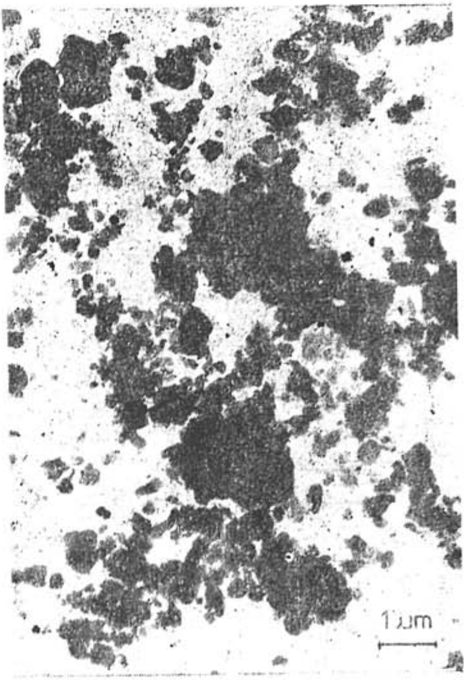


Fig. 1. Electron micrograph of kaoline Mesa Alta, suspension, magnif. 7500 x.

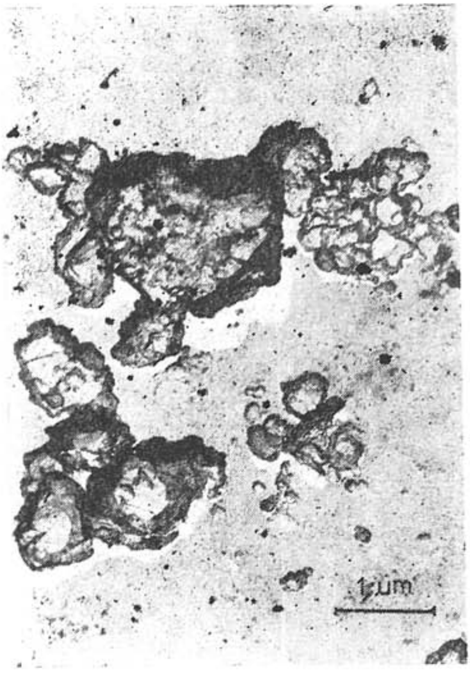


Fig. 2. Electron micrograph of kaoline Mesa Alta, replica from suspension, magnif. 13500 x.

Experimental

For morpology investigations were used the following samples:

1. Mesa Alta, separated from the standard kaoline API (No. 9) with mean particle diameter between 0.3—0.6 μm (a small portion only of these particles have pseudohexagonal shapes). Aggregates which constitute about 10—15 % of the sample reach the size of 2.5 μm and consist (according to a replica) from clay prticles. The original son—decomposed minerals are present in very small quantities, they occur in the fraction about 1 μm (Fig. 1, 2).

2, 3. The samples BZ and Wolfka are two technological types from the deposit Kemlitz (GDR). They are products of in situ weathering process in quartz porphyrys and in their tuffs. The type BZ represents development of kaolinite particles in the isometric forms of aggregates of clay minerals whose diameter is between 3—5 μm. Single crystallites occur rarely (2—3 μm) in the form of isolated tubes (halloysite?). (Fig. 3, 4). The type Wolfka has a dispersion character, most frequent are particles from 1.5 to 2.0 μm width pseudohexagonal structure and prismatic particles, length up to 2.5 μm and with 0.3—0.5 μm. This would indicate the presence of some other clay mineral, perhaps the admixture of illite or some mixed layered IM structures. Relatively frequently occur the original non-decomposed minerals (2—4 μm), (Fig. 5, 6).

