

## CHARACTERIZATION AND DIFFERENTIATION OF KAOLINITES FROM SELECTED CZECH DEPOSITS USING INFRARED SPECTROSCOPY AND DIFFERENTIAL THERMAL ANALYSIS

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### ABSTRACT

This paper reports the possibilities of using FTIR spectroscopy and simultaneous thermogravimetry and differential thermal analysis for examination of the structural order of four Czech kaolinite samples (Jimlikov, Sedlec, Olomucany and Unanov deposits) and one kaolinite standard KGa-1b from Georgia deposit obtained from the Source Clays Repository of The Clay Minerals Society (USA). FTIR spectroscopy was used for the classification of the degree of structural order of kaolinite samples by empirical (IR-E) and numerical (IR-N) classification. Differential thermal analysis was used for the determination of the kaolinite disorder degree according to decomposition peak temperature obtained from DTA curves. The resulting trend of decrease in orderliness is: KGA-1b (with the best orderliness) > Jimlikov > Sedlec > Olomucany > Unanov (with the worst orderliness).

**KEYWORDS:** kaolinite, degree of structural order, infrared spectroscopy, thermogravimetry and differential thermal analysis

### 1. INTRODUCTION

Important deposits of high quality kaolin in the Czech republic (sedimentary rock, with a significant proportion of kaolinite and other clay minerals) are in Karlovy Vary region. A more extensive deposits of kaolin are in the region of Horni Briza, Kaznejov, Chotikov and other places in the northern neighborhood of Pilsen. Low-quality kaolin deposits are situated in western Bohemia and also in Znojmo district. Kaolin is widely used in the paper industry for its high whiteness and low abrasion and it is also used in the other industry branches like construction, ceramics, rubber and porcelain manufacturing.

The empirical formula for kaolinite is  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  and the theoretical chemical composition is  $\text{SiO}_2$ , 46.54 %;  $\text{Al}_2\text{O}_3$ , 39.50 %; and  $\text{H}_2\text{O}$ , 13.96 %. Kaolinite has a 1:1 sheet structure consisted by tetrahedral and octahedral sheets. Type 1:1 minerals generally do not have the charge or its value is extremely low (Murray, 2007). The kaolinite layered structure 1:1 according to (Kühn and Zamarský, 1984) is shown in Figure 1.

The quality respectively the orderliness of kaolinites strongly influence their physical and chemical properties. The most often used method for examination of the degree of structural disorder or “crystallinity” of the kaolinite samples is X-ray powder diffraction. Kaolinite tetrahedral and octahedral network forms a single layer with

a thickness of approximately 7 Å. The poor structural order commonly observed in kaolinites can be explained in terms of a series of stacking faults or defects in the *ab* plane and along the *c*-axis. The XRD patterns of ordered kaolinite samples are significantly different from those of disorder. Ordered kaolinite shows sharp and narrow peaks, while its disordered counterpart gives less well-defined, broad, and asymmetrical peaks (Brigatti et al., 2006). The crystallinity indices given by many authors are widely used for determination of kaolinite disorder degree using various approaches based on X-ray diffraction (Brindley et al., 1963; Plancon and Zacharie, 1990; Aparicio and Galán, 1999; Chmielová and Weiss, 2002; Aparicio, 2006).

Less common used method for determination of kaolinite disorder degree is an infrared spectroscopy. The structural disorder of kaolinites can be detected by differences in position and relative intensity of OH stretching and bending bands in IR spectrum (Brindley, et al., 1986; Muller and Bocquier, 1987; Prost et al., 1989; Madejová et al., 1997). On the basis of change in the relative intensities of absorption bands corresponding to the stretching and bending vibrations of structural OH groups, it was possible to divide the analyzed samples into three groups: with ordered structure, partially ordered structure and poorly ordered structure.

