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MINERALOGICAL COMPOSITION AND DISTRIBUTION OF Si, Al, Fe, Mg, AND Ca IN THE FINE FRACTIONS OF SOME CZECH AND SLOVAK BENTONITES

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Abstract: Phase composition of the $<2\ \mu m$ fractions of eleven samples from nine Czech and Slovak bentonite deposits were studied by X-ray diffraction, infrared spectroscopy, thermal analysis, and acid dissolution (AD) techniques. Smectite was the main phase in all samples, but only one was monomineralic. The amount of non-smectitic phases varied between 18 and 51 mass %. Readily soluble (in 6M HCl at 95 °*C*) and insoluble components were found in all samples. Exchangeable calcium and hydrated forms of aluminium and of Fe(III) oxides and hydroxides are usually the main components of readily soluble phases, but Mg as a constituent of these phases cannot be excluded. Crystalline phases (kaolinite, anatase, cristobalite), a partly weathered hydrated volcanic glass and SiO_2 from smectite tetrahedra are expected in the insoluble components. Acid dissolution enables the calculation of reasonable structural formulas of smectites containing extraneous phases.

Key words: bentonite, smectite, structural formula, acid dissolution, XRD, infrared spectroscopy, DTA.

Introduction

The three main regions of bentonite deposits in Czechoslovakia are shown in Fig. 1. Their formation belongs to the young volcanics of the Neogene age.

The parent rocks of the Northwest-Bohemian deposits (region 1 in Fig. 1) are ultrabasic and basic effusives and pyroclastics of basanite, olivinic basalt, and tephrite types. The smectite components are mainly Fe-bearing members of the beidellite—nontronite series. Autohydrothermal decomposition of parent rocks is believed to be the leading process of their formation, while weathering processes were of secondary importance only (Franče 1983; Kraus & Kužvart 1987).

The Slovak bentonite deposits were reviewed recently by Kraus et al. (1989). The Central Slovakian deposits (region 2 in Fig. 1) are connected with two types of neovolcanic rocks: andesites (Hrochoť) and rhyolites (Stará Kremnička - Jelšový Potok). If parent rocks were andesitic pyroclastics, the smectite is a member of the beidellite-nontronite series. If the bentonites were developed from rhyolitic pyroclastics, montmorillonite is the main component. Kraus & Kužvart (1987) considered underwater weathering to be the most probable process of their formation.

The geological position and origin of East-Slovakian deposits (region 3 in Fig. 1) are similar to that of the Central-Slovakian deposits - parent rocks were mainly rhyolitic pyroclastics. Some contain as much as 40 mass % of cristobalite (Konta 1957; Horváth, 1966). Except for the three regions shown in Fig. 1, some minor bentonite and bentonitic clay deposits are dispersed all over the country.

The aim of this paper was (*1*) to present the mineralogical composition of the $<2\ \mu m$ particle-size fractions of eleven Czech and Slovak bentonites, (*2*) to investigate the distribution of individual elements among the phases present in these fractions, and (*3*) to compare the structural formulas obtained by usual recalculation of the bulk chemical analysis with those obtained from acid dissolution data.

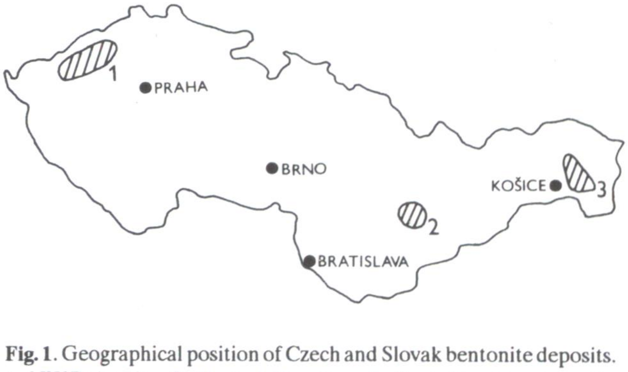

Fig. 1. Geographical position of Czech and Slovak bentonite deposits. 1 - NW Bohemian; 2 - Central-Slovakian; 3 - East-Slovakian deposits.

Material and methods

Eleven samples from nine Czech and Slovak deposits were chosen for this study. The materials used were Ca saturated with 0.5 M CaCl solution, fractionated to $<2\ \mu m$, washed free of excess ions using water and ethanol, air-dried at 60 °*C*, and

Table 1: Mineralogical composition of $< 2\,\mu m$ fractions of Ca- saturated Czech and Slovak bentonites.

