

Mineralogical and physico–chemical properties of bentonites from the Jastrabá Formation (Kremnické vrchy Mts., Western Carpathians)

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Abstract: In the past years an increasing demand for bentonites resulted in the opening of new bentonite deposits in the Jastrabá Formation. The shortage of information, in particular analytical data, on the bentonites from the newly opened Jastrabá Fm. deposits was the motivation for the current study. Smectite is the predominant mineral in all bulk bentonites from the new deposits. Its amount varied between 43 and 90 wt. %. The bulk bentonites also contain variable amounts (10–57 wt. %) of mineral admixtures such as feldspars, mica, opal-CT, kaolinite, quartz and sometimes goethite. The smectite mineral comprising the studied bentonites was montmorillonite. The octahedral Al in the structure of montmorillonite was partially substituted by Mg, and to a lesser extent by Fe. The interlayer space of montmorillonite is occupied predominantly by divalent exchangeable cations (Ca^{2+} and Mg^{2+}). The dehydroxylation temperature of smectites ($>600^\circ\text{C}$) determined on the DTG curves indicates the presence of the *cis*-vacant variety of montmorillonites. The mean crystallite thicknesses of smectites (T_{MEAN}) calculated by BWA analyses ranges from 7.2 to 11.5 nm. The shape of the crystallite thickness distributions (CTDs) for smectites is lognormal in all cases. Cation exchange capacity (CEC) and total specific surface area (TSSA) increases with increasing amount of smectite. The CEC of 101 meq/100g and TSSA of 616 m²/g correspond to bulk bentonite from the Stará Kremnička III deposit containing 89 wt. % of smectite.

Keywords: Deposit, mineralogy, Kremnické vrchy Mts., Jastrabá Formation, bentonite, smectite, montmorillonite.

Introduction

Bentonite is a raw material composed predominantly of clay minerals from the smectite group (e.g., montmorillonite, beidellite, saponite, nontronite and hectorite) (e.g., Christidis & Huff 2009). Smectites have characteristic 2:1 type of layered structure consisting of one octahedral sheet interlayered between two tetrahedral sheets. The octahedral sheet may be either dioctahedral or, less commonly, trioctahedral. The non-equivalent isomorphous substitution in the tetrahedral (Al^{3+} and/or Fe^{3+} for Si^{4+}) and octahedral (Mg^{2+} and/or Fe^{2+} for Al^{3+}) sheets give rise to a charge imbalance which is compensated by exchangeable cations (e.g., Na^+ , K^+ , Ca^{2+} , Mg^{2+}) located in the interlayer space. The exchangeable cations are only loosely held in the smectite interlayers and can be easily replaced by other cations. As such, smectites have relatively high cation exchange capacity ($\text{CEC}=80\text{--}150$ meq/100g; La Grega et al. 1994; Calarge et al. 2006). The swelling capacity of smectites enables a reversible increase/decrease in the basal spacing of the interlayer space. Smectites can increase their volume 12-times in contact with water (Galamboš et al. 2010). The small size of smectite particles results in high total specific surface area (TSSA), which may reach 800 m²/g (Środoń & McCarty 2008; Zhu et al. 2015).

Overall, the specific layered structure of smectites is responsible for their unique properties, such as high CEC and TSSA, swelling capacity, low hydraulic conductivity and high adsorption capacity. Due to these properties, smectites have been studied for many potential environmental applications, for example, as sealing material in landfill liners (Andrejkovičová et al. 2008), backfill material for construction of high-level nuclear waste (HLW) repositories (Pacovský et al. 2007; Stríček et al. 2009; Osacký et al. 2013), wastewater treatment (Viraraghavan & Kapoor 1994), adsorbent for heavy metals (Sheta et al. 2003; Rao et al. 2006; Andrejkovičová et al. 2010; Galindo et al. 2013) and organic compounds (Tiller et al. 1984). The bulk of the world's bentonite production in 2018 (~28 million t) is used as pet waste absorbents, drilling mud, foundry sand and ore pelletizing (U.S. Geological Survey 2019).

The formation of bentonite deposits is mainly associated with alteration of volcanic glass-rich rocks (Kraus et al. 1994; Moll 2001). The composition of the parent rocks (acidic rocks — rhyolites, intermediate rocks — andesites and basic rocks — basalts) may affect the crystal chemistry of smectites (Christidis & Dunham 1997; Osacký et al. 2012). For instance, the Fe^{3+} for Al^{3+} substitution controls the crystal chemistry of smectites derived from intermediate rocks, whereas Mg^{2+} for

Al³⁺ substitution seems to be more important for smectites derived from acidic precursors (Christidis & Dunham 1997). Slovak bentonite deposits were formed mainly by an alteration of rhyolitic (e.g., Stará Kremnička–Jelšový potok deposit) and andesitic (e.g., Lieskovec deposit) volcanoclastics in a lacustrine environment (Kraus et al. 1994). The majority of Slovak bentonite deposits are concentrated in the two areas in the Western Carpathians: Central Slovakia Volcanic Field (e.g., Stará Kremnička–Jelšový potok, Kopernica and Lieskovec deposits) and Eastern Slovakia Volcanic Field (e.g., Fintice, Lastovce and Kuzmice deposits).

In the present study, we examine bentonites from different deposits of the Jastrabá Formation (Fm.), located in the south-western part of the Kremnické vrchy Mts. in the Central Slovakia Volcanic Field. The Jastrabá Fm. is one of the most promising areas for the occurrence of non-metallic raw materials in the whole Western Carpathians (Šamajová et al. 1992). The economic accumulations of perlites, zeolites, bentonites (clay rocks rich in smectite) and K-bentonites (clay rocks rich in illite–smectite) on the south-western margin of the Kremnické vrchy Mts. were formed by an alteration of Miocene acidic vitric volcanoclastics of the Jastrabá Fm. (Kraus et al. 1994) and margins of rhyolite domes (Demko et al. 2010).

With the annual bentonite production of about 200 kt and total reserves more than 50,000 kt, Slovakia is one of the world's leading countries in bentonite exploitation (Baláž & Kušík 2015). It should be noted, that 13 of 30 bentonite deposits (43 % of all Slovak bentonite deposits) are located in the Jastrabá Fm. (Record of Mining Areas 2016). The best grade Slovak bentonites from the Stará Kremnička–Jelšový potok and Kopernica deposits (both belong to the Jastrabá Fm.) contain ~80 wt. % of smectite (Osacký et al. 2009).

Increasing demand for bentonites in the past years resulted in the opening of several new bentonite deposits in the Jastrabá Fm. (e.g., Stará Kremnička III, Lutilla I, Lutilla–Pod Klapou and Bartošova Lehôtka), most of which have never been studied in detail. As a consequence, the potential of recently mined Slovak bentonites from new deposits is not fully

determined. We believe that bentonites from the newly opened bentonite deposits of the Jastrabá Fm. are qualitatively equivalent to those from older bentonite deposits in this area (e.g., Stará Kremnička–Jelšový potok). However, this conjecture needs to be supported by analytical data. The comprehensive characterization of bentonites from new deposits is an essential primary step in assessing the qualitative and technological parameters and the optimal application of these bentonites.

The main goal of the present study is a comprehensive characterization of bentonites from the new deposits and their comparison with other Jastrabá Fm. deposits (e.g. Kopernica) as well as world bentonite deposits (e.g., Gonzales County, Texas; Crook County, Wyoming; Apache County, Arizona; Otay San Diego County, California; Crook County, Wyoming; all located in the United States). The obtained results provide a set of original data on mineralogy, chemistry, thermal and surface properties of bentonites from several new deposits located in the Jastrabá Fm., which may help to find a proper application for the bentonites, leading to a more rational and efficient utilization of this kind of raw material.

