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FOURIER TRANSFORM INFRARED SPECTROSCOPIC CHARACTERIZATION OF KAOLIN GROUP MINERALS FROM THE MAIN SLOVAK DEPOSITS

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Abstract: FTIR spectroscopy was used to study Slovak kaolinites and halloysites of various geological origin. Twenty seven samples ranging from well-ordered to very poorly-ordered kaolinites were examined to explore correlation between the degree of structural disorder (or crystallinity) and their geological origin. The highest degree of ordering was found for hydrothermal and sedimentary kaolinites. Poorly ordered kaolinites and halloysites belong to the group of weathered kaolins or to the kaolin clays. The degree of crystallinity, determined by IR spectroscopy (OH stretching and bending regions) was compared with that measured by XRD. Good relationship between IR and XRD measures of disorder was found for the kaolinites of hydrothermal and sedimentary origin, while only partial correlation was found for weathering kaolinites and kaolin clays.

Key words: kaolinite, halloysite, genetic origin, degree of crystallinity, FTIR, XRD.

Introduction

Kaolin group minerals occur in several different types of deposit in Slovakia (Kraus & Hano 1976; Kraus & Horváth 1978; Kraus 1989; Novotná et al. 1993). Three genetic groups of kaolin deposits, distinguished in this region, originated by weathering, hydrothermal activity or sedimentation. The kaolin clays were assigned to a separate group (Kraus 1989). From the petrological-genetic aspect, their position towards the kaolins of the weathering and hydrothermal origins is unambiguously distinguished. Sometimes it is difficult to set an exact boundary between the sedimentary kaolins and kaolin clays. Sedimentary kaolins represent a type of kaolin sands and gravels, which underwent short and rapid transport from the kaolin weathering crusts mostly to the continental basin and have narrow spacial relations to the parent rocks. The kaolin clays were usually transported over greater distances and therefore it was difficult to determine their source area and the parent rocks. The weathering and sedimentary kaolins offer essential information about the parent rocks, climate and character of topography. The kaolin clays are significant mainly to state the time stages of the kaolinization and to consider the kaolin weathering from the regional aspect (Kraus 1989).

Natural kaolinites have various degree of structural disorder or "crystallinity" which are often related to the conditions of genesis of these minerals (Brindley et al. 1986; Giese 1988). Variations in the degree of order–disorder of kaolin group minerals were recognized many years ago (Brindley & Robinson 1946), but more detailed studies revealed the true complexity of the situation (Mitra 1963; Noble 1971; Plancon & Tchoubar 1977a, 1977b). Attempts have been made to quantify the "crystallinity" of kaolin minerals in terms of indices based on X-ray diffraction (XRD) patterns (Hinckley 1963; Stoch 1974; Hughes & Brown 1979). The Hinckley index, commonly used as a semi-quantitative measure of crystallinity, is less useful for poorly ordered samples or for samples containing quartz. To overcome these problems new empirical indices of crystallinity for kaolins were derived. Poorly ordered kaolinites and halloysites are better characterized by the empirical crystallinity indices according to Hughes & Brown (1979). The values range from 4.8 for halloysite to 83 for well-ordered kaolinite. Stoch (1974) derived index of crystallinity for kaolins with quartz admixture. It attains about 0.7 for kaolinite of high degree of ordering and 1.5–1.8 for disordered kaolinite.

It is well known that the infrared spectra of more or less disordered natural kaolinites show appreciable differences