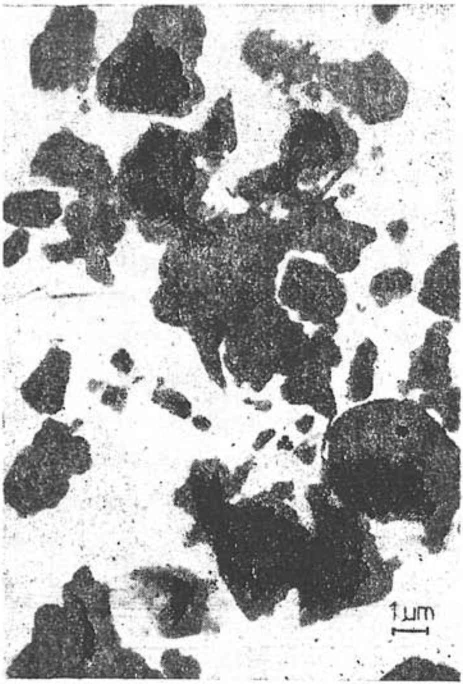


Fig. 3. Electron micrograph of kaoline Wolfka — Kemlitz, suspension, magnif. 4500 x.

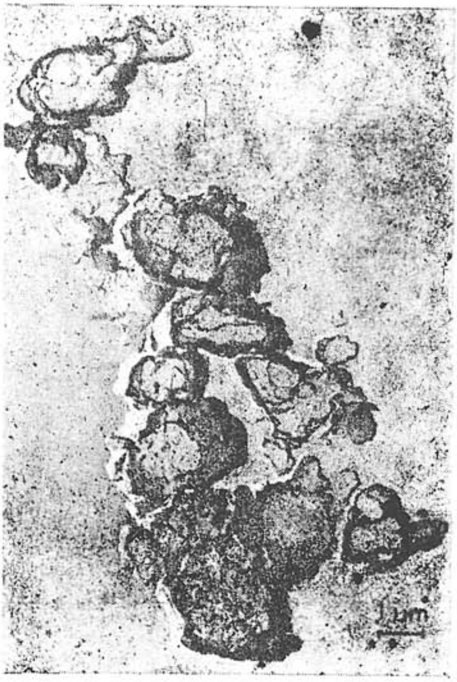


Fig. 4. Electron micrograph of kaoline Wolfka — Kemlitz, replica from suspension, magnif. 6000 x.

4. The kaoline Sedlec is a product of in situ weathering caused by climatic factors, of the Karlove Vary granite, with direct transitions into undecomposed rocks. We have to consider also the near hydrotherms of Karlove Vary, as well as the influence of percolating aggressive water from the near overlying brown coal seams. The particle diameter range from 1 to 1.5 μm, the aggregate size is 3 to 4 μm. Apart from kaolinite there are admixtures of illite or some mixed IM structures, from the original minerals small amounts of muscovite and quartz are present (Fig. 7, 8).

5. Clays from the Poltár formation arose by kaolinitic weathering of crystalline rocks — Veporides washed into a local sedimentation basin. For our analyses we used the kaolinite of fireclay type from the locality Halič-Kopáň. Beside clays, sands and organic particles, very frequent are fragments of non-decomposed minerals in nearly all fractions. The most frequent fraction is that of 0,3—0,6 μm. A smaller portion consists of particles of about 1 μm which sometimes have pseudohexagonal structure. In replicas the typical globular forms can be clearly observed (Fig. 9, 10).

The mineralogical composition of the investigated kaolinites determined by the quantitative X-ray phase analysis is shown in Table 1. The kaolinites are arranged in the order of their decreasing structure perfection as this was determined by the values HWB and HC. The criterion of the structural order