Geological setting

All investigated bentonites come from deposits located in the south-western part of the Kremnické vrchy Mts., in the Western Carpathians and belong to the same geological formation (Jastrabá Fm.) (Fig. 1). The Jastrabá Fm. consists of rhyolitic volcanism products represented by volcanic extrusions, lava flows, tuffs and epiclastics, which form a continuous, 100–300 m thick complex (Lexa et al. 1998). Early sporadic extrusive and explosive activity of rhyodacites is followed by a widespread activity of plagioclase and plagioclase–sanidine rhyolites; the late volcanic activity products are represented by plagioclase–quartz–sanidine rhyolites (Chernyshev et al. 2013). The biostratigraphic data suggest the Late Sarmatian to Early Pannonian age of the Jastrabá Fm. (Konečný et al. 1983). The results of K–Ar isotope dating of

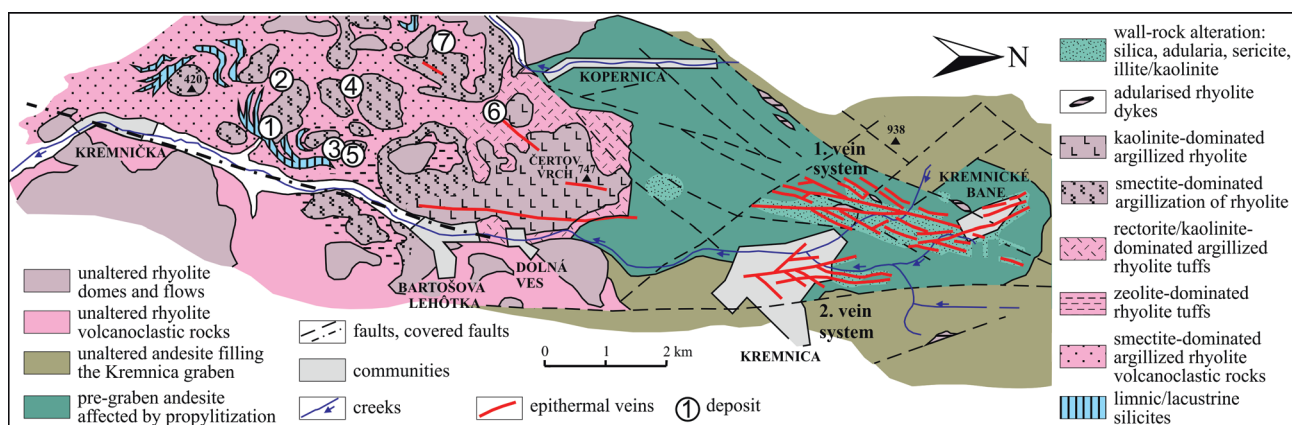


Fig. 1. Simplified geological map of the south-western margin of the Kremnické vrchy Mts. (Jastrabá Fm.) (modified from Kraus et al. 1994; Koděra et al. 2014). Bentonite deposits: Stará Kremnička–Jelšový potok (1); Stará Kremnička III (2); Lutilla I (3); Lutilla–Pod Klapou (4); Bartošova Lehôtka (5); Kopernica (6) and Dolná Ves (7).

the Jastrabá Fm. rhyolites yield ages ranging from 12.2 ± 0.3 Ma to 11.4 ± 0.4 Ma (Chernyshev et al. 1995, 2013). Permeable rhyolite volcanoclastic rocks of the Jastrabá Fm., rich in volcanic glass, are extensively altered into economic accumulations of bentonites, K-bentonites and zeolites (Šamajová et al. 1992). The northern part of the Jastrabá Fm., in the vicinity of the Kremnica ore vein system, is affected by regional illite–smectite alteration forming K-bentonite accumulations (e.g., Dolná Ves deposit; Kraus et al. 1994; Šucha et al. 2001) (Fig. 1). The alteration products in the southern part of the Jastrabá Fm. are composed mainly of smectite (montmorillonite), locally forming bentonite deposits (e.g., Stará Kremnička III, Stará Kremnička–Jelšový potok, Lutilla I, Lutilla–Pod Klapou, Bartošova Lehôtka, Kopernica) (Fig. 1). Bentonites consist predominantly of montmorillonite, accompanied by variable amounts of opal-C/CT, quartz, feldspars, mica, zeolites and kaolinite (Šamajová et al. 1992; Kraus et al. 1994; Osacký et al. 2009; Uhlík et al. 2012; Górniak et al. 2016, 2017). The thickness of bentonite beds ranges from a few metres up to 50 m (Šamajová et al. 1992). The bentonite beds are often interbedded with limnic/lacustrine silicites which are formed by SiO_2 discharge from the subsurface hydrothermal fluids upon reaching the local limnic/lacustrine basins (Koděra et al. 2014). The previous studies have reported that bentonite deposits of the Jastrabá Fm. are primarily formed by alteration of acidic vitric volcanoclastics during diagenesis of the volcanoclastics in a freshwater environment in an open or semi-closed hydrological system (Šamajová et al. 1992; Kraus et al. 1994). The results of recent studies have shown a strong effect of subsurface hydrothermal fluids (deeply-circulating, mostly meteoric waters, driven by heat from the contemporaneous rhyolite magma chamber) on the bentonitization of rhyolitic volcanoclastics from the Jastrabá Fm. (Demko et al. 2010; Koděra et al. 2014).

The nature of the volcanic precursors of bentonites of the Jastrabá Fm. has not been previously studied in detail. Kraus et al. (1982, 1994) proposed that the precursors of the bentonites from the Jastrabá Fm. were mostly redeposited and partly also autochthonous rhyolite tuffs. The results of recent studies have demonstrated that the textural and compositional variation of bentonites from the Jastrabá Fm. (e.g., Kopernica deposit) can be related to the formation of bentonites from genetically diversified volcanic materials such as ignimbrites, pyroclastic fall deposits and redeposited tuffs (e.g., Górniak et al. 2016). Demko et al. (2010) reported that the best grade bentonites (Stará Kremnička–Jelšový potok, Dolná Ves and Kopernica deposits) were formed by the alteration of marginal perlitic breccias of extrusive domes and cryptodomes.

Starting materials and methods

Starting materials

Eight bentonite samples were collected from the borehole VSK-11 ($48^\circ 38' 18.9''$ N, $18^\circ 53' 9.8''$ E) located in the Stará

Kremnička III deposit (1.5 m, 10.5 m, 16.5 m, 20.5 m, 30.5 m, 31.5 m, 40.5 m and 47 m). Point samples C87 and C88 also come from the Stará Kremnička III deposit ($48^\circ 38' 20.3''$ N, $18^\circ 53' 7.1''$ E); point samples C74, C85 and C86 are from the Lutilla I deposit ($48^\circ 37' 42.0''$ N, $18^\circ 52' 19.3''$ E); point samples C75 and C90 are from the Lutilla–Pod Klapou deposit; point samples C76, C77 and C78 are from the Stará Kremnička–Jelšový potok deposit ($48^\circ 37' 35.6''$ N, $18^\circ 53' 12.0''$ E); and point sample C89 is from the Bartošova Lehôtka deposit ($48^\circ 38' 38.1''$ N, $18^\circ 53' 35.5''$ E).

The samples were dried for 3 days at 60°C . Solids were manually homogenized and separated into several size fractions. Prior to the size separation, the bulk solids were sonicated in distilled water for 10 min and then stirred for an additional 24 h at room temperature. The $>160\ \mu\text{m}$ particle size fraction was isolated from the bulk solids by wet sieving using a Fritsch sieve shaker and distilled water. The sub-sieve fraction ($<160\ \mu\text{m}$) was divided into two size fractions ($2\text{--}160\ \mu\text{m}$ and $<2\ \mu\text{m}$) by settling in distilled water. All separated size fractions were dried overnight at 60°C , weighed and analysed.

A portion of the $<2\ \mu\text{m}$ fractions was treated three times overnight with 1 M NaCl in order to prepare Na-saturated smectites. Excess soluble salts were removed by centrifugation, followed by dialysis. Na-saturated solids were dried overnight at 60°C , passed through a $250\ \mu\text{m}$ sieve and analysed by BWA and thermal analyses.

Methods

The X-ray diffraction (XRD) patterns of oriented (air-dried and ethylene glycol solvated) and randomly oriented preparations were recorded using a Phillips PW1710 diffractometer with Cu $K\alpha$ radiation and graphite monochromator at 20 mA and 35 kV. The step size for all analyses was $0.02^\circ\ 2\theta$. The oriented preparations were made by dispersing 150 mg of $<2\ \mu\text{m}$ fraction in 2 ml of distilled water, pipetting the suspension onto a glass slide and drying at room temperature. The XRD patterns of oriented preparations with an exposure time of 0.80 s per step were utilized for clay mineral identification (from the $00l$ series of reflections). The ethylene glycol (EG) solvation of oriented preparations was carried out overnight at 60°C .