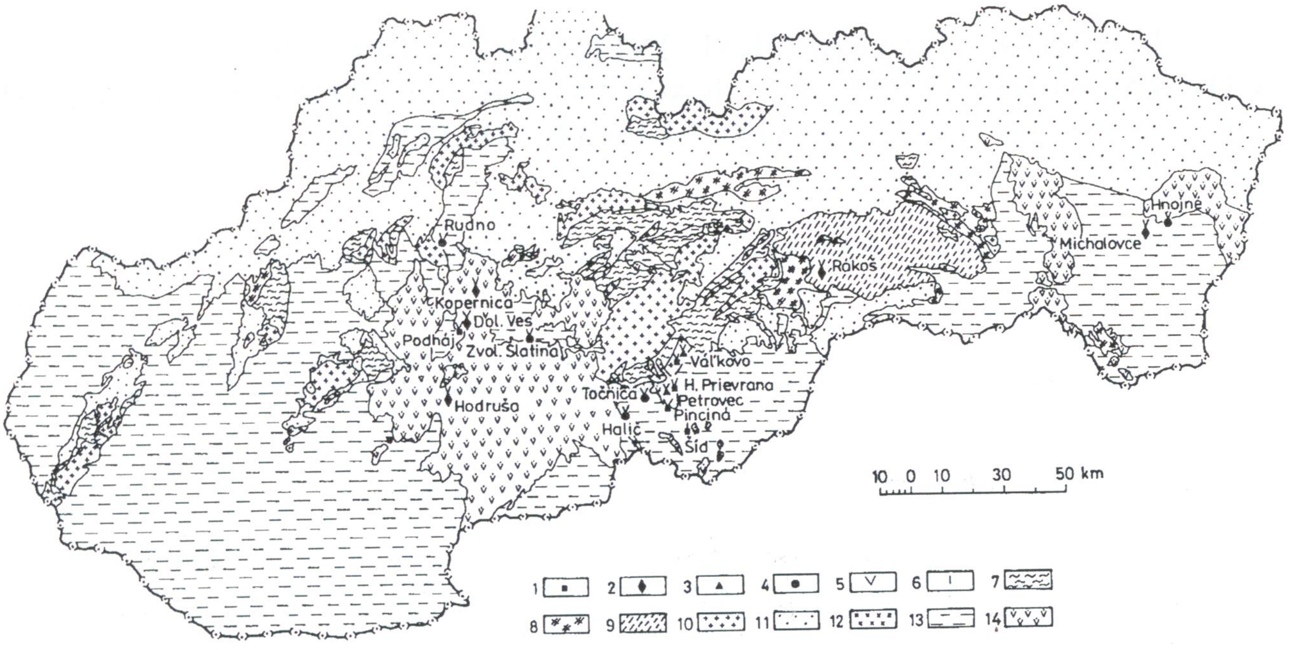

Fig. 1. Localization of kaolin group minerals from the Slovak deposits and occurrences. Genetic type: 1—weathering kaolin; 2—hydrothermal kaolin; 3—sedimentary kaolin; 4—kaolin clay. Time of origin: 5—Miocene; 6—Pliocene; 7—metamorphites of Precambrian or Paleozoic; 8—non-metamorphosed rocks of Paleozoic; 9—metamorphosed rocks of Paleozoic; 10—granitoids of Paleozoic; 11—sediments of Mesozoic and Paleogene; 12—granitoids of Mesozoic; 13—sediments of Neogene; 14—neovolcanites.

in the OH stretching region (Parker 1969; Brindley et al. 1986; Prost et al.1989). Three absorption bands assigned to stretching vibrations of inner surface hydroxyl groups at 3697, 3669 and 3652 cm^{-1} and a band at 3620 cm^{-1} attributed to the vibrations of inner hydroxyl groups are observed in the spectra of well-crystallized kaolinites (Farmer 1974). The intensity of the bands at 3669 and 3652 cm^{-1} is much weaker than those at 3697 and 3620 cm^{-1}. Samples from different deposits show considerable variation in the relative intensities of these bands, which appear to be affected by the degree of structural disorder. In a disordered Pugu kaolinite the decrease of the intensity at 3701 cm^{-1} and the development of only one single band at 3652 cm^{-1} was observed. The IR pattern given by most halloysites have often no distinct features between 3697 and 3620 cm^{-1} (Farmer 1974).

X-ray diffraction was the main technique used for characterization of degree of ordering of Slovak kaolinites (Kraus 1989; Kraus & Horváth 1978; Novotná et al. 1993). Infrared (IR) spectroscopy provides valuable information in the clay research and has been extensively applied also in investigation of Slovak bentonites (Čičel et al. 1992; Madejová et al. 1992, 1995; Šucha et al. 1990, 1994). The purpose of this study was to investigate Slovak kaolinites and halloysites of different origin by FTIR spectroscopy and to show the possibility of this method to determine the degree of structural disorder in their fine fractions. The results obtained by IR spectroscopy were correlated with the X-ray diffraction results.

Geological setting

The scheme for the subdivision of deposits and occurrences of kaolin in Slovakia is setting out from a genetic classification (Fig. 1). The most significant deposits of weathering origin were found in the Lučenská kotlina Depression. A kaolin deposit of economic importance is located in Horná Prievrana near Poltár, where kaolin of the best technological properties was formed by weathering of metarhyolites (sample HP1) and various phyllites (sample HP2). Imperfectly ordered kaolinites were formed by weathering on granitoids (VA1) and phyllites (VA2) at the locality Váľkovo or by weathering of the neovolcanic rocks in the deposits Pinciná (PI, Lučenská kotlina Depression) and Šíd (SI, Cerová vrchovina Upland.).

The kaolin deposits of hydrothermal origin are located in the central Slovakia at the locality Kopernica (KO), Hodruša (HO) and Dolná Ves (DV), while the hydrothermal deposit Rákoš (RK) is situated in the SW part of Spišsko-Gemerské Rudohorie Mts. The alteration of rhyolite led to the formation of well-ordered kaolinite at the deposit Kopernica and Dolná Ves. Kaolinites occur as cavity filling of the veins at the deposit Rákoš and Hodruša.

Table 1: Locality, mineral composition and genesis of the samples studied.