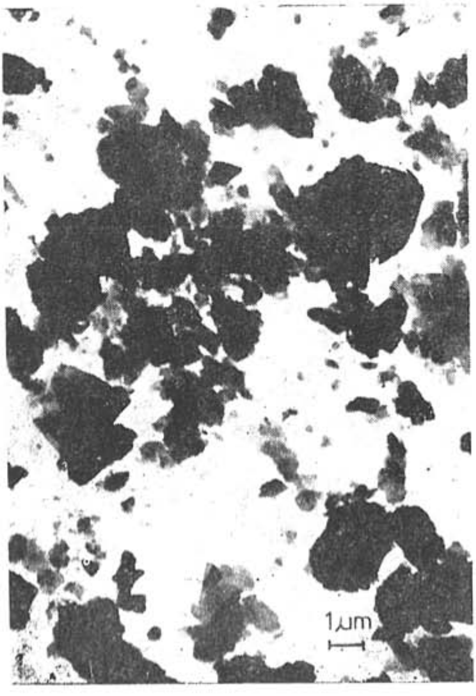
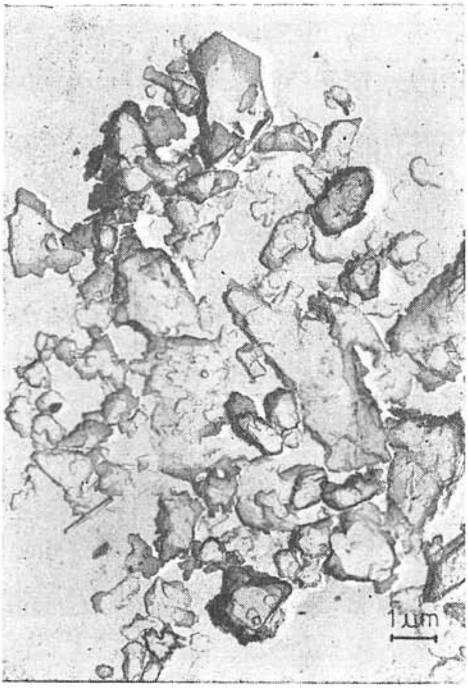


Fig. 5. Electron micrograph of kaoline BZ — Kemlitz, suspension, magnif. 4500 x.

Fig. 6. Electron micrograph of kaoline BZ — Kemlitz, replica from suspension, magnif. 6000 x.

Fig. 7. Electron micrograph of kaoline Sedlec, suspension, magnif. 4500 x.



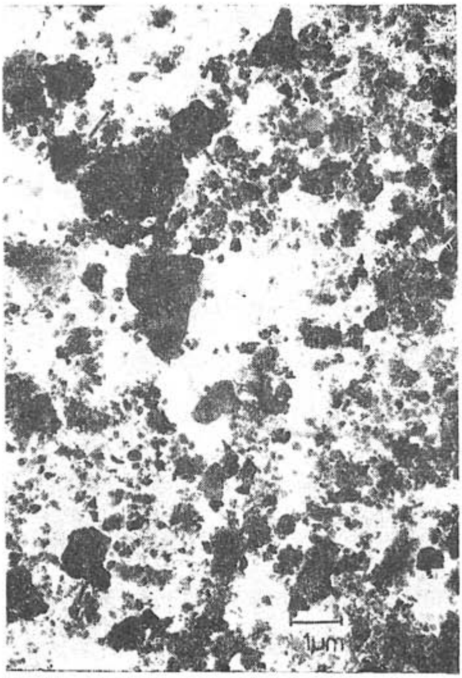


Fig. 8. Electron micrograph of kaoline Sedlec, replica from suspension, magnif. 6000 x.

Fig. 9. Electron micrograph of kaoline Halič — Kopáň, suspension, magnif. 6000 x.

Fig. 10. Electron micrograph of kaoline Halič — Kopáň, replica from suspension, magnif. 6000 x.

Table 1

Locality	% Content			HWB	HC	Specific surface ($m^2.g^{-1}$)
	kaolinite	quartzother				
Mesa Alta	95	3	1—2	8.3	1.17	10.0
BZ	80—84	12.5	3—5	8.5	1.235	13.1
Wolfka	85—87	13.5	2	9.8	0.825	13.3
Sedlec	84—87	2.3	11—13	10.3	0.828	15.7
Halič — Kopáň	90—94	0.8	7	26.9	0.082	35.1

+ Samples of kaolinites except for kaolinites and quartz contented also ingredients of further minerals mainly minerals of the smectite group.

