GEOLOGICKÝ ZBORNÍK — GEOLOGICA CARPATHICA 30, 4, BRATISLAVA, DECEMBER 1979

VLADIMÍR ŠTEFAN FAJNOR, JOZEF MASÁR*

HIGH-TEMPERATURE CLASSIFICATION OF MONTMORILLONITE FROM THREE SLOVAK LOCALITIES

(Fig. 1—3, Tab. 2)

Abstract: In the article the results of high-temperature investigation of montmorillonite from three localities of industrial importance are mentioned: Lastovce, Kuzmice and Jelšový Potok. The objective of the work was to range two East Slovakian and one Middle Slovakian localities to the high-temperature classification of monmorillonite according to R. E. Grim anh G. Kulbicki. The experimental results lead to the conclusion that montmorillonite of Cheto type is found at neither locality and all three localities may be ranged to the type Wyoming with some reservations.

Резюме: В статье приводятся результаты высокотемпературного исследования монтмориллонита из трех промышленно важных локалит (местонахождений) Ластовце, Кузмице и Ельшовый Поток. Целью работы было определить положение двух восточнословацких и одного среднесловацкого местонахождения в высокотемпературной классификации монтмориллонита согласно Р. Е. Грима и Г. Кулбицкого. Экспериментальные результаты ведут к заключению, что монтмориллонит типа Чето не находится ни в одном из этих трех местонахождений и все три местонахождения можно включить с определенными условиями в тип Вайоминг.

1. Introduction

The first more detailed report about the influence of high-temperature on the clay mineral montmorillonite was published by R. E. Grim and W. F. Bradley (1940). They have found out that destruction of montmorillonite three-layers terminates at the temperature interval 800 to 850 °C and at temperature 850 °C as a new phase spinel appears, which melts at the temperature around 1300 °C. The further phase mullite appears at the temperature above 1050 °C and remains up to the highest temperature employed (1400 °C). At temperature 950 °C quartz appears, which recrystallizes to cristobalite after rising temperature.

At the beginning of the following decade W. F. Bradley and R. E. Grim (1951) published a more extensive work about the influence of high-temperature on clay minerals, in which they mentioned DTA curves of eight various samples of montmorillonite and identified their high-temperature phases by X-ray diffraction analysis. They came to the significant conclusion that from the viewpoint of high-temperature part of DTA curves the latter may be divided into two groups. In the first group the exothermic peak follows immediately after the endothermic one, in the second group it is distinctly separated. This difference was also confirmed by the fact that after destruction of montmorillonite structure in the first group of samples spinel forms whereas quartz

---

* RNDr. V. Š. Fajnor, CSc. — Prof. RNDr. J. Masár, CSc. Department of Inorganic Chemistry of Natural Science Faculty, Comenius University, 816 31 Bratislava, Pavilion CH

forms in the second group. The results of J. W. Earley. I. H. Milne and McVeagh (1953) were in agreement with this fact.

R. E. Grim and G. Kulbicki (1957) proved a strong influence of interchangiable cations on development of high-temperature phase of montmorillonite.

On the basis of detailed investigation of 38 various montmorillonite samples from localities at five continents R. E. Grim and G. Kulbicki (1961) published a high-temperature classification of montmorillonite, included in all more voluminous monographs from the field of thermal analysis in the following years – e. g. D. Schultze (1969), R. C. Mackenzie (1970) and mineralogy of clays – e. g. R. E. Grim (1968), M. Gregor and B. Číčel (1969).

According to this classification montmorillonite may be divided into two types or mixture of these types:

In the first type the crystalline structure preserved up to the temperature of 850 to 900 °C, then it crystallizes as the first high-temperature phase β-quartz, which recrystallizes to cristobalite. The third high-temperature phase cordierite forms at temperature when the structure of cristobalite already disappears (1200 to 1300 °C). The samples are melting at temperature interval 1400–1500 °C where all X-ray diffraction lines disappear. DTA curve of this montmorillonite type, designated as Cheto type by the authors, is characterized by separation of the exothermic peak from the preceding endothermic peak by temperature interval 50 to 150 °C. The second exothermic peak appears at temperature 1100 °C and the third at temperature interval 1200 to 1300 °C.