Deposit	Main mineral	Admixture	Origin
Király–Hegy (KH)	kaolinite	Q	hydrothermal
Horní Bříza (HB)	kaolinite	–	weathered
Sedlec (SE)	kaolinite	Q, I	weathered
Georgia (KGa–2)	kaolinite	–	sedimentary
Horná Prievrana (HP1)	kaolinite	Q, I	weathered
Horná Prievrana (HP2)	kaolinite	I	weathered
Váľkovo (VA1)	kaolinite	–	weathered
Váľkovo (VA2)	kaolinite	–	weathered
Pinciná (PI)	kaolinite	–	weathered
Šíd (SI)	kaolinite	–	weathered
Podháj (PO)	kaolinite	–	weathered
Kopernica (KO)	kaolinite	–	hydrothermal
Hodruša (HO)	kaolinite	–	hydrothermal
Dolná Ves (DV)	kaolinite	–	hydrothermal
Rákoš (RK)	kaolinite	–	hydrothermal
Rudno (RU)	kaolinite	–	sedimentary
Vyšný Petrovec (VP)	kaolinite	–	sedimentary
Točnica Podrečany (TP)	kaolinite	–	kaolin clays
Breznička (BE)	kaolinite	I	kaolin clays
Váľkovo (VA3)	kaolinite	–	kaolin clays
Halič–Kopáň (HK)	kaolinite	–	kaolin clays
Hnojné (HN1)	kaolinite	Sm	kaolin clays
Hnojné (HN2)	kaolinite	Cr, H	kaolin clays
Michalovce (MI)	halloysite		hydrothermal
Rákoš (RH)	halloysite	–	kaolin clays
Kalinovo–Hrabovo KA)	halloysite	–	kaolin clays
Zvolenská Slatina (ZS)	halloysite	I	kaolin clays

Q – quartz
I – illite
Sm – smectite
Cr – cristobalite
H – halloysite

Hydrothermal alteration of East Slovak neovolcanites produced the halloysite deposit Michalovce–Biela hora (MI), which represents unique occurrence of halloysite on European scale. The sedimentary kaolin deposits Rudno (RU) and Vyšný Petrovec (VP) were formed by redeposition of the primary kaolins originated by weathering on granitoids and phyllites, respectively.

In the Poltár Sequence of the Lučenská kotlina Depression kaolin clays with poorly ordered kaolinite as dominant mineral are located in Točnica–Podrečany (TP), Breznička (BE) and Váľkovo (VA3). Halloysite was found in the complex of kaolin sands at the locality Kalinovo–Hrabovo (KA) and halloysite formed on andesites is present at the locality Zvolenská Slatina (ZS). The kaolin clay group includes also halloysite from the oxidation zone of the hydrothermal mercury deposit Rákoš (RH). In the East Slovak kaolin clays (locality Hnojné –HN1, HN2) cristobalite and an insignificant admixture of halloysite were identified in addition to the predominating highly disordered kaolinite.

Materials and methods

Kaolinites and halloysites from the main Slovak deposits were investigated. Four well-known kaolinites, representing different origin (Horní Bříza and Sedlec, Bohemia — weathered, Király–Hegy, Hungary — hydrothermal and Georgia, USA — sedimentary) have been selected as reference samples containing kaolinites with different degree of ordering. The coarse samples were ground to pass a 0.2 mm sieve. The fine fractions (less than 2 μm) were separated by centrifugation after disaggregation in distilled water. Table 1 lists the locality, mineral composition and genesis of the samples studied.

The spectra were recorded on FTIR spectrometer Nicolet Magna 750 equipped with a DTGS detector. For each sample 256 scans were recorded in the 4000–400 cm^{-1} spectral range with a resolution of 4 cm^{-1}. The FTIR spectra were obtained in absorbance mode on pellets containing 1 mg (for OH stretching) or 0.5 mg (for 1200 – 400 cm^{-1} region) sample in 200 mg KBr.

Two approaches were used to determine the degree of structural disorder of kaolinites from the FTIR spectra:

1. **Empirical (IR–E)** — based on the resolution and relative intensities of the bands in the OH stretching and bending regions. The samples were classified as:
   - — ordered (or well-ordered) if the OH stretching and bending bands were clearly resolved;
   - — partially ordered — if the individual bands at 3670, 3650 and 938 cm^{-1} could be identified but their intensities were low; and
   - — poorly ordered (or disordered) — if only one band near 3660 cm^{-1} or inflexions near 3670, 3650 and 938 cm^{-1} were observed in the spectra.

   The presence of only two bands near 3700 and 3620 cm^{-1} indicated highly disordered structure or halloysite.
2. **Numerical (IR–N)** — based on crystallinity indices CI_1 and CI_2 calculated from the intensities of selected vibration modes (Brindley et al. 1986; Al-Khalissi & Worrall 1982; Plastinina et al. 1979). Two crystallinity indices (CI) were used to determine the degree of disorder:

$$CI_1 = \frac{I_{(\nu_1)}}{I_{(\nu_3)}} \qquad CI_2 = \frac{I_{(\nu_4)}}{I_{(\nu_1)}}$$

where $I(\nu_1)$ and $I(\nu_4)$ are the intensities of the OH stretching bands at 3690 cm^{-1} and 3620 cm^{-1} and $I(\nu_3)$ is the intensity of the OH bending band at 915 cm^{-1}. The base-line method was used to obtain the intensities 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 ($CI_1 > 0.8$, $CI_2 < 0.9$).