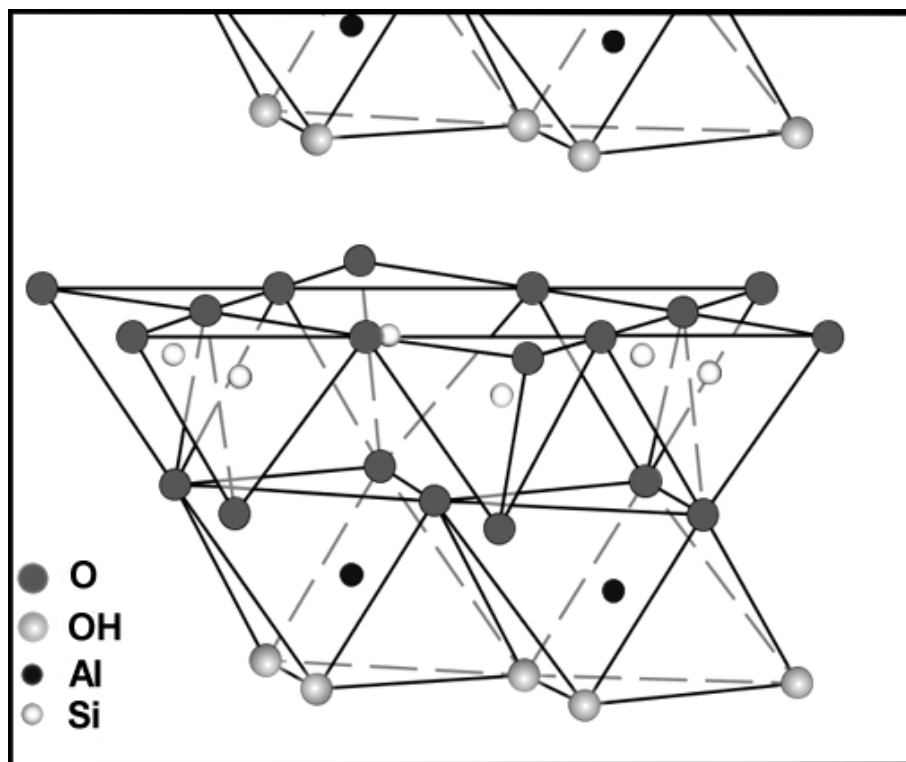


Fig. 1 The kaolinite layered structure 1:1.

The least common used method for determination of kaolinite disorder degree is simultaneous thermogravimetry and differential thermal analysis. The DTA curves show the endothermic and exothermic reactions in a kaolinite sample during heating, such as desorption of surface water ( $H_2O$ ), dehydroxilation (structural  $OH^-$  groups) and the transformation to mullite and cristobalite (Földvári, 1997; Hatakeyama and Liu, 1998; Guggenheim and Koster van Groos, 2001). The obtained temperature effects of dehydroxilation and polymorphic transformation are strongly dependent on kaolinite sample structural order (Smykatz-Kloss, 1974; Kristóf et al., 2002).

In the present paper is incorporated a detailed study of the degree of structural disorder for four Czech kaolinite samples (Jimlikov, Sedlec, Olomucany and Unanov deposits) and one kaolinite standard KGa-1b from Georgia deposit obtained from the Source Clays Repository of The Clay Minerals Society (USA). The kaolinite standard KGa-1b is the aim of the interest of many authors because of its purity and its special properties (Pruett and Webb, 1993; Berezniński et al., 1998; Sanchez-Soto et al., 2000; Mermut and Cano, 2001; Traoré, 2006). This standard kaolinite was chosen for comparison with Czech selected kaolinites mentioned above. The detailed study has included mainly an numerical approach based on crystallinity indices  $CI_1$  and  $CI_2$  calculated from the intensities of selected vibrations

modes obtained by FTIR measurements as well as the determination of the disorder degree according to peak temperature values of kaolinite dehydroxilation and transformation obtained by differential thermal analysis.

## 2. SAMPLES AND EXPERIMENTAL METHODS

### 2.1. TESTED SAMPLES

Kaolinite samples (fraction under  $5\mu m$ ) from several different Czech kaolin deposit were used for analysis:

- kaolinite sample from Karlovy Vary region, formed by kaolinization of granite (Jimlikov u Chodova locality)
- kaolinite sample from Karlovy Vary region, formed by kaolinization of granite (Sedlec locality)
- kaolinite sample from Moravian Karst, represented kaolinized clayey-sandy sediments in fosil-karst depressions (Olomucany locality)
- kaolinite sample from Znojmo region, formed by kaolinization of granitoid rocks (Unanov locality)
- kaolinite sample KGa-1b from Georgia (USA), represented sedimentary kaolinite with well ordered structure.

Following Table 1 shows the volume of kaolinite and type of associated minerals signed as : Q - quartz, I - illite, Sm - smectite, D - dickite, F - feldspar.

**Table 1** Locality, mineralogical composition, genesis and classification according to XRD of tested kaolinite samples.