In the second type the crystalline structure preserves up to the temperature 900 to 950 °C, then cristobalite and mullite crystallize. X-ray diffraction lines of mullite remain preserved to melting of samples at temperature 1400 to 1500 °C. At DTA curves of this montmorillonite type, designated as Wyoming type by the authors, the endothermic peak (at temperature about 900 °C) is immediately followed by the exothermic peak. The second exothermic peak is at temperature 1100 to 1200 °C. The course of DTA curves above this temperature is largely variable.

Remarkable is the observation of the authors that the capacity of cation exchange of all Cheto type samples is higher than of Wyoming type samples.

The results of the works by J. Lucas and N. Trauth (1965) have fully confirmed this high-temperature classification.

A strong influence of interchangiable cations on the origin and development of high-temperature phases of montmorillonite was sherified by M. V. Ejerish, A. A. Dvoretchenskaya, N. F. Pshenitchnaja (1970), V. S. Komarov, A. T. Rozin, N. A. Akulič (1972), M. Hložek (1973) and V. Š. Fajnor, J. Masár (1976). From quantitative measurements for Li–, Na–, K–, Cs–, Ca– and Ba-montmorillonite, published by R. Gauglitz and H. E. Schwiete (1961), it has unambiguously been evident that the greatest change of enthalpy of the first exothermic reaction is in the case of Mg-montmorillonite. The results of Wiegmann, C. H. Horte and G. Kranz (1974) also have led to the conclusion that the most intense formation of high-temperature montmorillonite phases is in the case of occupation of exchange positions by magnesium cations.

In the work we therefore were focused on investigation of Mg-montmorillonite, which was isolated from bentonite of three localities of industrial importance in Slovakia:

a) East Slovakian locality near Lastovce is suitable especially for explotation of foundary bentonite, M. Gregor and B. Číčel (1969);

b) bentonite from the locality Kuzmice (northwest from Lastovce) is mainly suitable for purpose white potshred ceramics and galenic pharmacy, M. Gregor and B. Číčel (1969);

c) bentonite from the Middle Slovakian locality Jelšový Potok in the Žiarska kotlina basin is a raw material of high quality for foundry and for production of whitening earth, D. Očenáš, J. Zuberec (1972) and I. Kraus, J. Zuberec (1976).

2. *Preparation of samples and applied methods of investigation*

From bentonite of the localities Lastovce, Kuzmice and Jelšový Potok Na-montmorillonite was isolated by the method described by J. Masár and Š. Hollý (1968). From this monoionic Mg-montmorillonite was obtained by fivefold saturation with one-molar solution of magnesium acetate (pH adjusted to the value 5,5). The prepared samples of Mg-montmorillonite isolated from bentonite from the locality Lastovce (further Mg–LAS only), of Mg-montmorillonite isolated from bentonite of the locality Kuzmice (further Mg–KUZ only) and Mg-montmorillonite isolated from bentonite of the locality Jelšový Potok (further Mg/JEL only) were studied by vertical X-ray goniometer of the firm Philips and by high-temperature version of thermoanalyser Derivatograph of the firm MOM Budapest, under the following conditions:

material-reference $\alpha-Al_2O_3$
thermocouples-original Pt/Pt–Rh(10 %)
range of temperature – 20 to 1500 °C
crucibles-ceramic
atmosphere-statical, air
weight of sample-1000 mg
heating rate – 7,5 to 8,5 °C/min.

The capacity of cation exchange was established by fivefold pressing out of magnesium ions by tenth-molar solution of aniline chloride (250 ml/1g of sample). The amount of pressed out magnesium was found out by complexometric titration.

3. *Experimental results and discussion*

According to X-ray diffraction records the sample Mg–LAS contained an insignificant admixture of α quartz (below 2 %) and the sample Mg–KUZ a small admixture of α cristobalite (3–5 %). The sample Mg–JEL did not contain any crystalline substances besides montmorillonite.