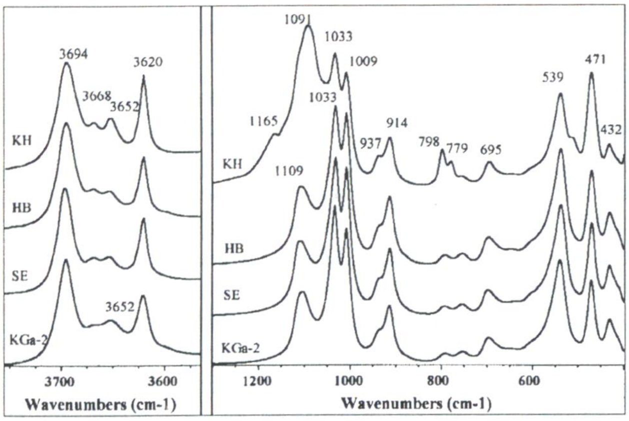

Fig. 2. IR spectra of Király-Hegy (KH), Horní Bříza (HB), Sedlec (SE) and Georgia (KGa-2) kaolinites.

The IR results were compared with the crystallinity indices calculated from the X-ray diffraction patterns of randomly oriented samples using the methods of Stoch (1974) for the kaolinites with high degree of ordering and of Hughes & Brown (1979) for the poorly ordered kaolinites and halloysites.

Results and discussion

The IR spectra of kaolin group minerals are shown in Figs. 2–9. The classification of kaolinites based on visual estimation of degree of crystallinity from the IR spectra (IR–E), calculated IR crystallinity indices CI_1 and CI_2 (IR–N) and XRD crystallinity indices CI–S (according to Stoch 1974) and CI – H&B (according to Hughes & Brown 1979) are given in Table 2.

Reference kaolinites

Four absorption bands at about 3695, 3670, 3650 and 3620 cm^{-1} were observed in the OH stretching region of kaolinites from Király–Hegy (KH), Horní Bříza (HB) and Sedlec (SE) (Fig. 2). Four clearly resolved bands reflect high structural ordering of the samples originated by weathering and hydrothermal activity. The crystallinity of kaolinites can be readily distinguished by differences in the relative intensities of the bands at 3670 and 3655 cm^{-1} (Russell & Fraser 1994). The higher intensity of the band at 3652 cm^{-1} observed for KH compared to HB and SE reflects the higher ordering of this kaolinite. The KH is classified as well-ordered, SE and HB as ordered kaolinites, respectively. The IR spectrum of a sedimentary kaolinite from Georgia (KGa–2) shows the replacement of the middle two bands by a single broad band at 3652 cm^{-1} with a shoulder near 3670 cm^{-1} indicating only partially ordered or disordered structure of this sample (Fig. 2).

Spectra of all reference kaolinites show a strong resemblance, particularly over the 1200–400 cm^{-1} region. The Si–O stretching vibrations give three strong bands in the 1100–1000 cm^{-1} range for HB, SE and KGa–2 kaolinites. The Si–O stretching band of KH displays a significant enhancement of absorption in the 1200–1100 cm^{-1} region which, together with doublet at 798 and 780 cm^{-1} and a shoulder near 512 cm^{-1} indicates the presence of relatively high content of quartz in the sample. The in–plane bending vibrations of inner hydroxyl groups absorb at 913 cm^{-1} and that of inner surface OH groups near 935 cm^{-1} (Fig. 2). The IR spectrum of KH kaolinite shows clearly resolved band at 938 cm^{-1} while the spectra of HB, SE and KGa–2 kaolinites show only shoulders in this region. This difference thus illustrates a higher degree of order of the KH kaolinite. Si–O bending vibrations contribute to the strong absorption in the region below 800 cm^{-1} (Farmer 1974). Absorption bands near 755 and 696 cm^{-1} probably involve vibrations of surface hydroxyl layer coupled with other lattice vibrations, the bands at 539 cm^{-1} and 470 cm^{-1} are assigned to the Al–O–Si and Si–O–Si bending vibrations, respectively.

The IR and XRD results are compared for reference kaolinites in Table 2. All methods indicate ordered structure for HB and SE, however discrepancy was found for KH. The IR–E and CI–S for KH reflect well-ordered kaolinite, while the IR–N and CI–H&B suggest "only" ordered structure. KH kaolin contains quartz, the presence of which affect the calculation of latter mentioned indices. Kaolinite with only partially ordered structure was confirmed for KGa–2 based on the IR–E and XRD results in contrary to the IR–N indices, which indicate ordered structure. The above mentioned discrepancies in the determination of the degree of disorder for KH and KGa–2 demonstrate the importance of the selection of the suitable method for classification of kaolinites.