<i>Deposit</i>	<i>Kaolinite (%)</i>	<i>Associated minerals</i>	<i>Origin</i>	<i>XRD</i>		
				<i>HI</i>	<i>AGFI</i>	<i>Class.</i>
Georgia (KGa-1b), USA	96	D	sedimentary	1.120	-	w-o
Jimlikov u Chodova, CZ	98	Q	weathered	1.060	1.180	o
Sedlec u K. Varu, CZ	97	Q,I,Sm	weathered	0.630	0.780	p-o
Olomucany, Blansko, CZ	97	Q,I,Sm	weathered	0.590	0.670	p-o
Unanov u Znojma, CZ	96	Q,I,F	weathered	0.480	0.640	p-o

*HI* - the method of Hinckley (1963)

*AGFI* - the method of Aparicio-Galán\_Ferrell (1999)

## 2.2. METHOD OF FTIR SPECTROSCOPY

The infrared spectra were recorded on Nicolet Avatar 320 FTIR spectrometer. The KBr pressed-disc technique was used for routine scanning of the spectra. Samples of 2 mg and 0.5 mg were dispersed in 200 mg of KBr to record optimal spectra in the regions of 4000-3000 and 4000-400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  and 64 scans. Discs for the 4000-3000  $\text{cm}^{-1}$  region were heated in the furnace overnight at 150  $^{\circ}\text{C}$  to minimize the water adsorbed on KBr and clay sample (Madejová et al., 1997).

Two approaches were used to determine the degree of structural disorder of selected kaolinites from IR spectra. The firstly step, an empirical approach (IR-E) on the basis of resolution and relative intensities of the bands in OH stretching and bending region was used. The samples were classified as:

- ordered (well - ordered) if the OH stretching and bending bands were clearly resolved;
- partially ordered if the individual OH bands at 3670, 3650 and 938  $\text{cm}^{-1}$  could be identified but their intensities were low; and
- poorly ordered if only one band near 3660 or inflexions near 3670, 3650 and 938  $\text{cm}^{-1}$  were observed in the spectra (Madejová et al., 1997).

A numerical approach (IR-N) based on crystallinity indices  $CI_1$  and  $CI_2$  calculated from the intensities of selected vibrations modes using the equations:

$$CI_1 = I(\nu_1) / I(\nu_3) \quad (1)$$

$$CI_2 = I(\nu_4) / I(\nu_1) \quad (2)$$

where  $I(\nu_1)$  and  $I(\nu_4)$  are intensities of the OH stretching bands at 3695  $\text{cm}^{-1}$  and 3620  $\text{cm}^{-1}$  and  $I(\nu_3)$  is the intensity of the OH bending band at 915  $\text{cm}^{-1}$ . The two-points baseline method was used to obtained the intensity of the OH bands. According to the obtained values of crystallinity indices kaolinites were

classified as poorly ordered structures ( $CI_1 < 0.7$ ,  $CI_2 > 1.2$ ); partially ordered structures ( $0.7 < CI_1 < 0.8$ ,  $0.9 < CI_2 < 1.2$ ) and ordered structures ( $CI_1 > 0.8$ ,  $CI_2 < 0.9$ ) (Russell and Fraser, 1994; Madejová and Komadel, 2001).

## 2.3. METHOD OF THERMAL ANALYSIS

Simultaneous thermogravimetry and differential thermal analysis was carried out using multimodular thermal analyzer SETSYS 12 - SETARAM instrument equipped with a measurement head TG ATD ROD according to below mentioned conditions. Measurement of each sample was carried five times to get predicative results.

Based on obtained DTA curves, respectively according to decomposition peak temperatures is possible to determine the degree of disorder in kaolinite samples. Well ordered sample has their decomposition peak temperature of quite high value ( $T_d > 571$   $^{\circ}\text{C}$ ), ordered sample has their decomposition peak temperature  $T_d$  at the temperature interval 561-570  $^{\circ}\text{C}$ . For poorly ordered sample, the temperature decomposition varies from 546 to 560  $^{\circ}\text{C}$  and disordered sample decomposition temperature values is up to 545  $^{\circ}\text{C}$ . The decomposition peak below 540  $^{\circ}\text{C}$  seems to be quite low according to published DTA data of kaolinites and belong to only a very few naturally occurring, extremely disordered samples.