Quantitative X-ray diffraction (QXRD) was performed on randomly oriented preparations and evaluated using the RockJock software (Eberl 2003). RockJock determines the quantitative content of minerals in powdered samples by comparing integrated reflection intensities of individual minerals with the intensities for pure standard minerals and an internal standard (corundum). Samples were prepared according to the method modified by Omotoso & Eberl (2009) from that reported by Środoń et al. (2001). The sample was passed through a $250\ \mu\text{m}$ sieve. Then 1 g of sample was mixed with 0.250 g of corundum and ground with 4 ml of denatured alcohol in a McCrone Micronizing Mill for 5 min using zirconia grinding cylinders. The mixture was dried overnight at 60°C .

The sample/corundum mixture was then shaken for 10 min in a plastic vial (25 ml) with 3 plastic balls (9 mm diameter) using a Retsch MM 200 mill. Hexane was added to the mixture in the ratio of 0.5 ml hexane to 1 g of pure clay and the vial was shaken for an additional 10 min. The powder was then side loaded into an XRD holder and X-rayed (from 4° to 65° 2 θ , 2 s per step).

The chemical composition was determined at ACME Analytical Laboratories Ltd. (Vancouver, British Columbia, Canada) by inductively coupled plasma (ICP) analysis after digestion of samples using lithium metaborate fusion, followed by nitric acid leaching. The analytical procedure followed the standard methods of the laboratories.

The structural formula of smectites was calculated using the method outlined by Čičel & Komadel (1994). The input data from the chemical analyses were corrected for the presence of mineral admixtures determined by QXRD analyses (RockJock).

The mean crystallite thicknesses and crystallite thickness distributions of smectite particles (Na-saturated <2 μ m fractions) were calculated by the Bertaut-Warren-Averbach (BWA) analysis (Drits et al. 1998) using the MudMaster program (Eberl et al. 1996), from XRD patterns of oriented EG preparations. This method is based on the observation that XRD reflections are broadened regularly as a function of decreasing particle size. The thickness of the coherently scattering domains was derived from the 001 basal reflection of smectites.

Cation exchange capacity (CEC) was determined by the copper(II) triethylenetetramine [Cu(Trien)]²⁺ method. The 0.01 M solution of [Cu(Trien)]²⁺ was prepared according to Meier & Kahr (1999). An oven-dried sample (105 °C/overnight), approximately 120 mg in weight, was added to 50 ml of distilled water and 10 ml of the [Cu(Trien)]²⁺. The suspension was dispersed by an ultrasonic treatment for 5 min and shaken for an additional 1 h. The suspension was then centrifuged at 4500 rpm for 20 min and the concentration of Cu²⁺ ions in the collected supernatant was determined by UV-VIS spectrophotometry (Cary 100, Varian) at 578 nm. The CEC was calculated according to the equation reported by Pentrák et al. (2012). The Pearson correlation between CEC and smectite contents in bentonites (QXRD analysis) was performed using the Origin software.

Fourier transform infrared (FTIR) spectra in the middle infrared region (4000–400 cm⁻¹) were obtained using a Nicolet 6700 spectrometer. The KBr pressed-disc technique was used for transmission measurements. Samples of 1 mg were dispersed in 200 mg of KBr to record optimal spectra. Discs were heated overnight at 150 °C to minimize water absorption on KBr pellets. For each sample 128 scans were recorded with a resolution of 4 cm⁻¹. Spectral manipulations were performed using the OMNIC software package. The assignment of the bands in FTIR spectra followed Farmer (1974).

Total specific surface area (TSSA) of the samples was determined using the ethylene glycol monoethyl ether (EGME) method. Samples, ~250 mg in weight, were placed into glass weighing bottles and dried to a constant mass in a desiccator over P₂O₅ under evacuation. Then several drops of EGME were added to the samples before storing them under vacuum in a desiccator over ignited CaCl₂. The samples were weighed every 90 min until constant mass was achieved and the TSSA was then calculated according to Novák & Čičel (1972).

Thermal analyses (TG, DTG and DTA) were performed using a Netzsch STA 449 F3 Jupiter analyser. Prior to thermal analyses, the samples (Na-saturated <2 μ m fractions) were stored at ambient laboratory conditions (22 °C and ~30 % RH). The moisture was removed by holding the sample in a Pt–Ir crucible at 105 °C for 60 min. For all measurements, 40 mg of samples was utilized and a heating rate of 10 K/min and a N₂ flow rate 50 ml/min were maintained.

Results and discussion

Mineral composition

The XRD results revealed that the bulk bentonites from all studied deposits consisted of similar mineral constituents, in particular smectite, feldspars, mica, opal-CT, kaolinite, quartz, sometimes goethite. The main differences were observed, however, in the quantity of these mineral constituents for the samples from different deposits and even for the samples from a single deposit. Fig. 2 shows XRD patterns of randomly

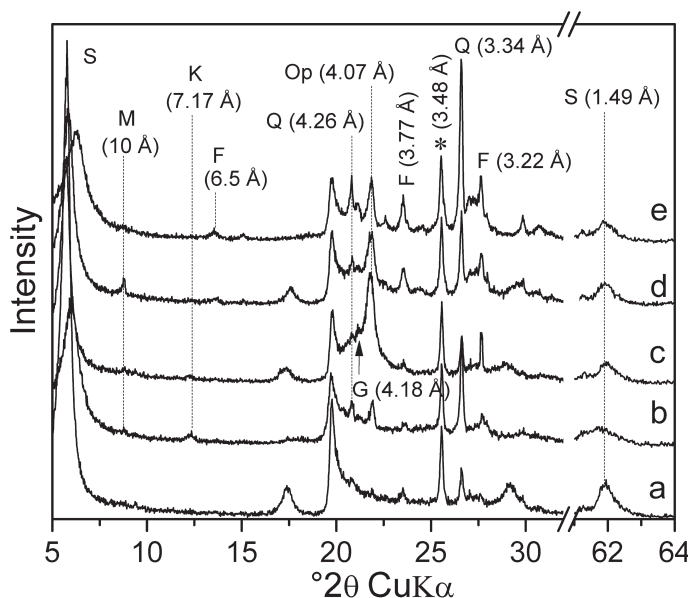


Fig. 2. XRD patterns of randomly oriented preparations of bulk samples VSK-11 10.5 m (Stará Kremnička III) (a), C86 (Lutilla I) (b), VSK-11 30.5 m (Stará Kremnička III) (c), C89 (Bartošova Lehôtka) (d), and C78 (Stará Kremnička–Jelšovský potok) (e). S — smectite, M — mica, K — kaolinite, F — feldspars, Q — quartz, Op — opal-CT, G — goethite, * — corundum (internal standard).

oriented preparations of five representative samples to demonstrate the main differences in mineralogy among the studied bentonites. The results of quantitative mineralogy (QXRD analysis) of all bentonites are reported in Table 1.

Smectite was the predominant mineral in all samples. The majority of the studied bulk samples contained ≥ 80 wt. % of smectite, as documented by bentonites from the Stará Kremnička III (VSK-11 1.5 m, 10.5 m, 16.5 m; C87 and C88), Stará Kremnička–Jelšový potok (C76 and C77), Lutilla I (C85) and Lutilla–Pod Klapou (C75) deposits (Table 1). Bulk bentonites, containing between 70 and 80 wt. % of smectite, were found in the Stará Kremnička III (VSK-11 20.5 m, 31.5 m, 40.5 m and 47 m), Lutilla I (C74) and Lutilla–Pod Klapou (C90) deposits (Table 1). Bulk bentonites with low amounts of smectite (≤ 61 wt. %) were found in the Stará Kremnička III (VSK-11 30.5 m), Stará Kremnička–Jelšový potok (C78), Lutilla I (C86) and Bartošova Lehôtka (C89) deposits (Table 1).