(HWB) was calculated by the method of J. Wiegmann et al. (1969), based on the following data obtained from X-ray diagrams of powder specimens:

a) values d_{001}

b) relations between the height of the diffraction maxima 110, in the region 020 and the minimum between 020 and 110,

c) relations of the diffractions maxima 110, 111 with regard to the minima between 110, 111 and 111,

d) relation between the height of the first and third diffraction maximum of the triplet between 0.255 and 0.249 nm,

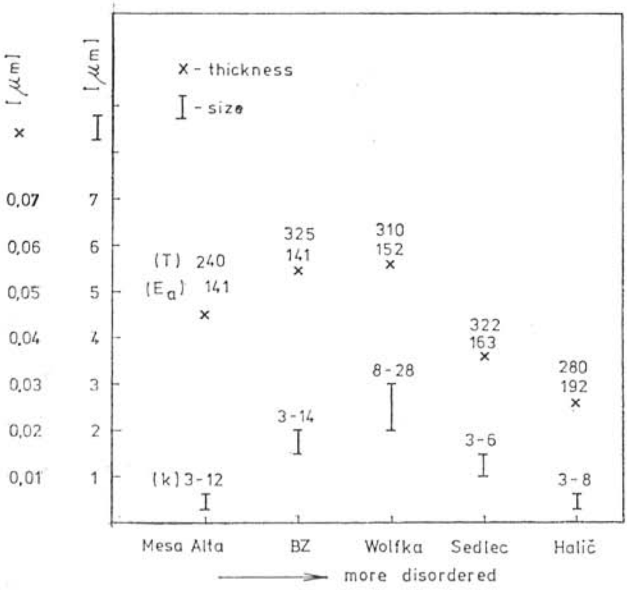


Fig. 11. Characteristics of kaolinites particles.
T = The temperature (C°) of the beginning of the dehydroxylation process; E_a = Activation energy (kJ.mol^{-1}) of the dehydroxylation process; k = The rate const.k.10^4 (min^{-1}) for three dimensional diffusion of the H_2O mols formed during the dehydroxylation.

e) width of the diffraction maximum 001 in the middle of its height.

Kaolinites with perfectly ordered structure reach the value of HWB about 8, disordered kaolinites about 30.

For comparison, in Table 1 for all types also the values HC, which represent the known Hinckley index of crystallinity (D. N. Hinckley, 1963), and the values of the specific surface ($m^2 . g^{-1}$) are listed.

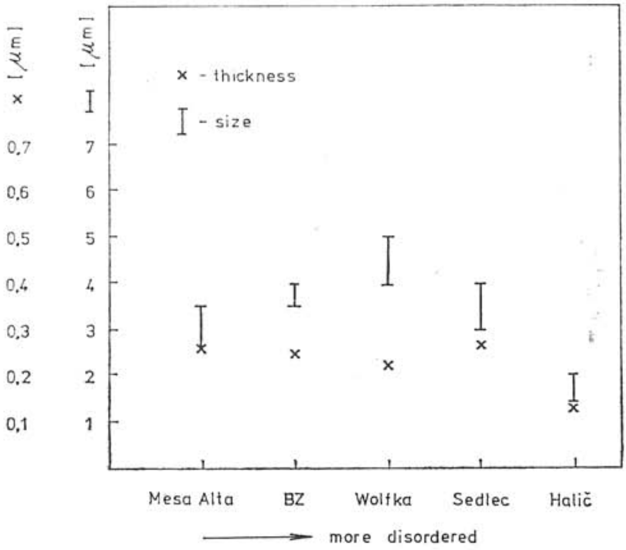


Fig. 12. Characteristics of the kaolinites aggregates.

Insvestigations on morphology and diameter characteristics of kaolinites were made with the aid of transmission electron microscopy. The samples were first desintegrated with ultrasound (2 min. at 18 kHz). Two methods of preparations were used: methods of suspensions and that of replicas from suspensions. The method of suspensions makes it possible to obtain basic diameter characteristics of elementary particles, information on their crystallographic properties an approximative mineralogical identification (fireclay, halloysite, kaolinite, illite, mixed-layer-minerals and finaly an estimation of the quantity of nondecomposed original minerals. The method of replicas from suspension, with regard to the angle of metal shadowing — 35° — makes it possible to determine the dimensions of the individual crystals and aggregates. The aggregates of clay minerals form intergrowths that could not be dispersed by ultrasound.