The differentiation mentioned above can be used for the determination of the disorder degree of kaolinites if the analysis were under the proposed conditions : heating rate 10  $^{\circ}\text{C} \cdot \text{min}^{-1}$ , sample fraction under 5  $\mu\text{m}$  (the fraction from 0.5 to 5  $\mu\text{m}$  with maximum in their grain size distribution curves laying for the fraction 2 – 3  $\mu\text{m}$ ), sample mass about 50 mg, thermocouple Pt-Pt<sub>90</sub>/Rh<sub>10</sub>, inert material Al<sub>2</sub>O<sub>3</sub>, no pressing in crucible (loose packed), air atmosphere. With different conditions, the dehydroxilation peak temperature  $T_d$  can vary, so the temperature interval of disorder degree can differ too. The most influencing factor for the  $T_d$  temperature value is the heating rate

**Table 2** Possition and assignment of the absorption bands in IR spectra of tested kaolinites.

<i>Assignment</i>	<i>KGa-1b</i>	<i>Jimlikov</i>	<i>Sedlec</i>	<i>Olomucany</i>	<i>Unanov</i>
OH stretching of inner-surface hydroxyl groups <sup>1</sup>	3694	3695	3696	3696	3696
OH stretching of inner-surface hydroxyl groups <sup>2</sup>	3669	3669	3668	3668(s)	3669
OH stretching of inner-surface hydroxyl groups <sup>2</sup>	3653	3652	3653	3654	3652
OH stretching of inner hydroxyl groups	3618	3620	3620	3620	3620
Si-O stretching (longitudinal mode)	1113(s)	1112	1113	1111	1114
Si-O stretching (perpendicular mode)	1098	-	-	-	-
in-plane Si-O stretching	1033	1032	1032	1032	1032
in-plane Si-O stretching	1009	1008	1007	1006	1007
OH deformation of inner-surface hydroxyl groups	937	935	937	936	935
OH deformation of inner hydroxyl groups	913	913	913	913	912
Si-O	791	793	793	793	794
Si-O, perpendicular	752	755	755	755	754
Si-O, perpendicular	694	699	699	698	697
Si-O	645	647	641	645	644
Al-O-Si deformation	540	538	537	538	537
Si-O-Si deformation	468	470	469	470	469
Si-O deformation	433	430	430	430	429

*1* - in plane vibration with a transition moment nearly perpendicular to the (001) plane

*2* - anti-phase vibration with a transition moment lying in the (001) plane.

(s) - shoulder of absorption band

(Gabbott, 2008). The difference between the dehydroxilation temperature with heating rates  $3\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  and  $30\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  for the same kaolinite sample is over  $50\text{ }^{\circ}\text{C}$ . Therefore the evaluation of the disorder degree of kaolinites by thermal analysis must be always adjusted to measurement conditions (Smykatz-Kloss, 1974).

### 3. RESULTS AND DISCUSSION

#### 3.1. FTIR SPECTROSCOPY

The infrared spectra of tested kaolinites are shown in Figures 2 and 3. The complete assignment of the absorption bands in measured IR spectra is summarized in Table 2.

Determination of degree of structural disorder from IR spectra of kaolinites based on visual estimation of specific features (IR-E) and calculated

