IDENTIFICATION OF CLAY MINERALS AND MICAS IN SEDIMENTARY ROCKS

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ABSTRACT
Real possibilities of FTIR-spectroscopy application along with thermal analysis (TG/DTA) for examining clay minerals in rocks are presented. These methods were used for determination of mineral composition in sedimentary rock samples from the shaft No.4 Frenštát -West, Northern Moravia, CZ.
Previously, the samples representing the basic clay mineral specimen were investigated by means of the following methods. In order to provide an adequate characterization of these samples, X-ray diffraction and X-ray fluorescence spectroscopy were utilized. As the individual clay minerals often occur in a form of mixed-layer clay minerals with various ratios of individual components, IR spectra and TG/DTA curves of mixtures (either natural or synthetic) were recorded, too.
Clay minerals represented mainly by fine-crystalline illite (muscovite) with traces of kaolinite were predominant. Besides, carbonates (calcite, ankerite) and silica minerals occured in these samples, too. A presence of pyrites and coal matter was confirmed only by thermal analysis. Traces of feldspars were detected by means of FTIR spectroscopy in some rock samples.

KEYWORDS: clay mineral, mixed-layer clay minerals, FTIR-spectroscopy, thermal analysis (TG/DTA)

1. INTRODUCTION

The nature and the content of clay minerals (i.e. kaolinites, illites, montmorillonites and chlorites) and micas (i.e., muscovites, glauconites) have a significant influence on behaviour and properties of rocks as well as the whole rock massif. The exact identification of clay minerals (micas) in real rock samples by means of conventional analytical methods is rather complicated. The grain size of such samples (below 0.002 mm) is one of the reasons. Another reason consists in the fact that the individual clay minerals occur in a form of mixed-layer clay structures with various ratios of the individual components. In this paper real possibilities of FTIR-spectroscopy application along with thermal analysis (TG/DTA) for examining clay minerals (micas) in sedimentary rocks are presented. FTIR-spectroscopy enables to obtain necessary information about individual minerals, noncrystalline admixtures and, simultaneously, to detect presence of organic matter. Absorption of infrared radiation by clay minerals depends critically on atomic mass, and the length, strength and force constants of inter-atomic bonds in the structures of these minerals. It is also controlled by constraints of the overall symmetry of the unit cell, and the local site symmetry of each atom within the unit cell (Russell and Fraser, 1994; Farmer, 1974). Absorption of infrared radiation is also strongly influenced by a degree of crystalline order (Lazarev, 1974) and by size and shape of the mineral particles (Farmer and Russell, 1966).

In general, the constituent units of clay minerals include hydroxyl groups, tetrahedral silicate/aluminate anions, octahedral metal cations, and interlayer cations. In IR-spectra OH-stretching modes lie in the spectral region of 3400-3750 cm^{-1}. Metal-O-H bending modes occur in the 600-950 cm^{-1} region. Si-O and Al-O stretching modes are found in the 700-1200 cm^{-1} range. Si-O and Al-O bending modes dominate the 150-600 cm^{-1}. Lattice vibrational modes in the far-IR range (33 to 333 cm^{-1}) are related to the interlayer cations (Schroeder, 2002).

Application of thermal methods for study of clay minerals and rocks has a history as long as that of thermal analysis itself. Thermal analysis is widely used in an investigation of minerals, mainly identification, quantitative analysis and water existence (Blažek, 1974).

The principal thermal reactions of clay minerals and the approximate temperature ranges in which they occur are generally considered in following categories:

- *low temperature bellow 400°C:* loss of adsorbed water and molecular water between layers

- *intermediate temperature 400 – 750 °C:* dehydroxylation and the formation of quasi-stable dehydroxylated phases

- *high temperature above 750°C:* recrystallization and formation of new phases.

   A problem of using thermal analysis is that clay minerals generally exist as mixtures, so the thermal reactions are those of mixtures. In view of these complications, it is reasonable first to consider optimum conditions for mainly monomineral phases with "well known" chemical and structure composition. Then with more information, it is simpler to consider more complex behaviour of such mixed system (Hatakeyama, 1998). The system of behaviour depends not only on the initial mineral compostion but also on the products formed at different temperatures, kinetics and reaction mechanism as well as crystal-chemical relations between the phases. The resultant TG/ DTA curves, especially peak temperatures, are also influenced not only with number and character of mixed components but also with mass and particle size of sample and heating rate (Langier-Kuzniarowa, 1993).

2.   ANALYTICAL PROCEDURE

   The basic clay mineral specimens (kaolinite, illite, montmorillonite, chlorite, micas) and the associated minerals (quartz, calcite, feldspar) were examined by FTIR-spectroscopy and thermal analysis (TG/DTA). Standards of minerals were obtained from the collection of minerals available in the Institute of Geonics. If it was possible, minerals were selected with regard to their high purity and authenticity. The important compilations of IR spectra have been published by van der Marel and Beutelspacher (1976), Moenke (1962, 1966), Ferraro (1982) and Kodama (1985).

   Thirty one real sedimentary rock samples were taken from the Silesian Unit (Těšín-Hradiště Fm., Hradiště Lower Cretaceous, Lower Barremian) from the depth 170 –230 m. The dark grey and light grey sandstones, fine up to medium grained, dominated over dark grey claystones with variable content of silt and carbonate component.

   Whole rock samples were ground in the planetary mill "Pulverissete 5" Fritsch GmbH to pass under 0.2 mm sieve. More detailed information was presented elsewhere (Martinec, 1986).