The bulk bentonites also contain admixture of feldspars (5–15 wt. %), mica (0–5 wt. %), opal-CT (0–6 wt. %), quartz (<1 –6 wt. %) and kaolinite (0–2 wt. %). A small amount (4 wt. %) of goethite was detected only in VSK-11 30.5 m (Table 1). In a few samples, elevated amounts of mineral impurities were detected; 11–35 wt. % of opal-CT (C86, C78, C89 and VSK11 30.5 m), 20–27 wt. % of feldspars (C89 and C78), 9–13 wt. % of mica (C90 and 89), 8 wt. % of kaolinite (C86) and 8 wt. % of quartz (C78). Overall, the QXRD results revealed a heterogeneous nature of bulk bentonites from the studied deposits.

Heterogeneous nature of bentonite beds, in terms of mineral composition and thickness, was also reported for bentonites STx-1 (Ca-montmorillonite, Gonzales County, Texas, USA) and SWy-2 (Na-montmorillonite, Crook County, Wyoming,

USA) which are among the deposits producing the world's best-grade bentonites (Moll 2001). Elzea & Murray (1990) reported that the characteristics of the Wyoming bentonite can vary significantly across the deposit due to differences in the volcanic ash composition, different depositional environment and weathering conditions.

The bulk fraction of STx-1, SWy-2 and SAz-1 (Ca-montmorillonite 'Cheto', Apache County, Arizona, USA) bentonites contained 67, 75 and 98 wt. % of smectite, respectively (Chipera & Bish 2001). The above smectite contents were similar to those of Slovak bentonites examined in the present study (Table 1) or reported previously (e.g., Górniak et al. 2016). The clay size fraction ($<2 \mu\text{m}$) of SWy-2, SAz-1, SCA-3 (montmorillonite 'Otay', Otay San Diego County, California, USA) and SWa-1 (ferruginous smectite, Grant County, Washington, USA) bentonites usually contained ≥ 93 wt. % of smectite (Osacký et al. 2013; Geramian et al. 2016). The results obtained in the present study (Table 1) along with published data (e.g., Osacký et al. 2013; Górniak et al. 2016; Pentrák et al. 2018) show that the same size fraction ($<2 \mu\text{m}$) of the Slovak bentonites contained usually ≤ 93 wt. % of smectite, due to higher amounts of mineral admixtures (e.g., feldspars, quartz, opal-CT, kaolinite and mica).

The particle size distribution results (Table 2) for bentonites from the Stará Kremnička III deposit (VSK-11 samples) show that the $<2 \mu\text{m}$ and 2–160 μm size fractions account for 15–34 wt. % and 42–69 wt. % of the total weight of the samples, respectively. Although the $<2 \mu\text{m}$ fractions of bentonites had elevated smectite contents compared with the bulk samples (Table 1), the amount of this fraction was low. Substantially higher amounts of the $<2 \mu\text{m}$ fractions were expected for the studied bentonites. The low amounts of the $<2 \mu\text{m}$

Table 1: Mineral composition (in wt. %) of the bulk and $<2 \mu\text{m}$ fraction of bentonites determined by RockJock.

Sample	Quartz	Feldspars	Opal-CT	Kaolinite	Mica	Smectite	Goethite	Deposit
Bulk								
VSK-11 1.5 m	1	9	4	–	2	84	–	Stará Kremnička III
VSK-11 10.5 m	2	5	3	–	<1	89	–	Stará Kremnička III
VSK-11 16.5 m	2	9	5	–	<1	83	–	Stará Kremnička III
VSK-11 20.5 m	3	9	5	1	2	80	–	Stará Kremnička III
VSK-11 30.5 m	1	5	35	1	2	52	4	Stará Kremnička III
VSK-11 31.5 m	4	10	5	1	2	78	–	Stará Kremnička III
VSK-11 40.5 m	2	12	6	2	1	77	–	Stará Kremnička III
VSK-11 47 m	3	15	5	2	1	74	–	Stará Kremnička III
C87	1	9	–	–	–	90	–	Stará Kremnička III
C88	3	12	2	–	–	83	–	Stará Kremnička III
C76	3	7	5	1	3	81	–	Stará Kremnička–Jelšový potok
C77	2	7	6	–	3	82	–	Stará Kremnička–Jelšový potok
C78	8	27	13	–	–	52	–	Stará Kremnička–Jelšový potok
C74	5	10	4	2	5	74	–	Lutilla I
C85	4	8	–	<1	5	82	–	Lutilla I
C86	6	12	11	8	2	61	–	Lutilla I
C75	1	6	5	1	3	84	–	Lutilla–Pod Klapou
C90	<1	11	4	–	9	75	–	Lutilla–Pod Klapou
C89	2	20	21	<1	13	43	–	Bartošova Lehôtka
$<2 \mu\text{m}$								
VSK-11 10.5 m	1	5	–	–	<1	93	–	Stará Kremnička III
VSK-11 31.5 m	<1	8	2	1	–	88	–	Stará Kremnička III

Table 2: Particle size distribution (in wt. %) of bentonites.

Sample	Size fraction (µm)		
	>160	2–160	<2
VSK-11 1.5 m	15	63	22
VSK-11 10.5 m	13	69	18
VSK-11 16.5 m	19	47	34
VSK-11 20.5 m	20	62	18
VSK-11 30.5 m	39	42	19
VSK-11 31.5 m	29	57	14
VSK-11 40.5 m	34	51	15
VSK-11 47 m	31	47	22

fractions indicate that some portion of smectite in bentonites from the Stará Kremnička III deposit was present in the form of aggregates (mainly between 2 and 160 µm in size) which resisted the applied size separation process (drying, homogenization, sonication and stirring). A similar behaviour was observed for Slovak bentonites from the Hliník nad Hronom (Uhlík et al. 2012; Górníak et al. 2017) and Kopernica deposits (Górníak et al. 2016) and STx-1 bentonite (Chipera & Bish 2001). The smectite aggregates in bentonites were often coated and/or intergrown with silica minerals (e.g., opal-CT, K-feldspars and zeolites) (Chipera & Bish 2001; Górníak et al. 2016, 2017). Furthermore, opal-CT and feldspars were common mineral admixtures identified in the studied bentonites from different Slovak deposits (e.g. Stará Kremnička III, Stará Kremnička–Jelšovský potok, Lutilla I, Bartošova Lehôtka), sometimes present in significant amounts (e.g., 35 wt. % of opal-CT for VSK-11 30.5 m, 27 wt. % of feldspars C78, Table 1). Opal-CT, in amounts up to 45 wt. %, was reported in bentonites from other Slovak deposits (Hliník nad Hronom and Kopernica) (Uhlík et al. 2012; Górníak et al. 2016, 2017). The presence of these minerals even in the <2 µm fractions of bentonites (up to 10 wt. %, Table 1) indicates their association mainly with smectite.

The laboratory experiments simulating alteration of volcanic glass in open systems showed that the precipitation rate of free SiO₂ decreased with the increasing rate of fluids flowing through the volcanic glass (Daux et al. 1997). Analogically, bentonites coexisting with SiO₂ polymorphs (e.g., opal-CT) were preferentially formed from acidic pyroclastic rocks deposited at low temperatures, which could not sustain high rates of fluid flow migrating through pyroclastic rocks; as a consequence, fluids have reached saturation by Si leached from pyroclastic rocks and amorphous SiO₂ has precipitated (Christidis & Huff 2009).

The formation of Slovak bentonite deposits of the Jastrabá Fm. (Kremnické vrchy Mts.) is still not fully understood mainly due to the complex geological–tectonic structure of the studied area and several mutually overlapping alteration processes. Kraus et al. (1994) proposed the model for the alteration of the rocks from the south-western part of the Kremnické vrchy Mts. (Jastrabá Fm.) based on the existence of three mutually associated processes of different origin: the diagenetic alteration of rhyolite tuffs, hydrothermal alteration of rhyolites and hydrothermal alteration of andesites and rhyolite

tuffs in the vicinity of the Kremnica ore veins. According to previous studies (Šamajová et al. 1992; Kraus et al. 1994) the largest economic accumulations of bentonites exploited in the Jastrabá Fm. (Stará Kremnička–Jelšovský potok deposit) were associated mainly with the diagenetic alteration of rhyolite tuffs. The concept about diagenetic alteration of rhyolite tuffs is based on the vertical mineral zonation (perlite, smectite and zeolite zone) distinguished in the vicinity of the bentonite deposit Jelšovský potok (Šamajová et al. 1992, Kraus et al. 1994). The same authors reported that the redeposited and partially also autochthonous rhyolite tuffs were altered into bentonites in a shallow water lacustrine environment (lakes and swamps) in an open or semi-closed hydrological system. Diagenetic mineral zones were formed as a result of gradual changes in chemical composition and pH of pore solutions percolating through vitric tuffs (Kraus et al. 1994). Due to the gradual hydration and hydrolysis of the vitric component and simultaneous formation of smectites in the upper zone, pore solutions became enriched in alkalies and silicon eventually attaining the mineralization and pH sufficient for clinoptilolite crystallization in the lower zone (Šamajová et al. 1992).