The average values of cation exchange capacity of the studied samples (with standard deviation from the average and values given by M. Gregor and B. Číčel – (1969)* and D. Očenáš and J. Zuberec (1972)** for corresponding bentonite are in Table 1.

Cation exchange capacity of montmorillonite
and bentonite from three localities of Slovakia.

Regarding to the fact that capacity values of cation exchange of montmorillonite of Wyoming type varied within the interval 0,89 to 1,09 mol/kg and in the interval 1,14 to 1,33 mol/kg in the Cheto type in the work by R. E. Grim and G. Kulbicki (1961), the mentioned results indicate affinity of all three investigated samples with montmorillonite of Wyoming type.

Derivative thermogravimetric, differential thermoanalytical, thermogravimetric and temperature curves of the investigated samples are given in Figs. 1, 2 and 3. Calibration of the apparatus is described by Š. Hollý and V. Š. Fajnor (1976).

In the products of thermoanalytical measurements only mullite, in sample Mg–KUZ also α cristobalite, present as original admixture in the sample, were found by X-ray phase analysis. Thus it has turned out that cristobalite originated by thermal disintegration of montmorillonite, disappears with annealing up to temperature 1500 °C, when, however, it is found as admixture in mont-

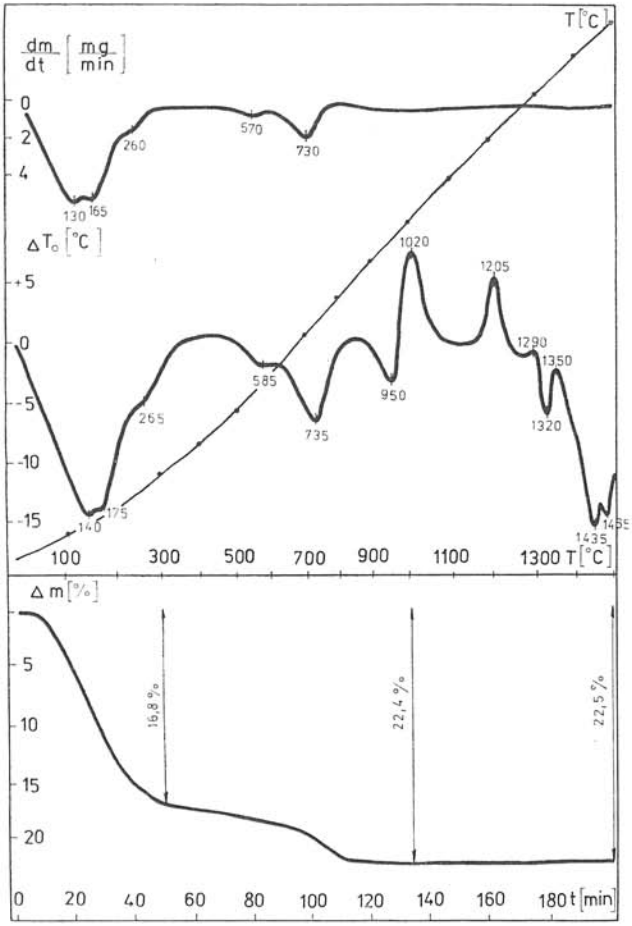

Fig. 1. DTG, DTA, TG and T curves of Mg-Montmorillonite, isolated from bentonite of the locality Lastovce.

morillonite, its crystalline structure remains preserved up to this temperature. (Of course, with given rate of heating – thus around 8 °C . min^{-1}.)

Interpretation of TG and DTG curves

The water from the three investigated montmorillonite samples escapes in two main stages. In the girst – temperature interval nearly 50 to 350 °C – surface-bound water, water from interlayer spaces and water from hydration covers of interchangeable cations escape. Water in form of H_2O molecules releases in three distinct steps (see DTG curves). The maximum rate of water escape from the coordination sphere of magnesium ions is at temperature (180 ± 5) °C. Its value does not exceed 6 mg/min. Total decrease to temperature 300 °C, conventionally considered as the amount of sorbed water, is shown in in the Figures. These values confirm a high sorption capacity and purity of sample Mg–JEL.