2.1. INFRARED SPECTROSCOPY

   The infrared spectra were recorded on Nicolet Avatar 320 FTIR spectrometer equipped with DTGS KBr detector. For each sample 64 scans were measured in the 4000-400 cm^{-1} spectral range in the transmission mode with a resolution of 4 cm^{-1}. The KBr pressed-disc technique was used for preparing a solid sample for routine scanning of the spectra. Samples of approximately 2 and 0.5 mg were dispersed in 200 mg of KBr to record optimal spectra

in the regions 4000-3000 and 4000-400 cm^{-1}, respectively. A diameter of the pellets, pressed from samples, was 13 mm. Discs for the 4000-3000 cm^{-1} region were heated in the furnace overnight at 150°C to minimize the water adsorbed on KBr and the clay sample, according to Madejová, Komadel (2001).

2.2. THERMAL ANALYSIS

   TG/DTA curves of rock samples and mineral standards were obtained with thermal instrument SETSYS 12, SETARAM with process conditions: heating rate 10 $K.min^{-1}$, final temperature 1150 °C, sample mass 50 ± 0.5 mg.

3.   RESULTS AND DISCUSSION
3.1. IDENTIFICATION OF CLAY MINERALS (MICAS) AND ASSOCIATED MINERALS
FTIR spectroscopy

   For illustrative purposes, infrared spectra of the most common clay minerals are given in Fig. 1- 5. The spectrum in Fig. 1 demonstrates well crystalline kaolinite. The sharp doublet at 3696 and 3620 cm^{-1} is characteristic for the kaolin group in general. The bands at 3696 cm^{-1}, and near 3620 arise from the internal surface OH groups (Balan, 2001). The OH deformation bands of kaolinite are situated at 938 and 913 cm^{-1}. Supporting bands at 794 (Si-O) and 698 cm^{-1} (Si-O) are diagnostic for kaolinite, too.

   The broad OH-stretching band near 3620 cm^{-1} coupled with the 829 cm^{-1}, 750 cm^{-1} doublet (Fig. 2) indicates illite. These bands originate from Al-Mg-OH deformation and, by analogy with muscovite (Fig. 3) (Farmer, 1974), Al-O-Si in-plane vibration. It can be difficult to identify illite, but 825, 750 cm^{-1} doublet certainly confirms its presence in most cases. The infrared spectrum of muscovite (Fig. 3) is very similar to spectrum of illite (Fig.2). Fig. 4 shows the typically broad OH-stretching band at 3624 cm^{-1}, which is an average envelope for wide range of Al-Al-OH and Al-Mg-OH environments in the highly substituted and distorted structure of montmorillonite. This band occurs close to the inner OH groups in kaolinite (Fig. 1), but can be distinguished by its much greater breadth. However, the well-resolved OH deformation bands at 915 cm^{-1} (Al-Al-OH) and 843 cm^{-1} (Al-Mg-OH) are more characteristic, their assignments were confirmed by deuteration (Russel, Farmer and Velde, 1970). The absorption near 620 cm^{-1} is characteristic for Al-rich montmorillonites. Fig. 5 demonstrates the spectrum of chlorite. The IR spectra of chlorites exhibit many alternatives. Fig. 6 - 8 show infrared spectra of the typical associated minerals present in clays (quartz, calcite and Na,K- feldspar).