The constant angle of shadowing made it possible to measure the thickness of particles and of aggregates according to the equation:

$$h = l . \operatorname{tg} \alpha$$

where h is the thickness of the crystal, l is the lenght of the shadow in μm, α is the angle metal shadowing.

On each sample about 100 measurements were performed. Results are listed in Table 2.

Table 2

Locality	% composition of		Average frequency of dimensions of			
			particles		aggregates	
	particles	aggre-gates	size (in μm)	thickness (in μm)	size (in μm)	thickness (in μm)
Mesa Alta	80—85	15—20	0.3 — 0.6	0.045	2.5 — 3.5	0.258
BZ—Kemmlitz	70—80	20—30	1.5 — 2	0.055	3.5 — 4	0.251
Wolfka—Kemlitz	70—80	20—30	2 — 3	0.056	4 — 5	0.223
Sedlec	75—80	20—25	1 — 1.5	0.037	4 — 4	0.279
Halič—Kopáň	90—95	5—10	0.3 — 0.6	0.027	1.5 — 2	0.140

Particle size of kaolinitic crystals were correlated with data obtained by thermoanalytical investigation and with data on kinetics of dehydroxylation (I. Horváth — G. Kranz, 1979), — Fig. 11.

Dimensions of aggregates and crystal clusters of kaolinitic particles are shown in Fig. 12.

Discussion

It was found that morphology and particle diameter and on the other hand, the degree of structure order are two factors which do not depend on each other.

Comparison of kaolinites from Mesa Alta with those of Tomášovce-Halič supports the above assumption. These kaolinites form, in spite of differences in their structure, particles of nearly identical character and diameter, the only difference being in their thickness which, as we could observe it, is generally greater in kaolinites with higher degree of structure order.

Morphologic properties and structure of kaolinites depend greatly on rock genesis (M. F. Vikulova — V. A. Šitov, 1966). It is known that kaolinites with relatively greater crystals, and with better ordered structure arise in the course of hydrothermal transformation and on recrystallization of micas, i.e. the conditions of their formation are important. Kaolinites with lower degree of order are usually of sedimentary origin (the original rock is eroded, washed, away and resedimented). The kaolinite particles have to overcome a long transport in the course of which defects in structure and morphologic changes (e.g. defoliation of aggregates and decrease of particle thickness) take place. On defoliation destruction of bonds between the kaolinitic double layers can take place. These bonds are formed by hydrogen bonds between the hydroxyl groups and the opposite oxygen atoms in the tetrahedral layers in the kaolinite structure. Hence it follows that in the redeposited kaolinites there remain only the strongest bonds OH .... O which can be destructed e.g. by thermal decomposition of kaolinite.

The dehydroxylation of kaolinite is a high-temperature reaction in solid phase and from technological aspect it is important in production of ceramic body. Apart from some outer factors, such as temperature, pressure, p_{H_2O} in the reaction environment etc., the dehydroxylation process is influenced by the characteristics of the starting material, e.g. its structure, shape and size of the reacting crystals. As far as kinetics of kaolinite dehydroxylation are concerned, the diffusion of the formed molecules of H_2O inside the kaolinite crystal, which proceeds in the direction of the crystallographic axes X and Y, i.e. in the direction of arrangement of the kaolinitic layers, is supposed to be the slowest process (I. Horváth — G. Kranz, 1979; J. Holt et al., 1962).