In the second stage – temperature interval nearly 350 to 1000 °C – so called hydroxyl water, bound in the mineral structure, escapes. Water in form of

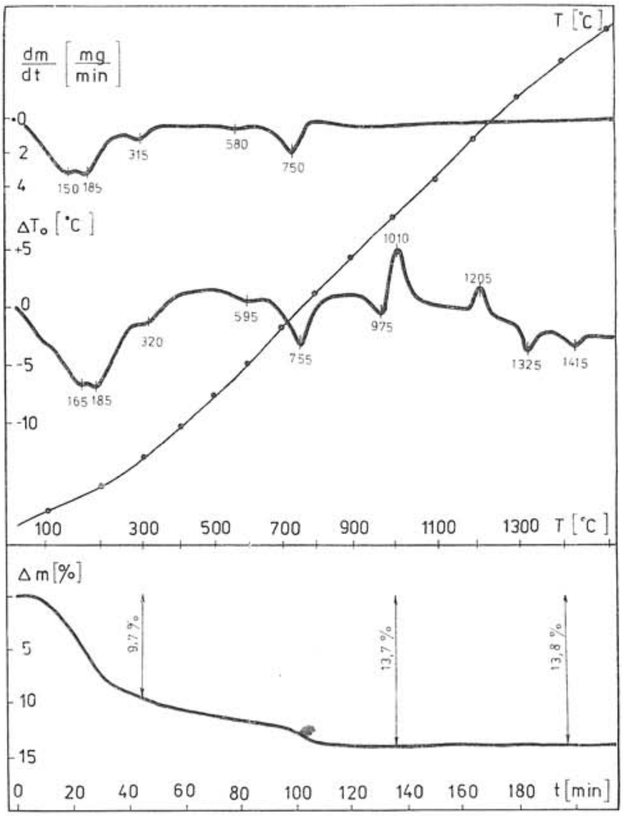

Fig. 2. DTG, DTA, TG and T curves of Mg-montmorillonite, isolated from bentonite of the locality Kuzmice.

OH-groups releases in two distinguishable steps (see DTG curves). In the first step only a small portion of water escapes, with maximum rate at temperature 570 °C. The main part of dehydroxylation process is around temperature 700 °C. Maximum rate of specific gravity change is at temperature 700 ° in sample Mg–LAS, at 730 °C in sample Mg–JEL and at 750 °C in sample Mg–KUZ. exchangiable cations have known ínfluence on dehydroxylation process. I. Horváth and B. Niklová (1973). In case of equal exchangeable cation the mentioned differences may be explained by various degrees of isomorphous replacements and various degree of crystal order of the studied montmorillonite samples. The loss of water in the second stage represents 4–5 % from weighed partions of samples, being in very good accordance with the generally accepted model of montmorillonite structure.