Thermal analyses
   TG/DTA curves shown in Fig. 9 - 13 demonstrate the standards of the most common clay minerals with their typical reactions: kaolinite (569 °C, 988 °C), illite (89 °C, 566 °C, 966 °C),
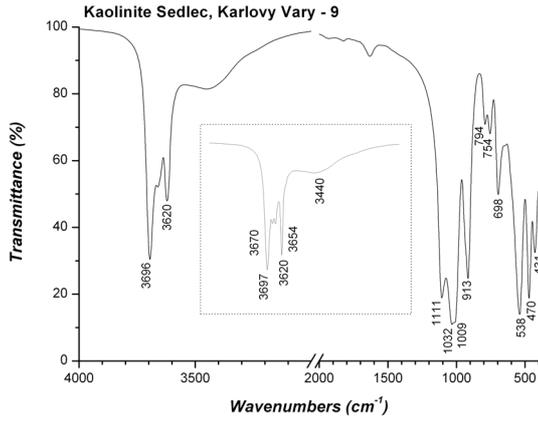
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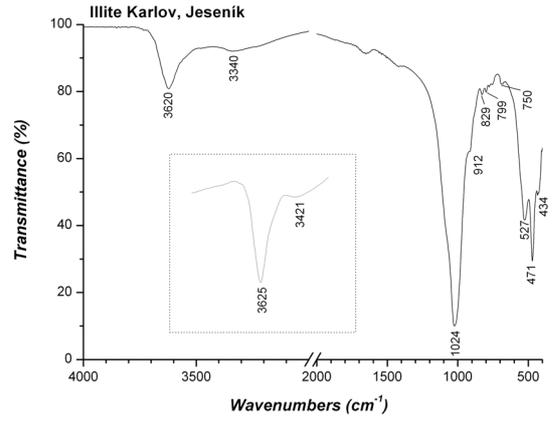
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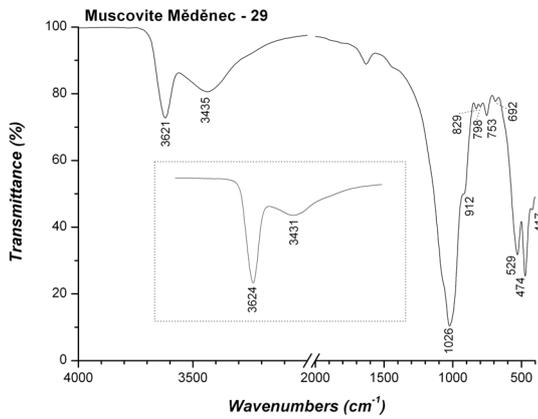
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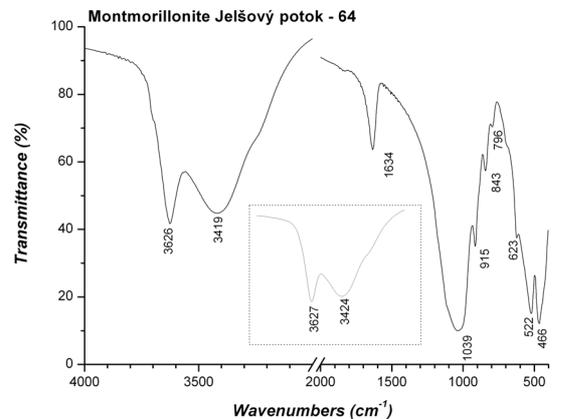
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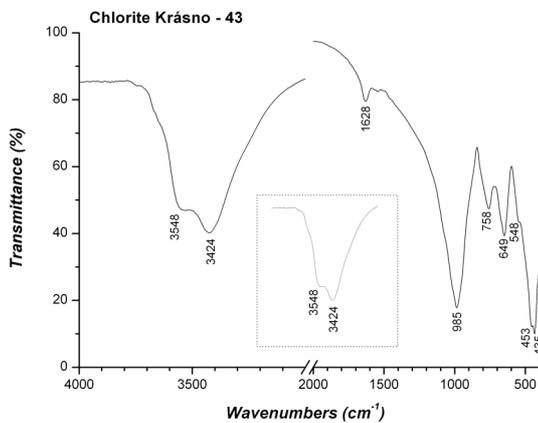