New data on fluid properties of the Kremnica hydrothermal system enabled reconstruction of the history of the spatial and temporal fluid evolution of individual parts of the ore vein system and shed new light on the formation of argillic alteration products from the south-western part of the Kremnické vrchy Mts. (Jastrabá Fm.) (Demko et al. 2010; Koděra et al. 2014). Stable isotope data of clay minerals (illites and illite–smectites) indicated isotopically homogenous sources of fluids (deeply-circulating, mostly meteoric waters, driven by heat from the contemporaneous rhyolite magma chamber) which are associated with the formation of illites and illite–smectites in the south-western part of the Kremnické vrchy Mts. (Jastrabá Fm.) (Demko et al. 2010). The isotope geothermometry results indicated that the lateral mineral zonation in the Jastrabá Fm., namely illite–smectite accumulations in the northern part (e.g., Dolná Ves deposit) and smectite accumulations in the southern part of the formation (e.g., Stará Kremnička–Jelšovský potok deposit), may be related to the gradual decrease in temperature of the hydrothermal fluids percolating through the rhyolite volcanoclastics from north to south (Demko et al. 2010). This finding was in line with previously published data showing an increase in the expandability of illite–smectites from north to south in the Dolná Ves hydrothermal deposit (Šucha et al. 1992). Demko et al. (2010) and Koděra et al. (2014) assume that the subsurface hydrothermal fluids migrating from north to south in permeable rhyolite volcanoclastic rocks of the Jastrabá Fm. played a key role in the alteration of the vitric component of rhyolite tuffs into (smectites) bentonites.

Chemical composition of bentonites and smectite crystal-chemistry

The position of the 060 reflection of smectite ($d=1.49$ Å, Fig. 2) indicates the presence of dioctahedral smectite in all

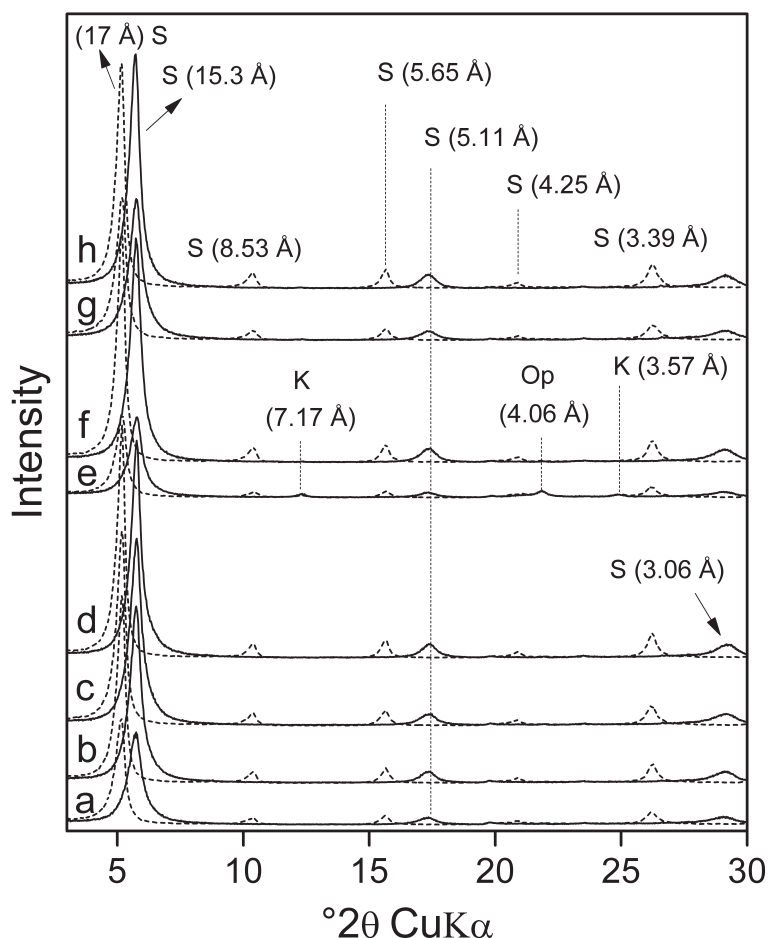
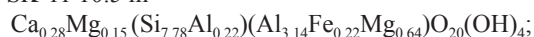


Fig. 3. XRD patterns of oriented air-dried (solid line) and ethylene glycolated (dash line) preparations (Stará Kremnička III) of samples VSK-11 1.5 m (a), 10.5 m (b), 16.5 m (c), 20.5 m (d), 30.5 m (e), 31.5 m (f), 40.5 m (g), and 47 m (h). S — smectite, K — kaolinite, Op — opal-CT.

studied samples. The 001 reflection of all studied smectites observed near 15.3 Å (Fig. 3), indicates the predominance of divalent exchangeable cations (most likely Ca^{2+} and Mg^{2+}) in the interlayer space of smectites. The comparison of air-dried and EG oriented XRD patterns showed that smectite was the only swelling clay mineral identified in the studied samples (Fig. 3). The observations above were in good agreement with the structural formulas of smectites, calculated from the <2 µm fraction of VSK-11 samples from the Stará Kremnička III deposit:

VSK-11 10.5 m



VSK-11 31.5 m



The formulas indicate that the layer charge of smectites arises mainly from Mg for Al substitutions in the octahedral sheet. Such dioctahedral Al-Mg rich smectites, with the layer charge arising mainly from non-equivalent isomorphous substitution of cations in the octahedral sheet, can be classified as montmorillonites (Brindley 1980). According to some authors,

the predominance of Ca and Mg cations in the interlayer space of montmorillonites may be related to the shallow lacustrine environment in which the vitric tuffs of the Jastrabá Fm. were altered into bentonites (Kraus et al. 1982, 1994).

The comparison of the above smectite formulas with those reported for smectites from other Jastrabá Fm. deposits, such as Stará Kremnička–Jelšovský potok (Čížek et al. 1974, 1992; Osacký et al. 2013) and Kopernica (Górniak et al. 2016; Pentrák et al. 2018) shows no significant differences. These findings indicate that: (i) the crystal-chemistry of smectites from the Jastrabá Fm. bentonite deposits is quite consistent and did not change significantly over years with bentonite exploitation, (ii) the similar crystal-chemistry of smectites from the Stará Kremnička III, Stará Kremnička–Jelšovský potok and Kopernica deposits suggests a similar composition of the parent rocks (acidic rhyolitic tuffs) and/or similar alteration conditions of bentonites from these Jastrabá Fm. deposits.

Previous studies showed that the composition of the parent rocks was an important parameter affecting the composition of smectites (e.g., Christidis 1998, 2006). For instance, the crystal-chemistry of smectites derived from acidic precursors (e.g., rhyolite) was controlled mainly by Mg for Al substitution, whereas Fe for Al substitution seemed to be more important for smectites derived from intermediate rocks (e.g., andesite) (Christidis & Dunham 1997). A typical example of a Slovak bentonite deposit formed by alteration of intermediate andesitic tuffs is the Lieskovec deposit in the Abčíná Fm., located in the south-eastern part of the Zvolen Basin (Šucha & Kraus 1999). Bulk bentonite from the Lieskovec deposit contained from 51 to 65 wt. % of dioctahedral Al-Fe rich smectite (montmorillonite) (Šucha & Kraus 1999; Andrejkovičová et al. 2006; Osacký et al. 2012).