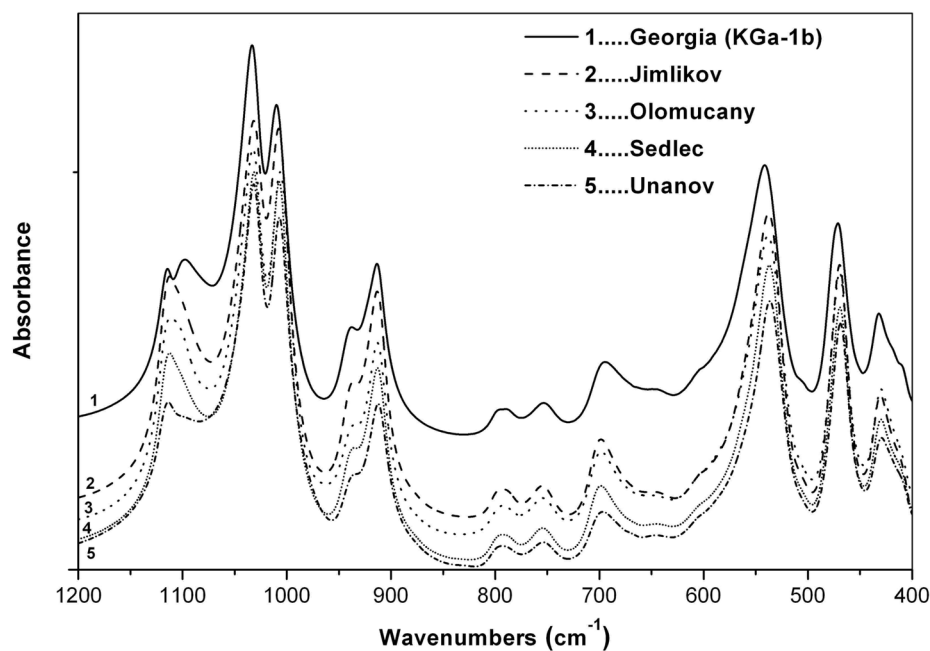


Fig. 2 The infrared spectra of kaolinites (400 to 1200  $\text{cm}^{-1}$ ).

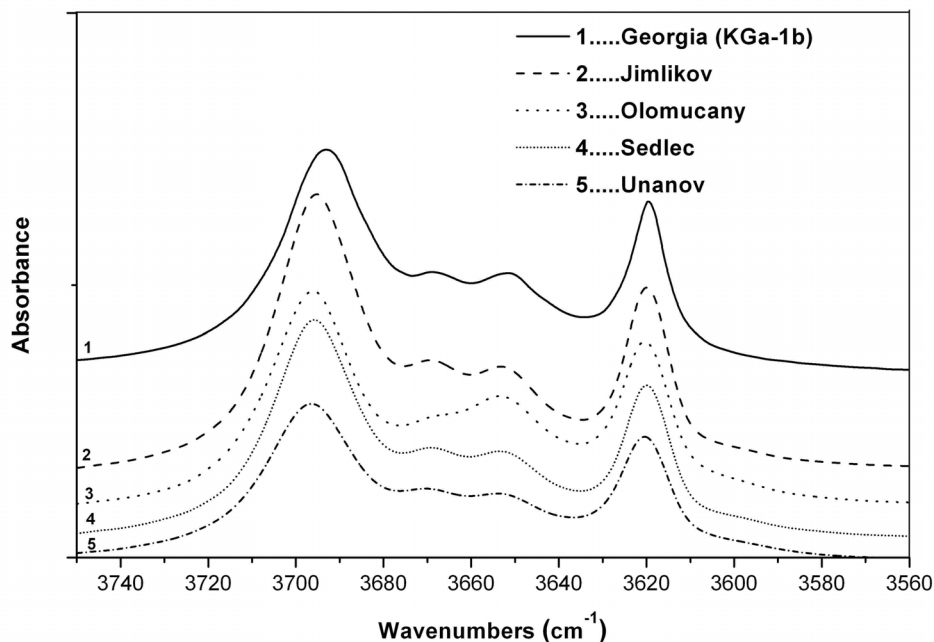


Fig. 3 The infrared spectra of kaolinites (3560 to 3750  $\text{cm}^{-1}$ ).

crystallinity indices  $CI_1$  and  $CI_2$  (IR-N) according to Neal and Worrall (1977) are given in Table 3.

The 3695, 3620  $\text{cm}^{-1}$  doublet is characteristic for the kaolin group general. Four clearly resolved absorption bands at about 3695, 3670, 3650 and 3620  $\text{cm}^{-1}$  reflect high structural ordering of the samples. Distinguishable four bands in OH stretching region were observed in IR spectrum of sample

KGa-1b, Jimlikov, Sedlec and Unanov. The IR spectrum of kaolinite from Olomucany deposit showed the replacement of the middle two bands by a single broad band at 3654  $\text{cm}^{-1}$  with a shoulder near 3668  $\text{cm}^{-1}$ , that indicates partially ordered structure of this sample (Fig. 3). IR spectrum of Unanov demonstrated general broadening of all bands (Fig. 2). This feature confirms high degree of disordering in



**Table 3** Classification of the degree of structural order of kaolinite samples using empirical (IR-E) and numerical (IR-N) classification.