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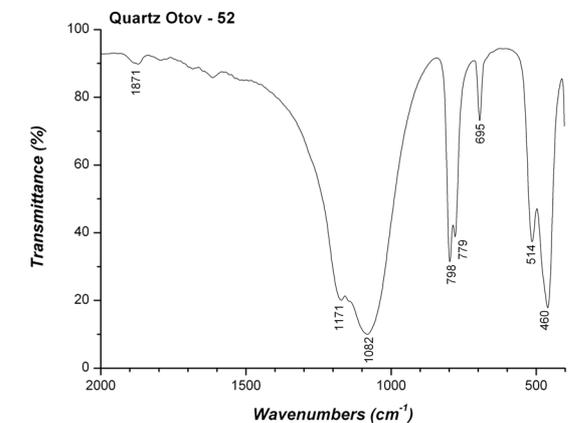
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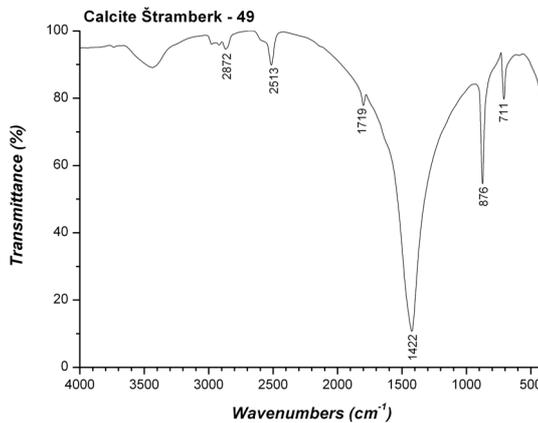
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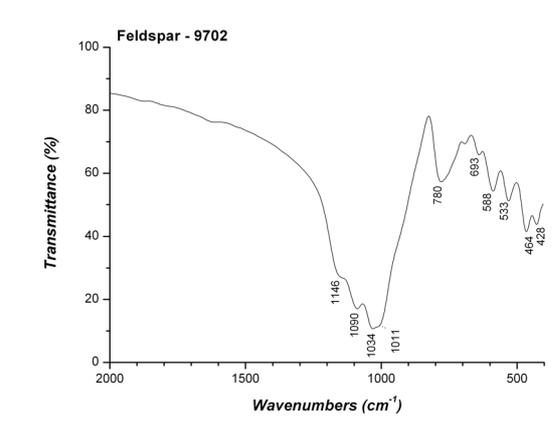
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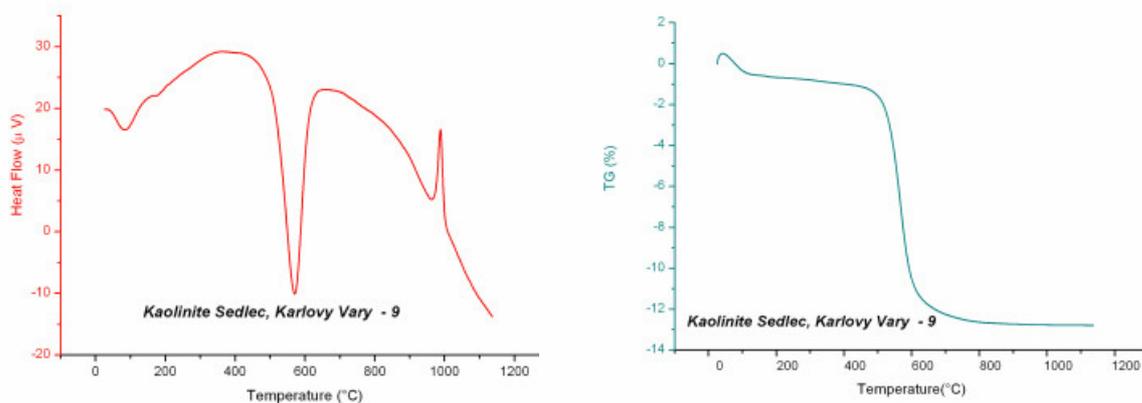
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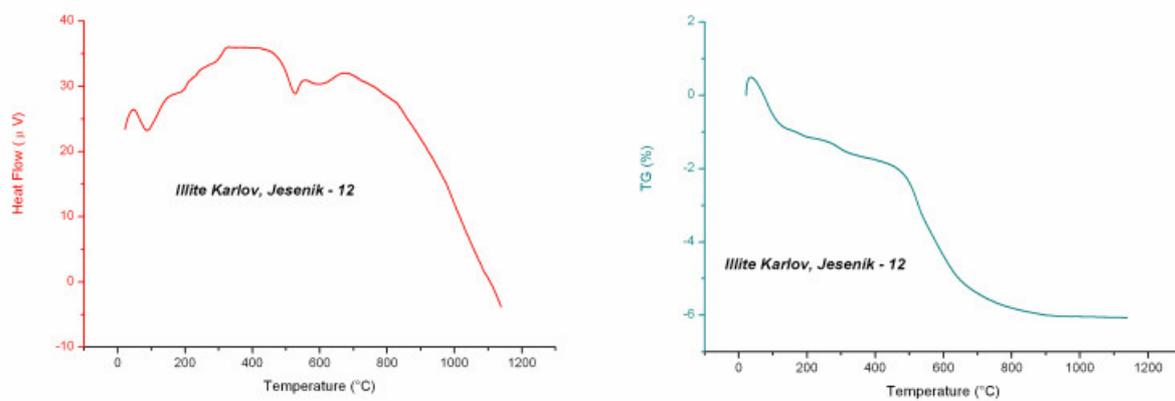
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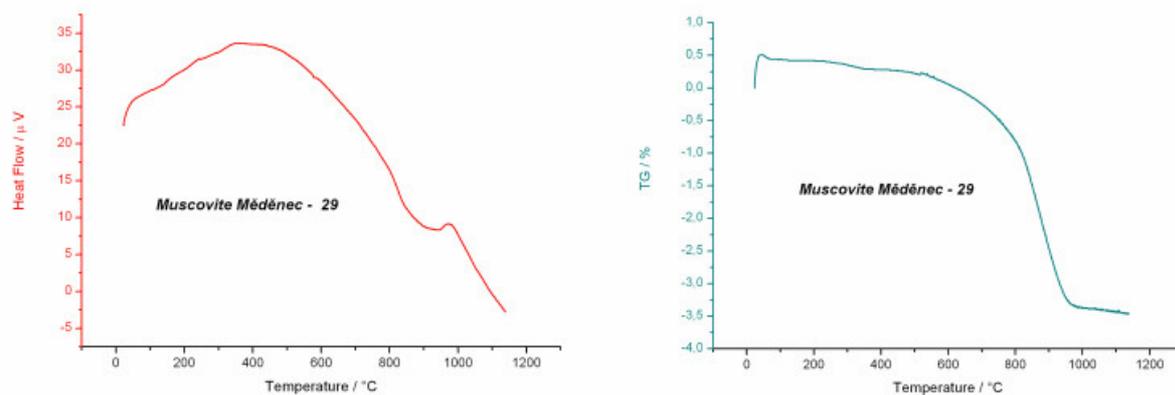
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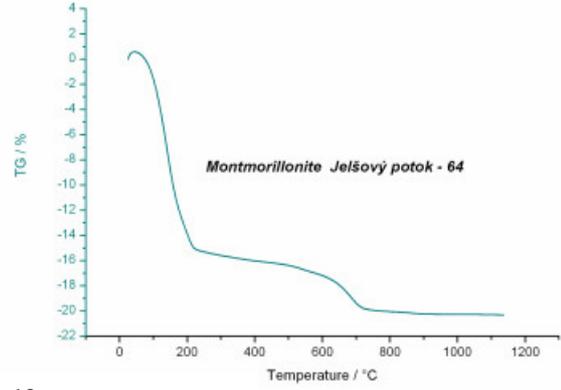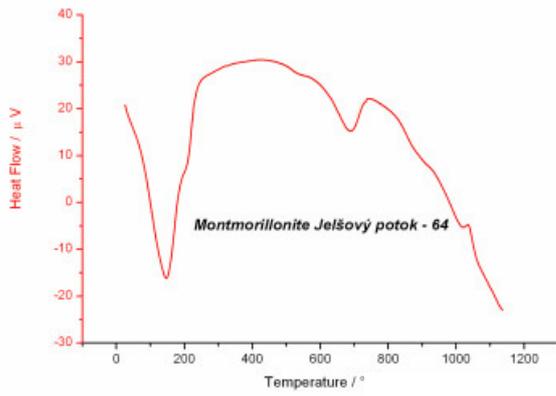