Kaolins of weathering origin

The IR spectra of samples from Horná Prievrana near Poltár (HP1, HP2) are similar and confirm that the dominant mineral is kaolinite (Fig. 3). The OH stretching re-

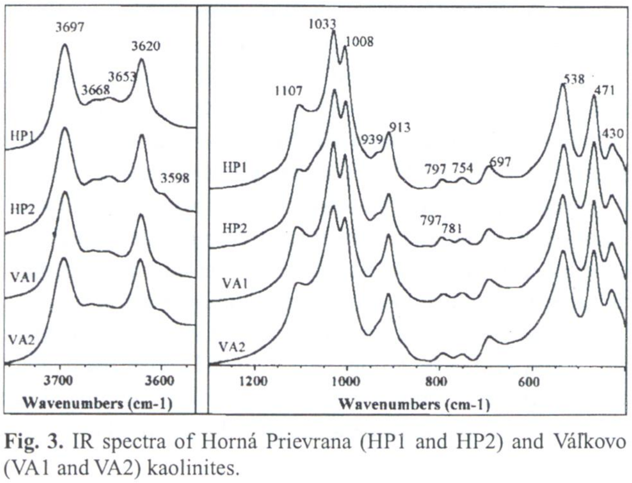

Fig. 3. IR spectra of Horná Prievrana (HP1 and HP2) and Váľkovo (VA1 and VA2) kaolinites.

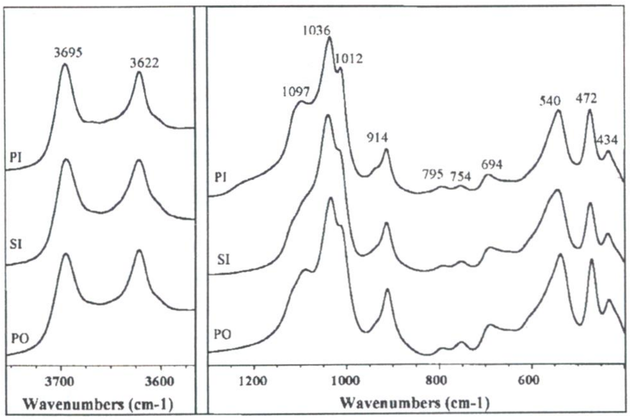

Fig. 4. IR spectra of Pinciná (PI), Šíd (SI) and Podháj (PO) kaolinites.

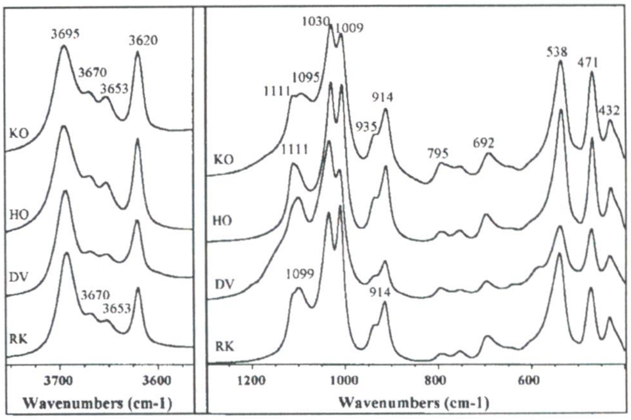

Fig. 5. IR spectra of Kopernica (KO), Hodruša (HO), Dolná Ves (DV) and Rákoš (RK) kaolinites.

gion shows two strong bands at about 3700 and 3620 cm^{-1} while the bands near 3670 and 3650 cm^{-1} are not clearly resolved, indicating partial ordered structure for HP1 and HP2. Small shoulders near 3598 and 875 cm^{-1} in sample HP2 are supposed to be due to AlFeOH vibrations of structural Fe^{3+} present in the octahedra (Petit & Decarreau 1990). However, the presence of other clay admixture (e.g. smectite) with AlFeOH groups, absorbing in the same ranges, cannot be excluded. The Si–O stretching band (1100–1000 cm^{-1}) of HP2 compared to HP1 is broader with less resolved bands. This feature and the doublet at 797 and 781 cm^{-1} indicates the presence of quartz in the sample.

The IR spectra of kaolins present in the locality Váľkovo (VA1, VA2) are shown in the Fig. 3. The low intensity OH stretching bands at 3668 and 3655 cm^{-1} reflect poorly ordered structure. Both spectra show a small shoulder near 3600 cm^{-1} due to structural Fe^{3+}.