The chemical composition of the studied bentonites is reported in Table 3. High SiO_2 and Al_2O_3 contents in all samples correspond to high amounts of aluminosilicates namely clay minerals (mainly smectite) and feldspars, and SiO_2 -bearing mineral phases namely opal-CT and quartz. The elevated SiO_2 content of VSK-11 30.5 m was due to an opal-CT admixture. The increased Fe_2O_3 contents may be related to the presence of biotite which is a common admixture in bentonites from the Jastrabá Fm. (Górniak et al. 2017) and/or montmorillonite (octahedral Fe). However, the elevated Fe_2O_3 content in VSK-11 30.5 m results from the presence of goethite. Increased Na_2O and K_2O contents in VSK-11 31.5 m and 47 m correspond to the higher amount of feldspars. Mica was another possible source of K_2O in the studied samples. The main source of MgO and CaO was likely smectite. The presence of Ti was likely due to the presence of accessory TiO_2 minerals

Table 3: Chemical composition (in wt. %) of the bulk and <2 µm fraction of bentonites determined by ICP.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	TiO ₂	LOI*
Bulk									
VSK-11 10.5 m	53.88	18.20	2.11	0.12	0.89	3.24	1.72	0.15	19.4
VSK-11 30.5 m	61.86	14.51	5.37	0.20	0.77	1.79	1.12	0.09	14.1
VSK-11 31.5 m	56.48	18.23	2.10	0.31	1.42	2.49	1.56	0.15	17.1
VSK-11 47 m	55.59	18.80	1.99	0.32	1.47	2.68	1.57	0.13	17.9
<2 µm									
VSK-11 10.5 m	52.41	18.88	1.86	0.03	0.29	3.42	1.78	0.11	21.0
VSK-11 31.5 m	52.41	20.80	1.95	0.07	0.38	2.86	1.71	0.12	20.2

*LOI — 1000 °C

(e.g., rutile and anatase) coming from parent volcanic rocks. The replacement of altered biotite crystals by Fe–Ti minerals in bentonites from the Jastrabá Fm was previously reported by Górníak et al. (2017). The LOI content is mainly related to the dehydroxylation of clay minerals. Samples with higher amounts of clay minerals (mainly smectite) show a higher LOI than those with lower amount of clay minerals. Overall, the results of chemical analyses are consistent with the QXRD data.

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra for all <2 µm fractions of VSK-11 bentonite samples (Fig. 4) display mainly bands related to the vibrations of smectite. The absorption bands near 3628 and 3421 cm⁻¹ correspond to the OH stretching vibrations of the structural OH groups and water molecules, respectively. The band at 3698 cm⁻¹, observed in the spectra of the sample VSK-11 30.5 m, is attributed to the OH stretching vibrations of kaolinite outer surface OH groups. The OH bending region of all VSK-11 samples with the absorptions at 915 cm⁻¹ (AlAlOH), 845 cm⁻¹ (AlMgOH) and an inflexion near 882 cm⁻¹ (AlFeOH) indicate that the octahedrally coordinated Al in the structure of smectites was partially substituted by Mg, and to a lesser extent by Fe. These findings are in good agreement with the structural formulas of VSK-11 10.5 m and 31.5 m smectites calculated from chemical analyses corrected for mineral impurities. A strong complex band near 1042 cm⁻¹ was due to Si–O stretching vibrations, whereas the bands at 524 and 468 cm⁻¹ are assigned to Al–O–Si and Si–O–Si bending vibrations, respectively. The bands at 1107 and 794 cm⁻¹ in the sample VSK-11 30.5 m indicate the presence of a silica admixture. This finding is in good agreement with QXRD analyses which confirmed 35 wt. % of opal-CT in this sample (Table 1).

Cation exchange capacity (CEC)

CEC values determined by the [Cu(Trien)]²⁺ method for oven-dried (105 °C/overnight) bulk bentonites and corresponding <2 µm fractions are shown in Table 4. CECs for studied samples ranged from 57 to 106 meq/100g. A significant positive correlation ($p < 0.0001$ and $R^2 = 0.919$, Fig. 5)

established between CEC values and smectite contents indicates that the CECs increases with increasing amount of smectite. The best-grade bulk bentonites (VSK-11 10.5 m and C87) contain 89–90 wt. % of Al–Mg montmorillonite and have a CEC of 99–100 meq/100g (Tables 1 and 4). The best-grade <2 µm fraction, obtained from the bulk sample VSK-11 10.5 m by conventional gravitational settling in water, contains slightly higher smectite content and CEC values (93 wt. % of Al–Mg montmorillonite and CEC=105 meq/100g, Tables 1 and 4). However, it should be noted that, in general, the amounts of <2 µm fractions of bentonites from the Jastrabá Fm. are low (Table 2) due to the presence of smectite aggregates coated/intergrown with silica minerals (e.g., feldspars and opal-CT) (e.g., Górníak et al. 2016, 2017).

For comparison, the <2 µm fraction of the SWy-2 bentonite with a similar smectite content (94 wt. % of smectite, Geramian et al. 2016) had lower CEC (93 meq/100 g, Pentrák et al. 2012) than the <2 µm fraction of VSK-11 10.5 m. This is due to the lower total layer charge of the SWy-2 montmorillonite, i.e. –0.70 for SWy-2 (Geramian et al. 2016) vs. –0.86 for VSK-11 10.5 m per O₂₀(OH)₄. On the other hand, the <2 µm fraction the of SAz-1 bentonite, containing 97 wt. % of smectite (Osacký et al. 2013) had higher CEC (121 meq/100 g, Pentrák et al. 2012) than the <2 µm fraction of VSK-11 10.5 m, due to slightly higher smectite content, and more importantly, substantially higher total layer charge of SAz-1 montmorillonite, namely –1.13 for SAz-1 (Osacký et al. 2013) vs. –0.86 for VSK-11 10.5 m per O₂₀(OH)₄.

In addition, we have calculated theoretical CECs from structural formulas (CEC_{sf}) of smectites VSK-11 10.5 m and 31.5 m (based on the exchangeable cations content). The CEC_{sf} of pure, dehydrated smectites VSK-11 10.5 m and 31.5 m were 124 and 121 meq/100 g, respectively. The CEC_{sf} values were then compared with the CECs determined by the [Cu(Trien)]²⁺ method for the <2 µm fractions of VSK-11

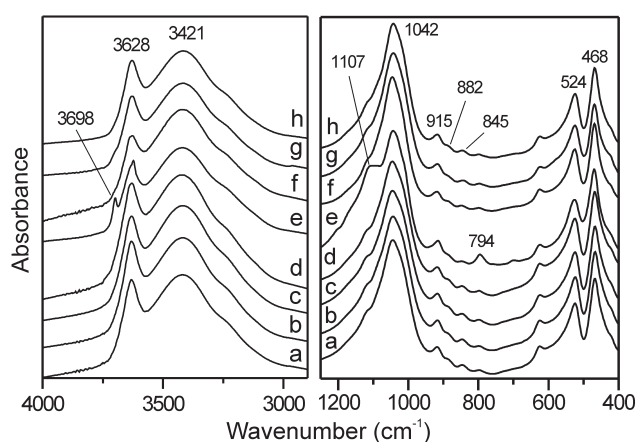
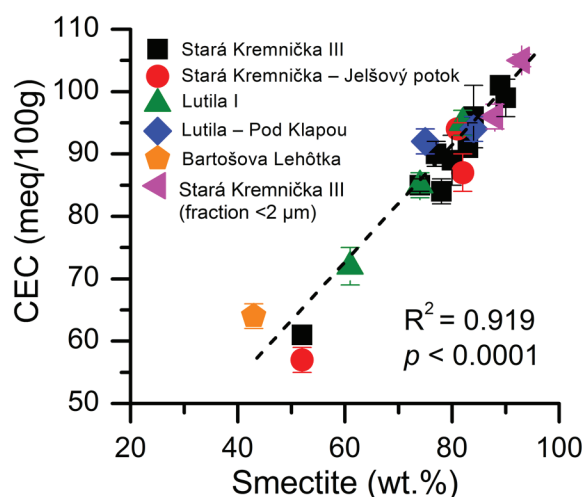


Fig. 4. FTIR spectra of <2 µm fractions (Stará Kremnička III) of samples VSK-11 1.5 m (a), 10.5 m (b), 16.5 m (c), 20.5 m (d), 30.5 m (e), 31.5 m (f), 40.5 m (g), and 47 m (h).