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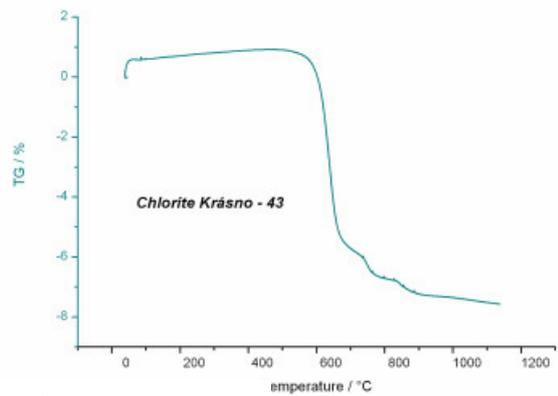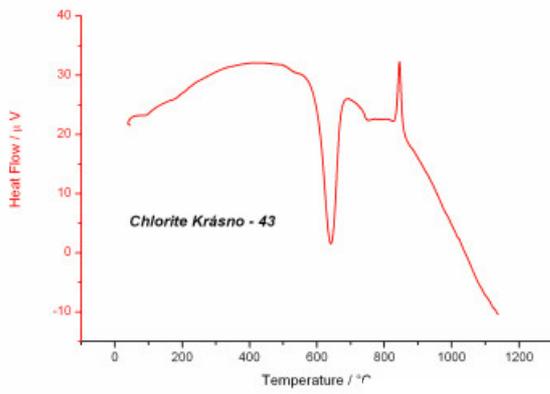
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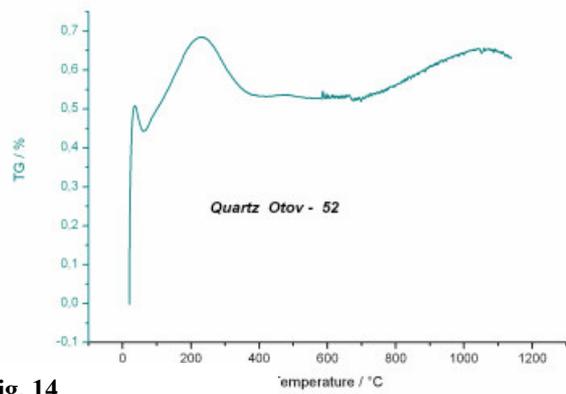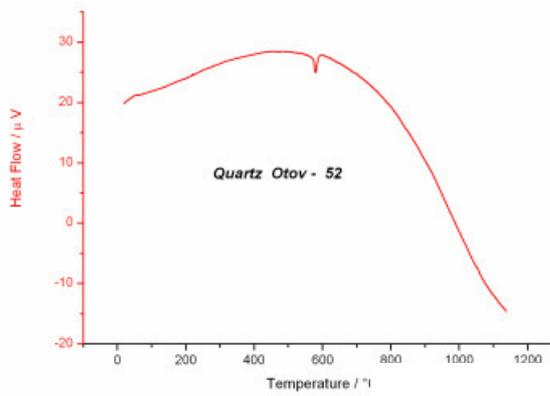
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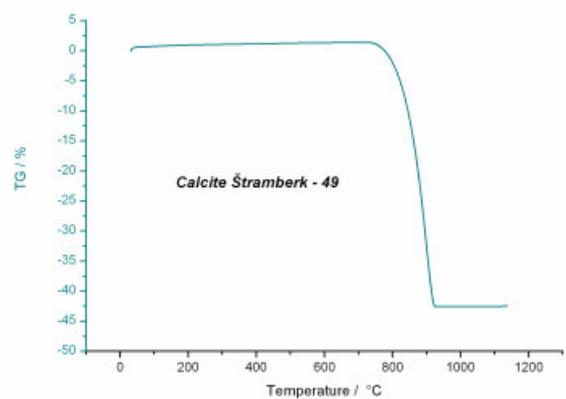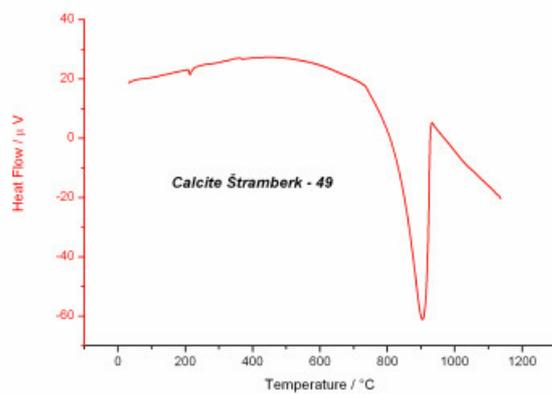
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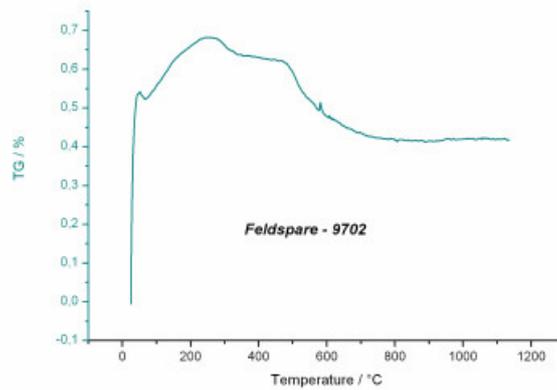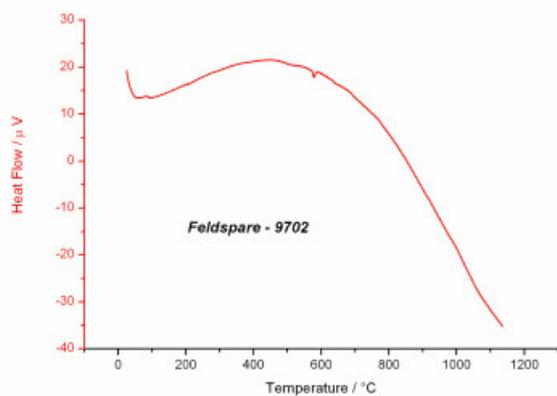