Weathering kaolins from the deposits Pinciná (PI, Lučenská kotlina Depression) and Šíd (SI, Cerová vrchovina Upland) have spectra with only two bands in the OH stretching region (near 3695 and 3620 cm^{-1}) and with poorly resolved bands related to Si–O stretching vibrations (Fig. 4). The IR spectroscopy can only hardly distinguish between kaolinite of highly disordered structure and halloysite, as the IR spectra of both show usually only two OH stretching bands. Because no halloysite was found in these deposits (Kraus 1989), the IR spectra are supposed to reflect highly disordered kaolinite.

The origin of kaolin in the deposit Podháj (PO) is not unambiguous as both hydrothermal and weathering origin were reported for this locality (Kraus 1989). The IR spectrum of PO with only two bands at 3695 and 3622 cm^{-1} and a broad Si–O stretching band with less detailed structure (Fig. 4) resembles those of Pinciná and Šíd. It seems likely that highly disordered kaolinite is present in Podháj and that weathering origin dominate in this deposit.

The IR–E classification of the crystallinity show only partial correlation with other two methods for weathering kaolinites (Table 2). The XRD indices indicate low crystallinity of these kaolinites while IR spectra revealed partially ordered structure for HP1, HP2 and poorly ordered structure for the other weathered kaolinites. The IR–N indicates partially ordered structure for HP1 and HP2 and poorly ordered structure for VA2, which is in accordance with the IR–E. However, ordered structure for VA1 and partially ordered for PI, SI and PO is in discrepancy not only with the IR–E but also with the XRD indices. The problem of different results obtained using three different methods for estimation of the degree of disorder is supposed to be connected with the different sensitivity of these methods to detect the admixtures (illite or halloysite) present in the kaolin samples.

Kaolins of hydrothermal origin

Four absorption bands occurring in the OH stretching region of the spectra of Kopernica (KO), Hodruša (HO), Dolná Ves (DV) and Rákoš (RK) kaolinites confirm clearly their ordered structure (Fig. 5). Moreover, not only the absorption at 913 cm^{-1} due to bending vibrations of inner hydroxyl groups but also the absorption at 936 cm^{-1} assigned to inner surface OH is seen in their spectra and confirm the ordered structure of the samples. The relative intensities of the bands at 3670, 3653 and 936 cm^{-1} for KO, HO and RK are only slightly lower as compared to the reference kaolinite Király–Hegy and indicate a kaolinite of a well-ordered structure. The OH bands for DV resemble the IR bands of reference kaolinite Horní Bříza and Sedlec and reflect an ordered structure. The IR–E results are in very good correlation with both IR and XRD crystallinity indices (Table 2). All methods show ordered structures for the kaolinites of hydrothermal origin.

The IR spectrum of the halloysite from the deposit Michalovce–Biela hora (MI) shows two absorption bands at 3695 and 3622 cm^{-1} in the OH stretching region (Fig. 6). A broad complex pattern of Si–O stretching absorptions with less resolved bands appears between 1100–1000 cm^{-1}.

Table 2: Classification of the degree of crystallinity of the samples based on different methods.

Deposit	**IR – E**	**IR – N**			**XRD**		
	Class.	**CI1**	**CI2**	**Class.**	**CI–S**	**CI–H&B**	**Class.**
Király–Hegy (KH)	w–o	0.886	0.888	o	0.69	36.0	w–o
Horní Bříza (HB)	o	1.091	0.685	o	0.87	48.9	o
Sedlec (SE)	o	1.020	0.721	o	0.98	37.1	o
Georgia (KGa–2)	pa–o	1.033	0.661	o	1.15	20.4	pa–o
Horná Prievrana (HP1)	pa–o	0.789	0.867	pa–o		11.5	p–o
Horná Prievrana (HP2)	pa–o	0.696	0.938	pa–o		10.5	p–o
Váľkovo (VA1)	p–o	0.863	0.802	o		11.4	p–o
Váľkovo (VA2)	p–o	0.685	0.994	p–o		11.2	p–o
Pinciná (PI)	p–o	0.828	0.924	pa–o		8.4	p–o
Šíd (SI)	p–o	0.874	0.992	pa–o		8.1	p–o
Podháj (PO)	p–o	0.732	1.035	pa–o		15.4	p–o
Kopernica (KO)	w–o	0.770	0.651	o	0.89		o
Hodruša (HO)	w–o	0.875	0.704	o	0.61	57.9	w–o
Dolná Ves (DV)	o	0.897	0.755	o	0.97	25.6	o
Rákoš (RK)	w–o	1.029	0.743	o	0.54	54.2	w–o
Rudno (RU)	w–o	1.021	0.706	o	0.70	38.6	w–o
Vyšný Petrovec (VP)	o	0.893	0.779	o	0.85	32.3	o
Točnica Podrečany (TP)	p–o	0.860	0.889	o		10.9	p–o
Breznička (BE)	p–o	0.646	1.074	p–o		10.7	p–o
Váľkovo (VA3)	p–o	0.765	0.928	pa–o		10.1	p–o
Halič–Kopáň (HK)	pa–o	0.776	0.938	pa–o		11.1	p–o
Hnojné (HN1)	p–o	0.858	0.892	pa–o		7.3	p–o
Hnojné (HN2)	p–o	0.749	0.970	pa–o		7.2	p–o
Michalovce (MI)	h	0.938	0.796	o		8.8	p–o
Rákoš (RH)	h	0.785	0.984	pa–o		8.5	p–o
Kalinovo–Hrabovo(KA)	h	0.830	0.926	pa–o		8.5	p–o
Zvolenska Slatina (ZS)	h	0.630	1.292	p–o		~5.5	p–o