Deposit	Attributes				IR-E	CI <sub>1</sub>	CI <sub>2</sub>	IR-N
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	class			class
Georgia (KGa-1b), USA	✓	✓	✓	✓	o	0.96	0.78	o
Jimlikov u Chodova, CZ	✓	✓	✓	✓	o	0.93	0.78	o
Sedlec u Karlových Varu, CZ	✓	✓	937 (s)	✓	pa-o	0.91	1.20	pa-o
Olomucany, Blansko, CZ	✗	✓	937 (s)	✓	p-o	0.74	0.82	pa-o
Unanov u Znojma, CZ	✓	✗	937 (s)	✓	p-o	0.72	0.81	pa-o

Attributes: 1<sup>st</sup> - distinguishable four bands 3695, 3670, 3650, 3620  
 2<sup>nd</sup> - general broadening of all bands is not observed  
 3<sup>rd</sup> - OH deformation bands 938 and 916 are visible  
 4<sup>th</sup> - two weak bands found at 795 and 758 are of about equal intensity  
 CI<sub>1</sub>, CI<sub>2</sub> - the method of Neal and Worrall (1977)

kaolinite. Two clearly resolved OH bending bands occurring at about 938 and 916 cm<sup>-1</sup> were observed in IR spectra of samples from Georgia (KGa-1b) and Jimlikov deposit (Fig. 2). Other samples in this spectral region showed only a very weak inflection located at 934 cm<sup>-1</sup>. In all IR spectra were found two weak bands at 795 and 758 cm<sup>-1</sup> with about equal intensity (Fig. 2). This attribute can help to distinguish between well-crystallized kaolinite and halloysite.

It is possible to divide tested kaolinites according to visual estimation of degree of crystallinity from IR spectra (IR-E) into three groups: ordered (well ordered), partially ordered and poorly ordered. First group is represented by kaolinite KGa-1b and Jimlikov whose IR spectra satisfy all the demands of IR-E classification. IR spectrum of Sedlec kaolinite without clearly resolved OH deformation band at 938 cm<sup>-1</sup> belongs to the second group with partial structural order. Kaolinite Olomucany and Unanov represent third group with poorly order structure. According to calculated values of IR-N classification, based on the ratio hydroxyl band absorbances 3695 and 915 cm<sup>-1</sup> (CI<sub>1</sub>); and 3695 cm<sup>-1</sup> (CI<sub>2</sub>), it is possible to divide the kaolinites into two groups: ordered (well ordered) and partially ordered. Among ordered (well ordered) kaolinites belong KGa-1b and Jimlikov. In this case data from IR-E classification correspond well with IR-N classification. Second group is represented by kaolinite Sedlec, Olomucany and Unanov, whose CI<sub>1</sub> and CI<sub>2</sub> crystallinity indices corresponded to partially ordered structures. Discrepancy between IR-N and IR-E classification arose probably thank to admixture of fine-grained illite or smectite present in kaolinite samples (see Table 1). Both minerals (illite and smectite) have their absorption bands at the same area and can contribute to the increasing of both OH bending absorption at 915 cm<sup>-1</sup> and OH stretching

absorption at 3695 cm<sup>-1</sup>. The problem is that their contribution to the absorption at 915 cm<sup>-1</sup> is significantly higher than to the absorption at 3695 cm<sup>-1</sup>. When calculating the ratio of CI<sub>2</sub> based on such affected values, the ratio can indicate an erroneously higher value for the crystallinity degree of the kaolinite.

### 3.2. THERMAL ANALYSIS

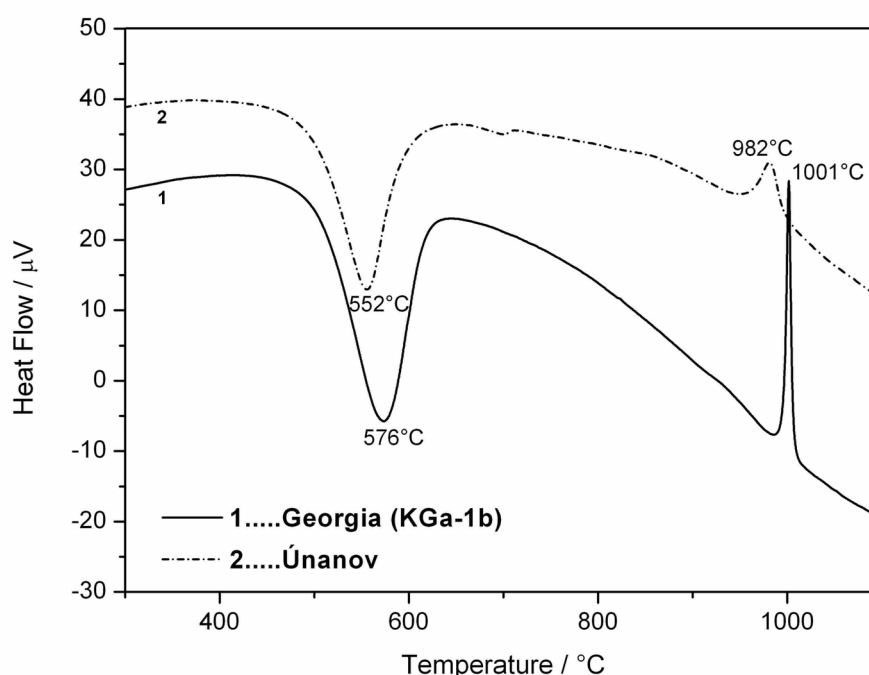
The measured DTA curves of tested kaolinites showed the following endothermic effects: desorption of surface water at low temperature interval 105-110 °C and releasing of constitution water and breaking of crystal lattice at higher temperature interval 552-576 °C. The recrystallization and transformation of dehydrated substance to mullite, cristobalite and quartz was observed as the exothermic effect at about 982-1001 °C.