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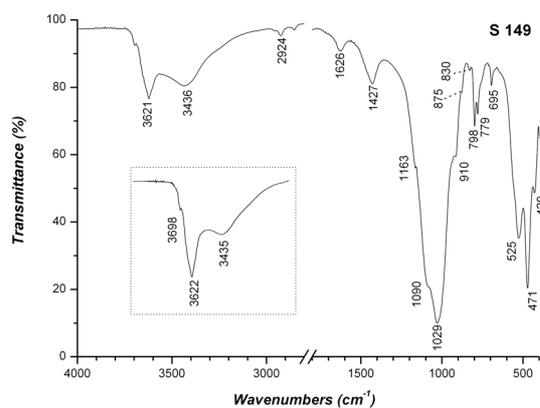
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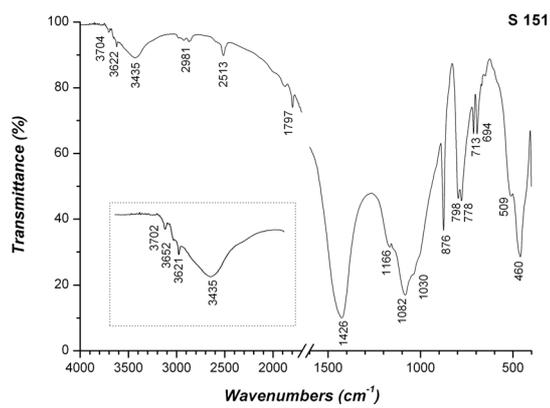
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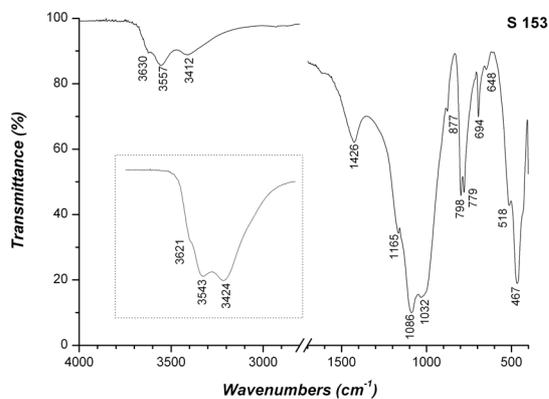
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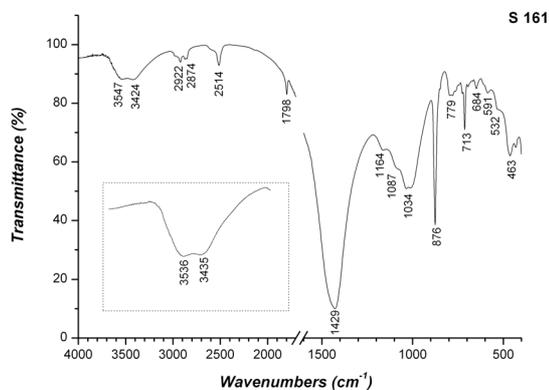
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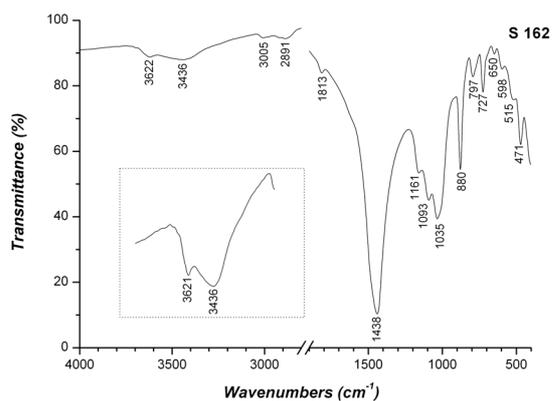
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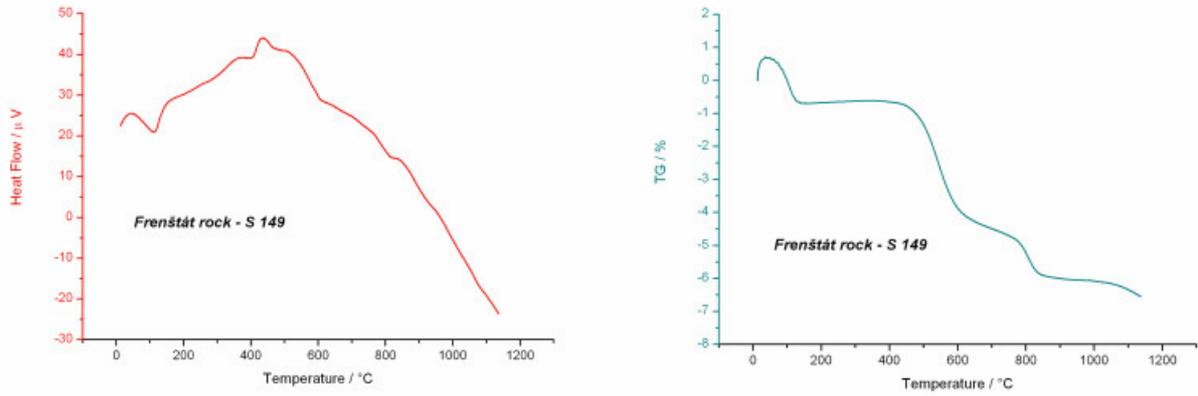
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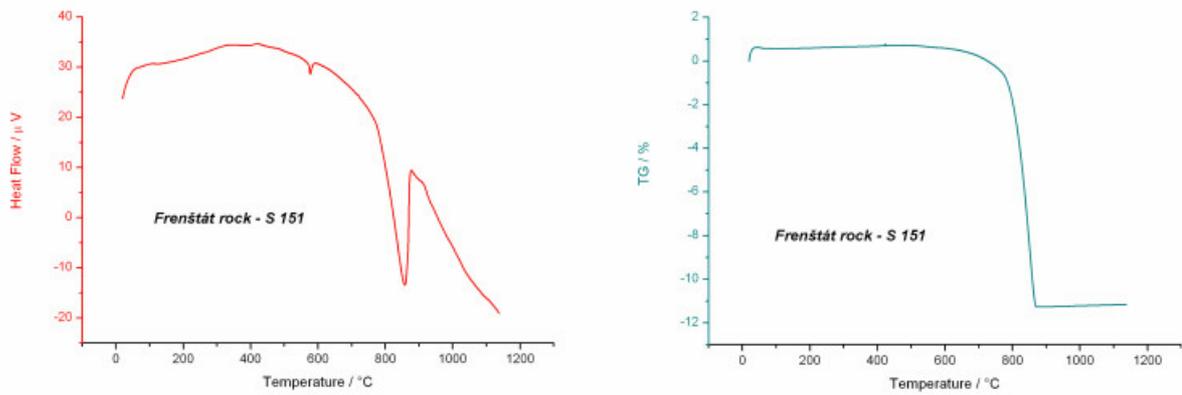