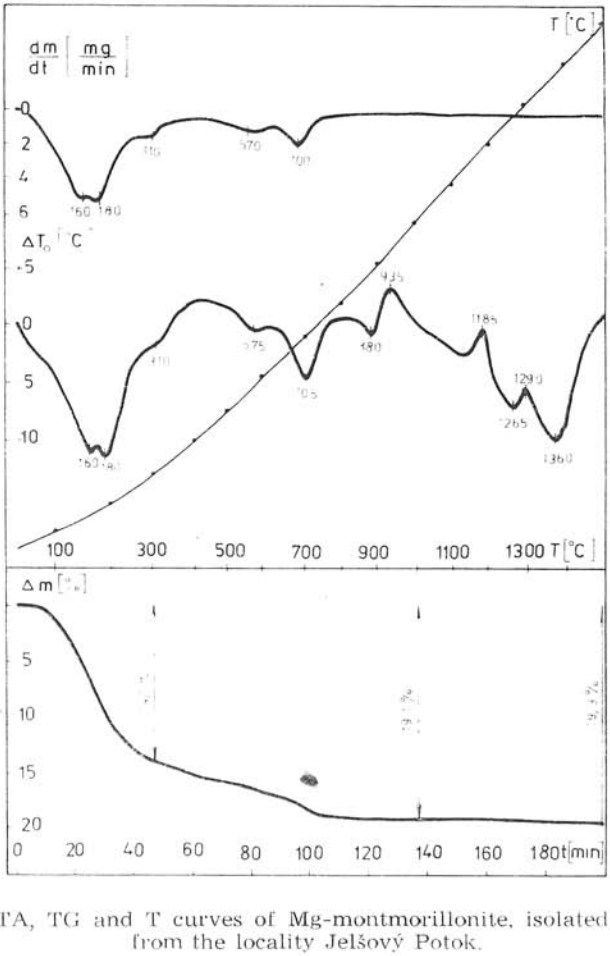

Fig. 3. DTG, DTA, TG and T curves of Mg-montmorillonite, isolated from bentonite from the locality Jelšový Potok.

Interpretation of DTA curves

The first three-stages endothermic peak on DTA curves corresponds to dehydration of montmorillonite. The difference of temperature between sample Mg–JEL and reference material reaches up to 15 °C. In sample Mg–KUZ the endothermic peak is lowest.

Another endothermic peak in temperature interval 550–600 °C is very little distinct and corresponds to endothermic reaction of the first stage of montmorillonite dehydroxylation. The following distinct endothermic peak corresponds to the intensive second stage.

The endothermic peak in temperature interval 800 to 1000 °C is often called as third in literature. It is conditioned by disappearance of the crystalline structure of montmorillonite and its maximum is in sample Mg–LAS at temperature 880 °C, in sample Mg–JEL at temperature 950 °C and in sample Mg–KUZ at 975 °C. Thermic stability of montmorillonite from various localities is distinctly different. It is suitable to mention that a lower thermal stability (sample Mg–LAS) is characteristic of Cheto type montmorillonite.

From the standpoint of high-temperature classification, however, the position of the first exothermic peak is decisive. The difference of temperature between the temperatures of maxima of the third endothermic peak and the first exothermic peak is 55 °C in sample Mg–LAS, 35 °C in sample Mg–KUZ and 70 °C in sample Mg–JEL. According to this criterion sample Mg–KUZ can be most convincingly ranged to the Wyoming type.

The second endothermic peak with maximum at temperature 1200 °C is ascribed to crystallization of cristobalite or mullite. Further exothermic peaks do not appear any more, with the exception of sample Mg–LAS. The endothermic peaks correspond to gradual disappearance of crystalline high-temperature phases and melting of samples.

For clearing up the essence of exothermic peak with maximum at temperature 1290 °C in sample Mg–LAS we gradually added 5,10 to 15 % MgO to this sample before thermoanalytical measurement. It has been shown that the temperature of peak maximum does not change but proportionally to the amount of MgO also height and area of the peak increase. We have confirmed by X-ray diffraction analysis that the third exothermic peak is connected with crystallization of cordierite.

Thermoanalytical curves of the studied samples unambiguosly prove that no sample belongs to montmorillonite of Cheto type, being also in good accordance with their values of cation exchange capacity (see Table 1).

Investigation of high – temperature phases

The studied samples were heated at temperatures 800, 1000 and 1200 °C for two hours. The time of annealing two hours was established as sufficient in the work by R. E. Grim and W. F. Bradley (1940); in the work by J. Lucas and N. Trauth (1965) even the time of annealing of one hour was used. The results of X-rays diffraction analysis of annealing products are summarized in Table 2.

As it is to be seen from the table, annealing of two hours at temperature 800 °C results in disappearance of diffraction lines of montmorillonite in all

Table 1

Montomorillonite	C. E. C. (mol. kg^{-1})	Bentonite	C. E. C. (mol. kg^{-1})
Mg–LAS	1,05 ± 0,05	Lastovce	0,40 – 0,50*
Mg–KUZ	1,03 ± 0,04	Kuzmice	0,40 – 0,85*
Mg–JEL	1,09 ± 0,04	Jel. Potok	0,63 – 0,73*