Table 4 shows the thermal data obtained from DTA curves including dehydroxilation peak temperature  $T_d$  and transformation peak temperature  $T_t$ . The first group of well ordered samples is represented by kaolinite KGa-1b with the highest decomposition peak temperature value (above 571 °C). The sample classified as ordered (from Jimlikov) belongs to the second group with middle decomposition peak temperature values. Among poorly-ordered samples in the third group belong kaolinite samples from Sedlec, Olomucany and Unanov with the lowest decomposition peak temperature values up to 560 °C.

From obtained data is evident, that with increasing of decomposition peak temperature value, respectively with increasing of orderliness, the transformation exothermic peak temperature also increase (Fig. 4). DTA curves show, that for well ordered samples, the transformation exothermic peaks

**Table 4** Thermal data including dehydroxilation peak temperature  $T_d$ , transformation peak temperature  $T_t$  and classification of disorder degree of kaolinite samples.

<i>Deposit</i>	$T_d$	$T_t$	<i>class</i>
Georgia (KGa-1b), USA	576	1001	w-o
Jimlikov u Chodova, CZ	570	992	o
Sedlec u Karlovyeh Varu, CZ	560	989	p-o
Olomucany, Blansko, CZ	558	988	p-o
Unanov u Znojma, CZ	552	982	p-o

**Fig. 4** DTA curves of kaolinite samples Georgia (KGa-1b) and Unanov.

are of the high intensity and quite narrow. For the poorly ordered sample, the transformation peaks are of low intensity, wider and smaller.

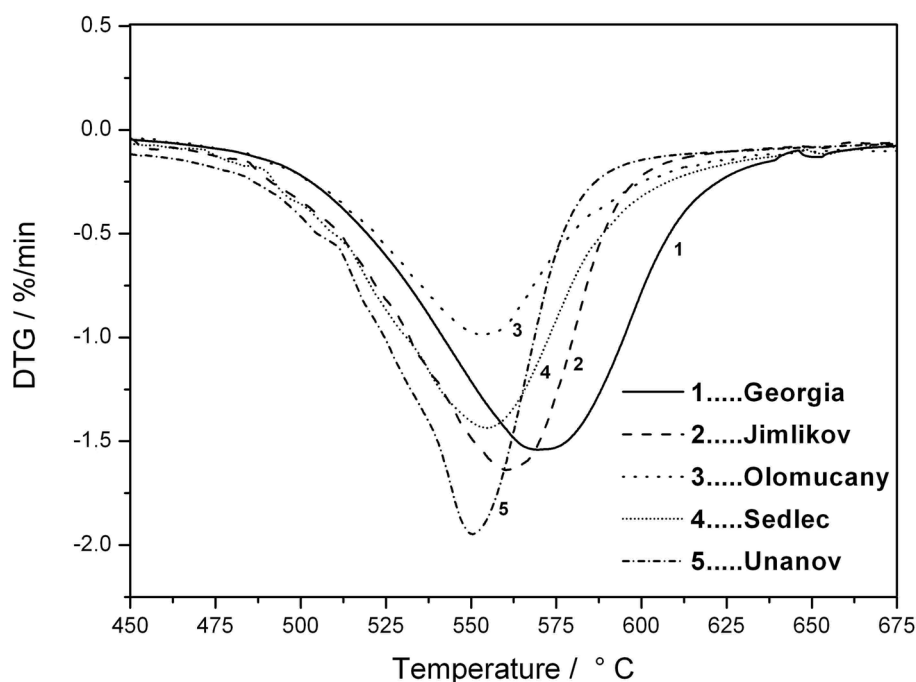
The kinetic parameters of decomposition was studied using the Arrhenius equation applied to solid state reactions. The activation energy for dehydroxilation was evaluated by Freeman-Carroll method which enables, from the exploitation of one DTG peak, to determine besides activation energy of reaction also the reaction order and the rate constant (Freeman and Carroll, 1958). Table 5 summarized thermal data including maximal reaction velocity temperature  $T_r$ , activation energy  $E_a$  with order reaction  $n$  and correlation factor  $R^2$ .