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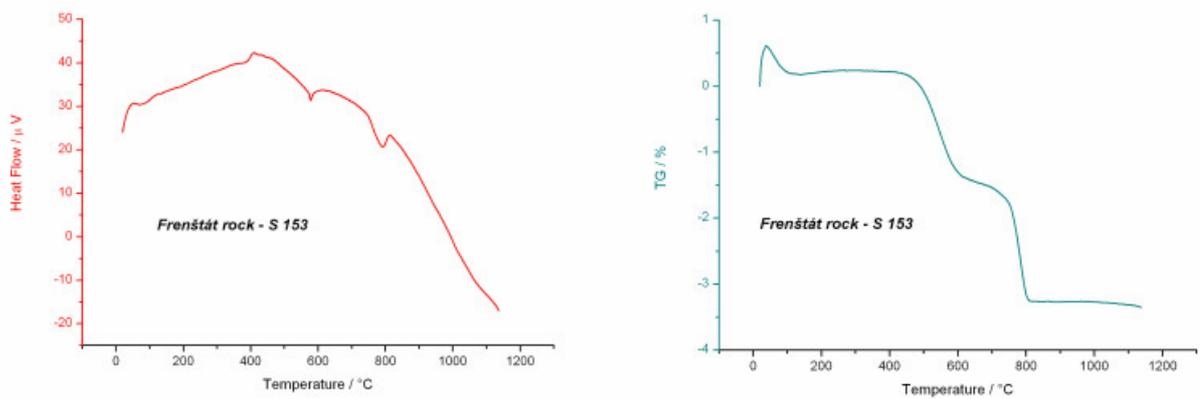
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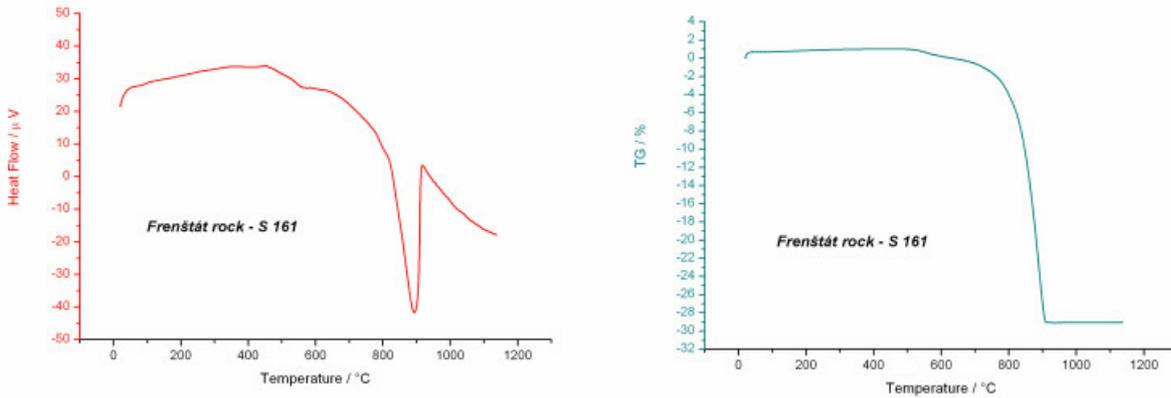
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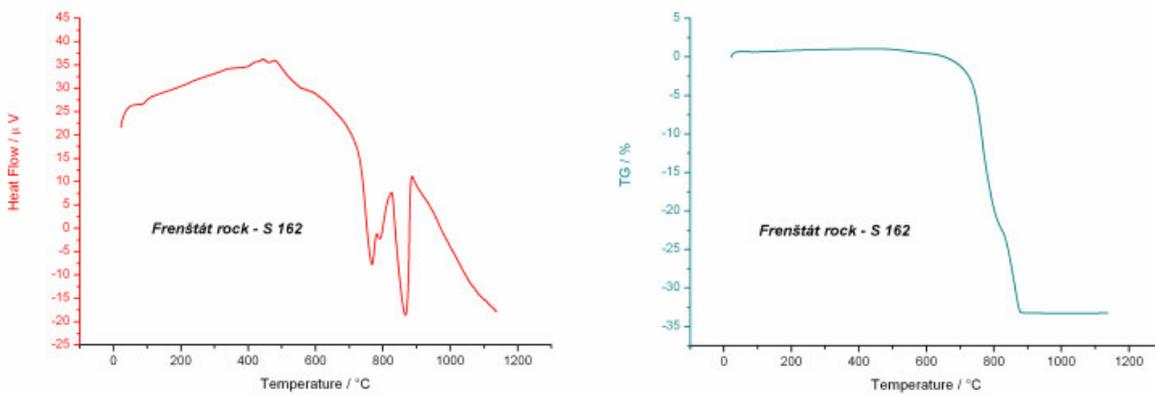
Fig. 26