IR–E — Empirical method based on IR spectra
IR–N — Numerical method based on IR crystallinity indices CI_1 and CI_2
CI–S, CI–H&B — XRD crystallinity indices by Stoch (1974) and Hughes & Brown (1979)
w–o — well ordered, o — ordered, pa–o — partially ordered, p–o — poorly ordered, h — halloysite

The OH bending band is present at 913 cm^{-1} with only a small inflexion near 936 cm^{-1}. The spectral features of sample Michalovce are in accordance with the presence of halloysite in this deposit.

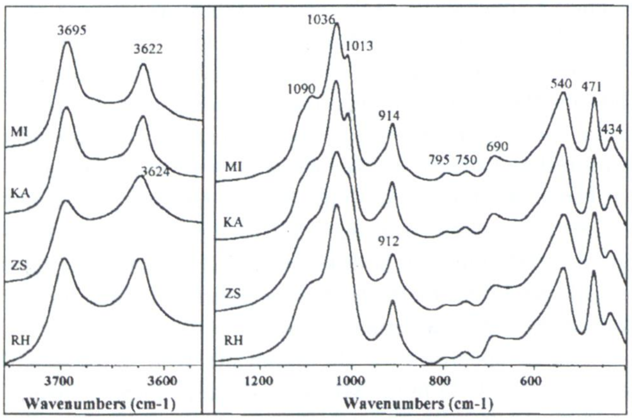

Fig. 6. IR spectra of Michalovce (MI), Kalinovo-Hrabovo (KA), Zvolenská Slatina (ZS) and Rákoš (RH) halloysites.

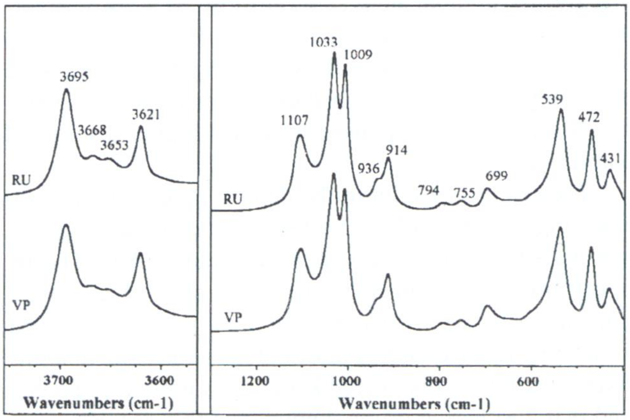

Fig. 7. IR spectra of Rudno (RU) and Vyšný Petrovec (VP) kaolinites.

Kaolins of sedimentary origin

Well crystallised kaolinites were found at deposit Rudno (RU) in the Turčianska kotlina Depression and Vyšný

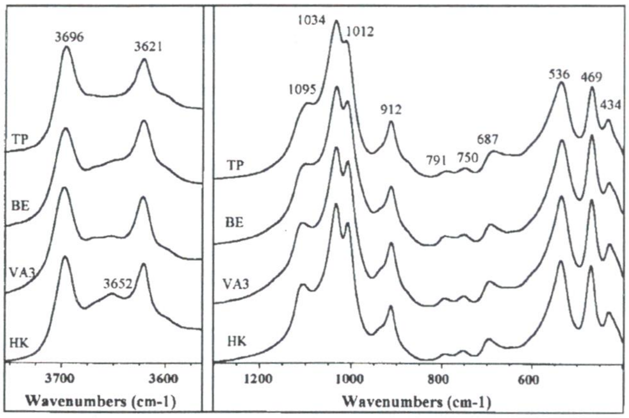

Fig. 8. IR spectra ofTočnica-Podrečany (TP), Breznička (BE), Váľkovo (VA3) and Halič-Kopáň (HK) kaolin clays.

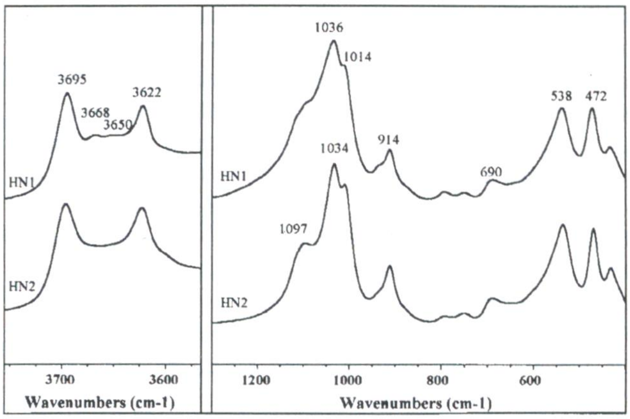

Fig. 9. IR spectra of Hnojné (HN1 and HN2) kaolin clays.