It is evident, that values of maximal reaction velocity temperature  $T_r$  obtained from DTG curve correspond to the decomposition peak temperature  $T_d$  obtained from DTA curves. Figure 5 shows the derivative thermogravimetric (DTG) curves for all

tested kaolinite samples at the heating rate  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . With increase of peak temperature on DTG curve, activation energy of dehydroxilation process decreased. The values of activation energy  $E_a$  varied from  $230\text{ kJ}\cdot\text{mol}^{-1}$  (well ordered kaolinite sample KGa-1b) to  $301\text{ kJ}\cdot\text{mol}^{-1}$  (the poorest ordered sample Unanov) with the reaction order  $n$  varied from 0.9 to 1.5. Obtained results show, that better ordered samples display lower activation energy for dehydroxilation process estimated by Freeman-Carroll method. The possibilities and comparison of Freeman-Carroll method with other used methods are described well by (Slovak, 2001). The disadvantage of this method can lay in the fact, that the calculation is performed from the difference of two discrete experimental points and consider rather homogenous character of reaction. MacKenzie (1978) and Cical et al. (1981) assume, that homogeneous and inhomogeneous mechanisms of the dehydroxilation

**Table 5** Thermal data including peak temperature  $T_r$ , activation energy  $E_a$  and reaction order  $n$ .

<i>Deposit</i>	$T_r$ °C	$E_a$ kJ.mol <sup>-1</sup>	$n$	$R^2$
Georgia (KGa-1b). USA	573	230	1.1	1.0000
Jimlikov u Chodova. CZ	568	242	1.4	0.9998
Sedlec u Karlovych Varu. CZ	563	277	1.5	0.9998
Olomucany. Blansko. CZ	559	274	1.0	0.9992
Unanov u Znojma. CZ	553	301	0.9	0.9996

**Fig. 5** DTG curves of kaolinite samples.

process is possible. Therefore if the heterogenous character of dehydraxilation process is supposed, the dependance of activation energy on structural order can differ, mainly if we consider that the dehydroxilation process is initiated in the defect places.

#### 4. CONCLUSIONS

The obtained results from infrared spectroscopy and differential thermal analysis were compared with XRD results previously published by Hinckley (1963) and Aparicio et al. (1999). Also according to Pruet and Webb (1993), kaolinite Georgia (KGa-1b) is signed as well-ordered and based on the calculated characteristic (Chmielová and Weiss, 2002), the kaolinites from Czech deposits can be divided into two groups. First group of medium-degree of structural order (ordered) samples contains kaolinite

Jimlikov, the second group of low-degree of structural order (poorly ordered) samples contains kaolinites from Sedlec, Olomucany and Unanov deposits. According to our DTA results, kaolinite Georgia (KGa-1b) belongs to well-ordered group, kaolinite Jimlikov to ordered group and other tested samples to poorly-ordered group. It is evident, that DTA data set a reasonable agreement with published data obtained by XRD diffraction method. In case of using FTIR spectroscopy, there is only a slight difference between IR data and data evaluated by DTA and XRD analysis. The OH stretching and bending vibrations of structural water are sensitive enough to distinguish ordered (well ordered), partially ordered and poorly ordered kaolinites. Visual IR-E method for structural order determination provides basic classification into three groups: ordered (well ordered), partially ordered and poorly ordered; while IR-N method divides



kaolinite samples into two groups: ordered (well ordered) and partially ordered. Unanov and Olomucany samples were evaluated as partially ordered kaolinite analogous to Sedlec. The cause of this discrepancy is probably the presence of clay mineral admixture (e.g. illite or smectite), which strongly influences the IR pattern in OH stretching and bending region. The OH bands are overlapped and thus may lead to incorrect degree of structural order. But even though all three used methods give a slightly different distribution of the structure classification, the order respectively the resulting trend of decrease in orderliness is the same for all three methods: KGA-1b (with the best orderliness) > Jimlikov > Sedlec > Olomucany > Unanov (with the worst orderliness).

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