Fig. 1 - 8 Infrared spectra of the most common clay minerals and of the typical associated minerals in clays.

Fig. 9-16 Thermal curves of kaolinite, illite, muscovite, montmorillonite, chlorite, quartz, calcite and feldspar (DTA on the left side, TG on the right side).

Fig. 17-21 Infrared spectra of sedimentary rock samples from the locality Frenštát (Northern Moravia).

Fig. 22-26 Thermal curves of sedimentary rock samples from the locality Frenštát (Northern Moravia) (DTA on the left side, TG on the right side)

muscovite, montmorillonite, chlorite and curves in Fig. 14 - 16 of some associated minerals: quartz, calcite and feldspar.

3.2. IDENTIFICATION OF CLAY MINERALS IN SEDIMENTARY ROCKS

FTIR spectroscopy

The measured infrared spectra of the sedimentary rock samples from Frenštát locality are shown in Fig. 17 - 21. These spectra represent five groups of sedimentary rocks, that seem to be very similar with regard to the character of their spectra.

S 149: illite/muscovite (3622, 3436, 1029, 910, 830, 525, 471, 429 cm^{-1}), quartz (1090, 798, 779, 695 cm^{-1}), traces of carbonates (1427, 875 cm^{-1}) and kaolinite (3698 cm^{-1}). This spectrum demonstrates essentially a poorly ordered illite.

S 151: carbonate (calcite) (2513, 1797, 1426, 876, 713 cm^{-1}), quartz (1082, 798, 778, 694 cm^{-1}), illite/muscovite (3622, 3435, 1030 cm^{-1}), traces of kaolinite (3704 cm^{-1}). Dominated minerals are carbonates with a calcite-type structure, illite/muscovite and quartz.

S 153: illite (1032 cm^{-1}), quartz (1086, 798, 779, 694, 467 cm^{-1}), traces of kaolinite (3621 cm^{-1}), smectites (3424 cm^{-1}), traces of carbonates (1426, 877 cm^{-1}). Due to very strong absorption of quartz in the region 1400-600 cm^{-1} it is very difficult to assign the characteristic bands to specific clay minerals.

S 161: carbonate (calcite) (2922, 2874, 2514, 1798, 1429, 876, 713 cm^{-1}), illite/muscovite (1034 cm^{-1}). On the basis of splitting absorption bands in the region 800 - 400 cm^{-1} it is possible to confirm presence of feldspars.

S 162: carbonate (ankerite) (3005, 2891, 1813, 1438, 880, 727 cm^{-1}), illite/muscovite (3621, 3436, 1035 cm^{-1}), feldspars (splitting bands in the region 800 - 400 cm^{-1}). This infrared spectrum is similar to that of the sample S 161. Carbonate is also predominant and probably exhibits the ankerite-type structure (1438, 727 cm^{-1}). The presence of feldspars was confirmed, too.

The measured infrared spectra were compared with records of the published spectra (van der Marel and Beutelspacher, 1976), (Moenke, 1966), (Farmer, 1974).

Thermal analysis

The TG/DTA curve of sample S 149 (Fig. 22) indicates the presence of illite, muscovite and maybe carbonate (calcite). On the basis of TG/DTA curve in Fig. 23, the sample S 151 contains quartz and dominant amount of carbonate (calcite). TG/DTA curve of sample S 153 (Fig. 24) shows the presence of quartz, carbonate (calcite) and implies the probable presence of illite traces. In the case of sample S 161 (Fig. 25), there is a dominant presence of calcite. The TG/DTA curve of sample S 162 (Fig. 26) indicates the presence of illite traces and dominant carbonate (probably ankerite).

Identification of analysed samples (Fig. 22 - 26) had a problem with the similarity in thermal effects of different clay minerals. Similarity in thermal behaviour is mainly connected with the origin, chemical variability and crystal structure (kaolinite, illite or chlorite). Additional complications were caused by overlapping thermal effects of different clays and associated minerals like calcite or quartz. It is possible to recognize them, but it just depends on their amount and proportion to clay minerals.

4. CONCLUSION

The basic clay mineral specimens and associated minerals were examined by FTIR-spectroscopy and thermal analysis (TG/DTA). Thirty one sedimentary rock samples from Frenštát locality, Northern Moravia, Czech Republic, were investigated by means of the mentioned methods.

The identification of analysed rock samples was connected with a problem of the similarity in thermal behavior and overlapping of thermal effects of different clays and associated minerals, like calcite or quartz. Splitting bands in OH region 4000-3000 cm^{-1} in infrared spectra complicated also the exact determination of individual clay minerals by FTIR-spectroscopy.

According to obtained data, sedimentary rocks represent five groups with a very similar character of their spectra and TG/DTA curves indicating the similar mineral composition. Clay minerals represented mainly by fine-crystalline illite with traces of kaolinite are predominant. Besides carbonates, the silica minerals occur in these samples, too.

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