Table 2

Sample	temperature 800 °C	temperature 1000 °C	temperature 1200 °C
Mg–LAS	α–Q, (Sp)	Cr, α–Q, Sp	Cr, Mu, Co
Mg–KUZ	Cr, (Sp)	Cr, Sp, Mu	Cr, Co, Mu
Mg–JEL	X-ray amorph.	β–Q, Sp, (Cr)	Cr, Mu

Annealing products of montmorillonite
Used symbols: Q-quartz, Cr-cristobalite,
Sp-spinel, Mu-mullite, Co-cordierite;
parentheses-indications of diffraction only.

three samples. The admixtures (α-quartz and cristobalite) do not change with annealing. At temperature 1000 °C spinel and cristobalite crystallized in all three samples. In sample Mg–KUZ already also mullite appearred, which is the main phase of high-temperature alteration of Wyoming type montmorillonite. Surprising was formation of β-quartz in sample Mg–JEL since β-quartz is the high-temperature phase of Cheto type montmorillonite.

The course of DTA curve in the temperature interval 900 to 1100 °C and formation of β-quartz indicate the possibility of share of Cheto type montmorillonite of Wyoming type in sample Mg–JEL. In order to verify this possibility (mixture of high-temperature types), we separated by sedimentation the fine-grained fraction (with radius of particles less than 1,25 μm) from sample Mg–JEL. X-rays diffraction measurements of the annealed fraction have shown distinctly stressed diffraction lines of spinel, an indication of mullite crystallization and a decrease in the intensity of diffraction lines of β-quartz, in contrast to the original sample. These results also confirmed the assumption of the authors of high-temperature classification that montmorillonite of Wyoming type is finer-grained than Cheto type montmorillonite.

Annaeling of samples at temperature 1200 °C resulted in formation of cristobalite and mullite in all samples, in samples Mg–LAS and Mg–KUZ also cordierite formed. At the same time diffraction lines of spinel disappeared in all samples. As R. E. Grim and G. Kulbicki (1961) investigated H-montmorillonite and not Mg-montmorillonite in their work, we pressed out magnesium cations from interchangiable layers of montmorillonite by solution of aniline chloride. When we annealed such samples at the temperature 1200 °C, X-ray measurements have shown that the height of diffraction lines of cordierite sank nearly to one half on the contrary to original annealed Mg-montmorillonites.

3. *Conclusion*

The results of high-temperature investigation of montmorillonite, isolated from bentonite of the localities Lastovce, Kuzmice and Jelšový Potok and transformed to monoionic Mg-montnorillonite show that in the first approach montmorillonite of Wyoming type is present in all three cases, confirmed also by the course of DTA curves and by the established cation exchange capacity. More detailed investigation, mainly investigation of high-temperature phases, however, leads to the conclusion, that there is not a completely pure Wyoming type (from the viewpoint of high-temperature classification of R. E. Grim and G. Kulbicki) and that mainly in the case of the locality Jelšový Potok also an admixture of Cheto type montmorillonite shows itself in montmorillonite of Wyoming type. It is obvious that besides two pure types of montmorillonite also various mixtures of these types may be found in nature, as it was finally established also by the authors of high-temperature classification themselves.

With regard to the fact that this classification is in close connection with crystallochemistry of montmorillonite, distinct differences in suitability of bentonite for concrete technological applications may by expected on the basis of it. It seems to be probable that just the admixture of Cheto type montmorillonite at the locality Jelšový Potok predestinates this locality as source of high quality raw material for production of whitening earth.

REFERENCES

BRADLEY, W. F. — GRIM, R. E., 1951: High temperature thermal effects of clay and related materials. Amer. Mineralogist (Washington), *36*, 3—4, p. 182—201.

EARLEY, J. W. — MILINE, I. H. — McVEAGH, W. J., 1953: Thermal, dehydration, and X-ray studies on montmorillonite. Amer. Mineralogist (Washington), *38*, 9—10, p. 770—783.

EJRISH, M. V. — DVORETCHENSKAYA, A. A. — PSHENITCHNAYA, N. F., 1970: Vlijanije sostava sorbirovanich kationov na obrazovanije vysokotemperaturnich faz v montmorillonitovich glinach. Zb. Issledovanije i ispolzovanije glin i glinistich mineralov. Alma-Ata, Izd. Nauka, 51 p.