Table 4: Cation exchange capacity (CEC), total specific surface area (TSSA) and mean crystallite thickness (T_{MEAN}) of the bulk and $< 2 \mu\text{m}$ fraction of bentonites.

Sample	CEC (meq/100g)		TSSA (m^2/g)		T_{MEAN} (nm)	Deposit
	Bulk	$< 2 \mu\text{m}$	Bulk	$< 2 \mu\text{m}$		
VSK-11 1.5 m	96 \pm 5	102 \pm 2	–	–	9.8	Stará Kremnička III
VSK-11 10.5 m	101 \pm 1	105 \pm 1	616	684	11.1	Stará Kremnička III
VSK-11 16.5 m	91 \pm 1	99 \pm 2	–	–	10.7	Stará Kremnička III
VSK-11 20.5 m	89 \pm 4	102 \pm 3	–	–	11.5	Stará Kremnička III
VSK-11 30.5 m	61 \pm 1	79 \pm 3	462	574	9.3	Stará Kremnička III
VSK-11 31.5 m	84 \pm 2	96 \pm 2	565	659	11.2	Stará Kremnička III
VSK-11 40.5 m	90 \pm 2	99 \pm 1	–	–	9.5	Stará Kremnička III
VSK-11 47 m	85 \pm 1	102 \pm 1	–	–	11.2	Stará Kremnička III
C87	99 \pm 3	100 \pm 3	–	–	9.1	Stará Kremnička III
C88	93 \pm 2	98 \pm 5	–	–	8.6	Stará Kremnička III
C76	94 \pm 1	105 \pm 2	–	–	8.7	Stará Kremnička–Jelšovský potok
C77	87 \pm 3	97 \pm 3	–	–	7.4	Stará Kremnička–Jelšovský potok
C78	57 \pm 2	96 \pm 8	–	–	7.7	Stará Kremnička–Jelšovský potok
C74	85 \pm 2	105 \pm 4	–	–	9.9	Lutila I
C85	95 \pm 2	106 \pm 3	–	–	8.4	Lutila I
C86	72 \pm 3	84 \pm 2	–	–	7.2	Lutila I
C75	94 \pm 2	101 \pm 2	–	–	8.7	Lutila–Pod Klapou
C90	92 \pm 2	102 \pm 4	–	–	9.2	Lutila–Pod Klapou
C89	64 \pm 2	85 \pm 1	–	–	9.0	Bartošova Lehôtka

**Fig. 5.** Cation exchange capacity (CEC) plotted versus smectite content of the studied bentonites.

10.5 m and 31.5 m, recalculated (based on the QXRD data, Table 1) to CEC of pure smectites (113 meq/100 g for pure VSK-11 10.5 m and 109 meq/100 g for pure VSK-11 31.5 m). The comparison shows that the CEC_{SF} values are slightly higher than the CECs measured by $[\text{Cu}(\text{Trien})]^{2+}$ (the difference being $< 10\%$). This small discrepancy is likely mainly because CEC_{SF} was calculated from an absolutely dry (ignited at 1000°C) basis, while CEC determined by $[\text{Cu}(\text{Trien})]^{2+}$ were measured after the sample was dried at 105°C /overnight, cooled in a desiccator, and then weighed. As a consequence, the H_2O left in the sample (mainly in smectite) at 105°C reduced the CEC values compared to CECs calculated from the H_2O -free basis (Środoń & McCarty 2008).

Total specific surface area (TSSA)

TSSA values for selected bulk bentonites and corresponding $< 2 \mu\text{m}$ fractions are reported in Table 4. TSSA increases with increasing amount of smectite in the studied bentonites. TSSA values gradually increase from 462 to 565 and $616 \text{ m}^2/\text{g}$ for bulk bentonites with the smectite content of 52 wt. % (VSK-11 30.5 m), 78 wt. % (VSK-11 31.5 m) and 89 wt. % (VSK-11 10.5 m), respectively. Similar TSSA values ($624\text{--}632 \text{ m}^2/\text{g}$) were reported for bulk Wyoming bentonites containing $\sim 89\text{--}91$ wt. % of smectite (Kiviranta & Kumpulainen 2011).

Thermal analysis

The results of thermal analyses (TG, DTG and DTA) for the selected bentonites (Na-saturated $< 2 \mu\text{m}$ fractions) are shown in Figure 6. For all samples, the mass loss from room temperature to 1000°C can be divided into three steps in the $< 300^\circ\text{C}$, $300\text{--}550^\circ\text{C}$ and $550\text{--}700^\circ\text{C}$ regions. At temperatures $< 300^\circ\text{C}$, the mass loss accounted for 8.9–11.8 % on the TG curves of the studied samples (Fig. 6) and it is mostly related to the desorption of surface H_2O (e.g., H_2O on exterior surfaces) and dehydration (e.g., interlayer H_2O) of clay minerals (mainly smectite). At elevated temperatures, $300\text{--}550^\circ\text{C}$ and $550\text{--}700^\circ\text{C}$, the mass loss was mainly due to the dehydroxylation (release of structural OH groups) of clay minerals, in particular smectite. The dehydroxylation of smectite was indicated by one broad peak with maximum at $\sim 640\text{--}660^\circ\text{C}$ on DTG curves (Fig. 6) suggesting the presence of *cis*-vacant dioctahedral smectites (Drits et al. 1995; Wolters & Emmerich 2007) in the studied bentonites. Generally, the *cis*-vacant smectites are primary products of weathered or hydrothermally altered volcanoclastic rocks of rhyolitic composition.

This conjecture is in line with the geological origin of the studied bentonites from the Jastrabá Fm. (e.g., Kraus et al. 1982, 1994; Koděra et al. 2014). The DTA curves of studied samples showed two endothermic events at 465–473 °C (mass loss = 1.2–1.9 %) and 630–655 °C (mass loss = 2.6–3.1 %) associated with the dehydroxylation of smectites (Fig. 6). Some contribution from kaolinite and mica was also possible because these are often present in the <2 µm fractions of studied bentonites in low amounts (~1 wt. %, Table 1).

The 739–762 °C endothermic events in the DTA of all samples (Fig. 6) were probably artefacts, related to the pretreatment of the samples (Meyer 1972; Wolters & Emmerich 2007)

and/or could represent carbonates (dolomite and/or calcite) decarbonation (Rowland 1955; Guggenheim & Van Groos 2001). The presence of carbonates was not confirmed by XRD and FTIR in the studied samples. In addition, no carbonates were previously reported for bentonites from the Jastrabá Fm. deposits. Thus, the endothermic events at 739–762 °C are most likely artefacts due to the pretreatment of the samples (size fractions separation, Na-saturation). Wolters & Emmerich (2007) reported that sodium might act as a flux causing partial sintering and retardation of released OH groups.

A weak endothermic event at 840–870 °C in the DTA curves for VSK-11 10.5 m and C85 (Fig. 6) is associated with the breakdown of anhydrous smectite (montmorillonite) structure to an amorphous material (Bradley & Grim 1951).

Bertaut–Warren–Averbach (BWA) analysis

The mean crystallite thicknesses (T_{MEAN}) and the crystallite thickness distributions (CTDs) for smectites (Na-saturated <2 µm fractions) are shown in Table 4 and Figure 7. The T_{MEAN} values calculated for smectites from studied bentonites range from 7.2 to 11.5 nm. The highest T_{MEAN} values (11.1–11.5 nm) were calculated for smectites from the Stará Kremnička III deposit. Besides that, no apparent relationships were found between the T_{MEAN} of smectites and the studied bentonite deposits. Figure 7 shows CTDs for seven representative samples with distinct T_{MEAN} values to demonstrate changes in the shape of CTDs due to different T_{MEAN} . The shape of CTDs for smectites is lognormal for all studied samples. The maxima of the CTDs gradually decreases in frequency, broadens and shifts to higher thicknesses with the gradual increase of T_{MEAN} values of smectites (Fig. 7).