Petrovec (VP) in the Lučenská kotlina Depression. The IR spectrum of RU reflects kaolinite of well-ordered structure (Fig. 7). The intensities of the OH stretching bands at 3669 and 3652 cm^{-1} are relatively high and the bending absorption of the inner surface OH groups at 936 cm^{-1} can be easily distinguished from the band of inner OH groups at 914 cm^{-1}. The IR spectrum of VP shows a strong resemblance to RU over the whole 4000–400 cm^{-1} region. Only slightly lower intensities of 3669 and 3653 cm^{-1} bands compared to RU indicate that this kaolinite can be classified as ordered.

The IR results (both IR–E and IR–N) show close correlation with both XRD indices (Table 2). The index of Stoch for RU (0.70) reflects a well-ordered kaolinite and that of VP (0.85) an ordered kaolinite.

Kaolin clays

The IR spectra of the samples from the kaolin clay deposits Točnica–Podrečany (TP), Breznička (BE), Váľkovo (VA3) and Halič–Kopáň (HK), located in the Lučenská kotlina Depression, are shown in Fig. 8. The positions of the most intensive OH bands (near 3696 and 3620 cm^{-1}) are almost the same for the samples from these localities, however, some differences in the absorptions were observed for these two bands. Only two absorption bands at 3696 and 3621 cm^{-1} and low resolution of the absorption near 930 cm^{-1} indicate that highly disordered kaolinite may be present in TP and BE. The higher intensity of the band at 3621 cm^{-1} compared to 3695 cm^{-1} indicates the presence of illite admixture in the sample BE. A broad band near 3650 cm^{-1} instead of two bands in the spectra of VA and HK reflects kaolinites of a poorly ordered or disordered structure.

Halloysite was found by TEM in the samples from Kalinovo–Hrabovo (KA), Zvolenská Slatina (ZS) and Rákoš (RH). The IR spectra with only two OH stretching bands confirm halloysite to be present in KA, ZS and RH (Fig. 6). For RH and ZS samples the higher intensity of the band at 3621 cm^{-1} compared to 3695 cm^{-1} and the broad Si–O stretching band indicate illite admixture.

A kaolinite with different admixtures was found in the East Slovak kaolin clays of Hnojné (Fig. 9). Four bands in the OH stretching region at the expected values (3695, 3668, 3650 and 3622 cm^{-1}) and a resolved absorption due to the OH bending vibrations of inner surface groups near 936 cm^{-1} suggest partially ordered kaolinite in HN1. The OH stretching region indicates smectite admixture, while a broad Si–O band with a less developed shoulder near 1100 cm^{-1} are in accordance with the presence of silica admixture in the HN1 sample. Only two OH stretching bands at 3696 and 3623 cm^{-1} present in the IR spectrum of sample HN2 indicate highly disordered kaolinite as the dominant mineral in this sample. Since the IR spectroscopy is not able to distinguish highly disordered kaolinite and mixture of poorly (or partially) disordered kaolinite and halloysite, this alternative should be also taken into consideration for HN2.

The IR spectra (IR–E) demonstrate that poorly ordered kaolinite and halloysite are the dominant minerals in the kaolin clays (Table 2). The Hughes and Brown indices ranges from 10.9 for TP to 5.5 for ZS, thus confirming that the kaolins in this group generally may be described as poorly ordered (or disordered) type. The classification of kaolin clays based on the IR indices differs slightly from the above mentioned methods (Table 2). In most samples IR indices suggest partially ordered structure.

Conclusions

Different genetic groups of Slovak kaolinites and halloysites have been analysed based on their FTIR spectra. The OH bands were sensitive enough to distinguish well-ordered, partially ordered and poorly ordered kaolinites, but failed to find the differences in the degree of crystallinity of halloysites. The highest degree of ordering was found for hydrothermal and sedimentary kaolins, poorly ordered kaolinite and halloysite belong to the group of weathered kaolins or to the kaolin clays.

The degree of crystallinity, determined by IR–E method was compared with the IR–N and XRD crystallinity indices. The method based on the IR indices (IR–N) provided basic classification into three groups — ordered, partially ordered and poorly ordered clays. A more detailed classification can be based on the total features of the IR spectra (IR–E). No principal discrepancies between the IR–N and IR–E methods were found. A reasonable agreement was found for the classification of kaolinite minerals based on IR and XRD methods. Certain differences arose for the samples on the border of the individual categories and for less ordered samples. The presence of clay admixture (e.g. illite or smectite) strongly influences the IR pattern in the OH stretching region. The OH bands are overlapped and thus may lead to incorrect degree of crystallinity.

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