FAJNOR, V. — MASÁR, J., 1976: Vysokoteplotné reakcie montmorillonitu „Jelšový Potok". Zborník VII. celošt. konf. o termickej analýze. Bratislava, Edič. stredisko SVŠT, S7 p.

GAUGLITZ, R. — SCHWIETE, H. E., 1961: Thermochemische Untersuchungen an Montmorillonit in Abhängigkeit von der Art, der Korngrösse und der Kationenbelegung. Ber. Deut. Keram. Ges. (Bonn), *38*, 2, p. 43—57.

GREGOR, M. — ČIČEL, B., 1979: Bentonit a jeho využitie. Bratislava, Vydav. SAV, 115 and 176 p.

GRIM, R. E., 1968: Clay mineralogy. New York—Toronto—London—Sydney, Mc Graw-Hill Book Co., 325 p.

GRIM, R. E. — BRADLEY, W. F., 1940: Investigation of the effect of heat on the clay minerals illite and montmorillonite. J. Amer. Ceram. Soc. (Columbus), *23*, 8, p. 242—248.

GRIM, R. E. — KULBICKI, G., 1957: Étude aux rayons X des reactions des mineraux argileux a haute température. Bull. Soc. Franc. Ceram. (Paris), 36, 16, p. 21—28.

GRIM, R. E. — KULBICKI, G., 1961: Montmorillonite: High temperature reactions and classification. Amer. Mineralogist (Washington), *46*, 11—12, p. 1329—1369.

HLOŽEK, M., 1973: Vliv vyměnitelných kationtů na průběh křivky DTA montmorillonitu v oblasti vzniku vysokoteplotných fází. Zborník VI. celošt. konf. o termickej analýze. Bratislava, Edič. stredisko SVŠT, S9 p.

HOLLÝ, Š. — FAJNOR, V., 1976: Kalibrácia termoanalytického prístroja „Derivatograph" (vysokoteplotná verzia). Chem. Listy (Praha), *70*, 1, p. 79—82.

HORVÁTH, I. — NIKOLOVÁ, B., 1973: Aktivačné energie dehydroxylácie monoiónových foriem montmorillonitu z termogravimetrických meraní. Zborník VI. celošt. konf. o termickej analýze. Bratislava, Edič. stredisko SVŠT, S3 p.

KOMAROV, V. S. — ROZIN, A. T. — AKULITCH, N. A., 1970: Vlijanije kratkovremennoj kislostnoj obrabotki na termičeskije prevrastchenija montmorillonita. Vesci Akad. Navuk Belarusk. SSR (Minsk), N. 6, p. 39—43.

KRAUS, I. — ZUBEREC, J., 1976: Bentonites and kaolins at the SW Margin of the Kremnické pohorie mts. in the neovolcanic region of central Slovakia. Seventh Conf. Clay Miner. Petrol. Praha—Karlovy Vary, p. 439—449.

LUCAS, J. — TRAUTH, N., 1965: Étude du comportement des montmorillonites a haute température. Bull. Serv. Carte géol. Als. Lorr. (Strasbourg), *18*, 4, p. 217—242.

MACKENZIE, R. C. (edit.), 1970: Differential Thermal Analysis. London—New York, Academic Press, 550 p.

MASÁR, J. — HOLLÝ, Š., 1968: Isolierung des Montmorillonite durch koloidchemische Methoden und dessen Struktursorptionseigenschaften. Acta Fac. Rerum. Nat. Univ. Comenianae, Chimia (Bratislava), *12*, 1, 179—192.

OČENÁŠ, D. — ZUBEREC, J., 1972: Ložisko bentonitu Jelšový Potok v Žiarskej kotline. Mineral. slovac. (Spišská Nová Ves), *4*, 15, p. 135—144.

WIEGMANN, J. — HORTE, C. H. — KRANZ, G., 1974: Personal announcement.

Review by I. HORVÁTH

Manuscript received February 21, 1979