The crystallite thickness of smectites depends on several factors. The structure of smectites is labile along the c direction due to the ability of smectites to accommodate water

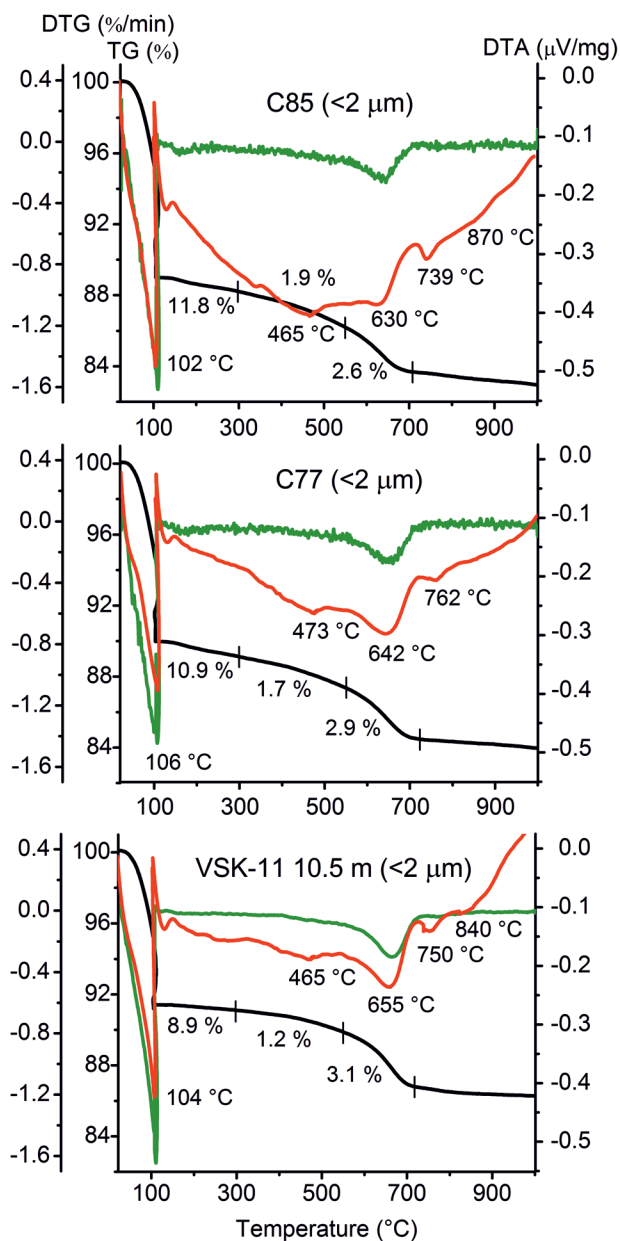


Fig. 6. TG, DTG and DTA curves of Na-saturated <2 µm fractions of samples C85 (Lutila I), C77 (Stará Kremnička–Jelšovský potok) and VSK-11 10.5 m (Stará Kremnička III).

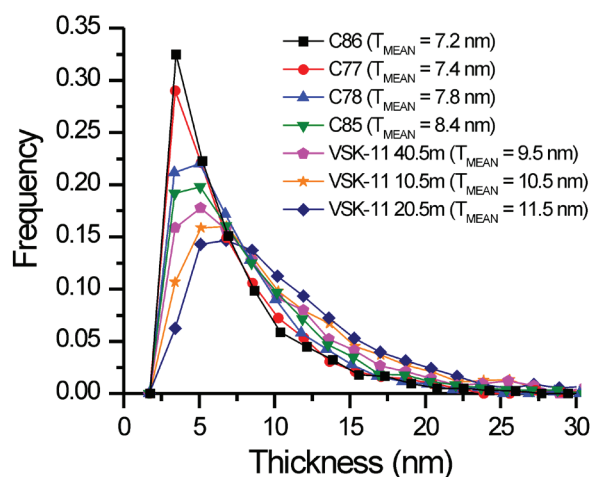


Fig. 7. Crystallite thickness distributions (CTDs) of smectites (Na-saturated <2 µm fractions) from the Lutila I (C86, C85), Stará Kremnička–Jelšovský potok (C77, C78) and Stará Kremnička III deposits (VSK-11 10.5 m, 20.5 m and 40.5 m) and corresponding mean crystallite thicknesses (T_{MEAN}).

molecules in the interlayer space. The subsequent change in the basal spacing due to the swelling produces changes in the crystallite thickness of smectites (e.g., Moore & Hower 1986; Mystkowski et al. 2000). At high humidity, smectite adsorbs water which splits some layers or sets of layers and this in turn, lowers the mean thickness which is a statistical description of the associations of layers that exist in a sample (Mystkowski et al. 2000). The effect of different pretreatment of smectitic samples on the mean crystallite thickness was previously studied by Mystkowski et al. (2000). The authors showed that different size fractions (<2 µm vs. <0.2 µm) and exchangeable cations (Na- vs. Ca-saturated forms) may also produce changes in the mean crystallite thickness of smectites calculated by BWA analyses.

The smectite crystallite thickness does not reflect a growth mechanism of smectite crystals (e.g., Mystkowski et al. 2000; Christidis 2001) as is the case of crystals of other clay minerals (e.g., illites, kaolinites), according to Eberl et al. (1998). The use of lateral *a-b* dimensions (length and width) instead of *c* dimension (thickness) of smectite particles was proposed by Christidis (2001) to study the growth mechanisms of smectites in bentonites. Mystkowski et al. (2000) showed a relationship between the *a-b* and *c* dimensions of the smectite crystallites; bigger crystallites (i.e. larger *a-b* dimensions) were statistically more likely to associate into thicker sets (i.e. larger *c* dimensions). In addition, the same authors believe that high thicknesses and large lateral dimensions of beidellite crystallites are related to the hydrothermal conditions in which the samples have crystallized. Šucha et al. (1996) observed that the redeposition of bentonites at a short distance reduced the crystallite thickness of smectites in comparison with the original bentonites formed by in situ alteration of andesitic volcanoclastics from the Zvolen Basin (Western Carpathians). Simić and Uhlík (2006) reported that the distinct smectite crystallite thicknesses determined for Serbian bentonites can be related to different geological environments in which the bentonites originated.

It would be interesting to discover the reason for the diversity of smectite crystallite thickness for the bentonites examined in the present study. All samples were pretreated in the same way (<2 µm fractions, Na-saturation) thus there must be some other factor than the samples pretreatment, which affects the smectite crystallite thickness of the studied samples.

Conclusions

The bulk bentonites from the Jastrabá Fm. consist of widely variable amounts of smectite, feldspars, mica, opal-CT, kaolinite, quartz, and sometimes goethite. Smectite was the predominant mineral in all samples and its amount varied between 43 and 90 wt. %. The clay size fractions (<2 µm) isolated from the bulk bentonites contain up to 93 wt. % of smectite. However, the amounts of the <2 µm fractions in the studied bentonites are rather low, compared to other studied

fractions, due to the presence of smectite aggregates associated with silica minerals (mainly feldspars and opal-CT). The calculated structural formulas revealed that smectites comprising the studied bentonites can be classified as montmorillonites. The layer charge of montmorillonites arises mainly from the Mg for Al substitutions in the octahedral sheet. The interlayer space of montmorillonites is occupied predominantly by divalent exchangeable cations (Ca²⁺ and Mg²⁺). The results of thermal analyses indicate the presence of *cis*-vacant variety of montmorillonites in the studied bentonites. The mean crystallite thickness (T_{MEAN}) of smectites calculated by BWA analyses ranges from 7.2 to 11.5 nm. The shape of crystallite thickness distributions (CTDs) for smectites is lognormal in all samples. Both cation exchange capacity (CEC) and total specific surface area (TSSA) increase with the increasing amount of smectite in the studied bentonites. The CEC of 101 meq/100g and TSSA of 616 m²/g correspond to bulk bentonite from the Stará Kremnička III deposit containing 89 wt. % of smectite.

The general consensus is that bentonites from the Jastrabá Fm. resulted from alteration of volcanoclastics of rhyolitic composition. The transformation mechanism, however, is controversial. The largest economic accumulation of bentonites in the Jastrabá Fm. (Stará Kremnička–Jeľšovský potok deposit) may be associated with the diagenetic and/or hydrothermal alteration of rhyolite tuffs whereas smaller occurrences of bentonites may be related to hydrothermal rather than diagenetic alteration. Further studies on the genesis of bentonite deposits are required. More comprehensive knowledge on the formation of bentonite deposits may contribute to the discovery of other prospective bentonite deposits on the south-western margin of the Kremnické vrchy Mts.

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