Correlation of the thermoanalytical and kinetic data with particle sizes of the investigated kaolinites showed (Fig. 11) that particle thickness varying in the interval 0.027 — 0.057 μm influence neither the rate constants nor the temperature of the beginning of dehydroxylation. Thus, e.g., particles of kaolinite from Mesa Alta with mean particle thickness of 0.045 μm strated to dehydroxylate at 240 °C, those from Sedlec with thickness of 0.037 μm at 322 °C and from Tomášovce-Halič with smallest thickness of 0.027 μm at 280 °C. It is possible to assume certain relations between the particle thickness and the values of the activation energy of dehydroxylation which decrease with the increasing thickness in the interval 192—141 kJ. $\text{mole}^{-1}H_2O$. This fact seems to be connected with the energy of bonds OH .... O between the kaolinitic double layers, which seem to be stronger in the less ordered structures (e.g. redeposited kaolinites). The stronger bond OH .... O, the diffusion of the H_2O molecules released on dehydroxylation occurring in the assumed direction of the stacking of layers, poses a greater resistance to them (higher activation energy). The influence of particle diameter of the investigated kaolinites between 0.5—3.0 μm on dehydroxylation parameters was not observed.

Conclusion

Research into morphology and particles sizes of kaolinites from five deposits showed:

a) the values of the activation energy of dehydroxylation of the investigated kaolinites increase with decreasing thickness of their particles, which supports the assumed mechanism of relase of H_2O molecules formed by dehydroxylation from the kaolinite,

b) the degree of structural order does not influence the diameter of particles, these are, however thicker, the better is the structure ordered. In kaolinites with differences in the periodic stacking of layers, in comparison with perfectly ordered structures, can arise stronger bonds OH .... O between the double layers as a consequence of changes in the length of this bond in the direction of the crystallographic axes „X" and „Y".

Translated by V. Šašková

REFERENCES

BRINDLEY, G. W. — ROBINSON, K., 1947: X-ray studies of some kaolinitic fireclays. Trans. Brit. Ceram. Soc. (Stoke on Trent). 46, p. 49—62.

HINCKLEY, D. N., 1963: Variability in „crystallinity" values among the kaolin deposits of the coastal plain of Georgia and South Carolina. Clays and Clay Minerals, New York, Proc. 11 th Nat. Conf., Pergamon Press, Oxford, p. 229—235.

HOLT, J. — CUTLER, I. B. — WADSWORTH, M. E., 1962: Rate of thermal dehydration of kaolinite in vacuum. Journal Amer. Ceram. Soc. (Easton) 45, p. 133—136.

HONJO, G. — KITAMURA, N. — MIHAWA, K., 1954: Study of clay minerals by single crystal electron diffraction diagrams the structure of tubular kaolin. Clay. Min. (Oxford—Edinburgh) 2, p. 133—141.

HORVÁTH, I. — KRANZ, G., 1979: Termoanalytické štúdium vysokoteplotnej dehydratácie kaolinitov s rôznym stupňom usporiadanosti. Silikáty (in press).

KUNZE, G. W. — BRADLEY, W. F., 1964: Occurrence of a tabular halloysite in Texas soil. Clays and Clay Minerals, Proc. of the 12 th Nat. Conf. New York, p. 523—527.

MURRAY, H. H. — LYONS, C. S., 1956: Degree of crystal perfection of kaolinite. Clays and Clay Minerals (Washington), Publ. 456, p. 31—40.

SOUZA SANTOS, P. — BRINDLEY, G. W. — SOUZA SANTOS, H., 1965: Mineralogical studies of kaolinite-halloysite clays. Amer. Min., (Washington), 50, p. 619—628.

VIKULOVA, M. F. — ŠITOV, V. A., 1966: Novyje dannyje po issledovaniju glinistych porod s pomoščju replik. Fizičeskije metody issledovanija mineralov osadočnych porod. Izd. Nauka, Moskva, p. 211—221.

WIEGMANN, J. — HORTE, C. H. — KRANZ, G., 1969: Zu kristallinen Fehlordnungserscheinungen an Kaolinit. Ber. deutsch. Ges. geol. Wiss. — B. Miner. Lagerstättenf. (Berlin), 14, 2, p. 190.

Review by P. ŠTEVULA

Manuscript received May 6, 1979