No.	Locality	Region in Fi1.	Geological unit	Minerals
1	Fintice	3	Košice Basin	S, Cr
2	St. Kremnička-JP	2	Kremnické hory Mts.	S
3	Braňany 1	1	České stedohorí Mts.	S, K
4	Hrochoť	2	Massif of Poľana	S, K
5	Blšany 1	1	Doupovské hory Mts.	S, A
6	Blšany 2	1	Doupovské hory Mts.	S, K, A
7	Braňany 2	1	České stedohorí Mts.	S, K, A
8	Hroznětín	1	Doupovské hory Mts.	S, K, A
9	Střimice	1	České stedohorí Mts.	S, K, A
10	Rokle	1	Doupovské hory Mts.	S, A
11	Černý vrch	1	České stedohorí Mts.	S, K, A

Stará Kremnička - Jelšový Potok,
S - smectite, K - kaolinite, Cr - cristobalite, A - anatase.

Table 2: Chemical composition of ignited $< 2\,\mu m$ fractions of Ca-saturated Czech and Slovak bentonites.

Sample	1	2	3	4	5	6	7	8	9	10	11
SiO_2	73.40	65.51	63.98	60.03	56.27	53.87	58.34	55.14	53.61	53.60	49.64
Al_2O_3	15.61	22.92	23.18	25.48	15.20	17.42	17.37	15.88	18.78	14.09	20.76
Fe_2O_3	3.50	3.81	5.03	8.03	12.88	13.12	13.80	8.49	16.75	18.84	20.44
FeO	0.04	0.03	0.17	0.04	0.04	0.10	0.06	5.40	0.53	0.06	0.06
TiO_2	1.06	0.29	1.25	1.31	5.28	5.83	4.71	5.59	3.70	5.48	3.90
MgO	3.38	3.33	2.52	2.05	3.92	2.85	2.30	3.21	2.93	2.90	2.75
CaO	3.00	3.35	2.40	2.49	4.73	4.10	3.14	4.56	1.98	3.39	1.30
Na_2O	n.a.	0.08	0.03	0.09	0.04	0.10	0.03	0.07	0.14	0.22	0.05
K_2O	n.a.	0.29	0.74	0.18	0.36	0.69	0.06	0.78	0.82	0.77	0.08

n.a. = not analyzed

ground so as to pass a 0.2 *mm* sieve. Mineralogical compositions given in Tab. 1 were obtained from analyses of these $<2\,\mu m$ samples, therefore they need not to be valid for the whole deposits. The chemical analyses recalculated on an ignited basis are presented in Tab. 2. Samples are numbered according to increasing Fe content.

Dissolution in HCl (AD)

One hundred cm^3 of 6 M HCl was heated to 95 °*C* in a 250 cm^3 glass reaction vessel placed in a thermostat. The reaction mixture was occasionally stirred and allowed to react for the desired time. After that it was filtered, washed with water, air-dried at 60 °*C*, and ground so as to pass a 0.2 *mm* sieve. The filtered liquid was combined with the washing solutions and analyzed for Al, Fe, Mg and Ca.

Calculation of structural formulas

Two sets of structural formulas (SF) were calculated. The first one was received from chemical analyses (SFCA) using the method of Kelley (1955). The second was based on acid dissolution data (SFAD) using a modified version (Číčel & Novák 1977) of Osthaus (1954). The dissolution data enabled estimation of the readily soluble (R) or the exchangeable (E) portions of the atoms, the portions bound in the octahedral sheets of the smectites (O), those bound in the tetrahedral sheets (T), and the insoluble components in the system (I), respectively. Only the portions E, O, and T were used for the calculation of SFAD.

Infrared spectroscopy

A Perkin-Elmer model 983 G spectrometer and the KBr pressed- disk technique (0.3 *mg* sample + 200 *mg* KBr) were used.

XRD analysis

A Philips model PW-1050 X-ray diffractometer (40 kV, 18 mA, CuKα - radiation, Ni-filter) was used to analyze either randomly oriented specimens or samples sedimented on to glass slides.

Differential thermal analysis

The DTA, TG, and DTG curves were obtained simultaneously using a Derivatograph Q 1500 D apparatus, with a heating rate of 10 °*C*.

Results and discussion

Mineralogical composition and structural formulas The mineralogical compositions of the samples are given in Tab. 1. XRD and IR analyses revealed that smectite was the dominant phase in all of the samples. Some samples contained minor admixtures of kaolinite and/or anatase (up to 5 mass %), cristobalite was identified in the sample Fintice.

Sole crystalline admixtures were reported in the $< 1\,\mu m$ fractions of Braňany (kaolinite - Shrbená & Vaněk 1981) and Rokle bentonites (anatase - Konta 1986). This is in good agreement with our samples Braňany 1 and Rokle (Tab. 1), while also anatase was identified in Braňany 2. Anatase, siderite, kaolinite and feldspar were found in five of the $< 1\,\mu m$ fractions of Černý vrch bentonite (Šindelář 1984). No siderite and/or feldspar is present in our Černý vrch sample (Tab. 2).

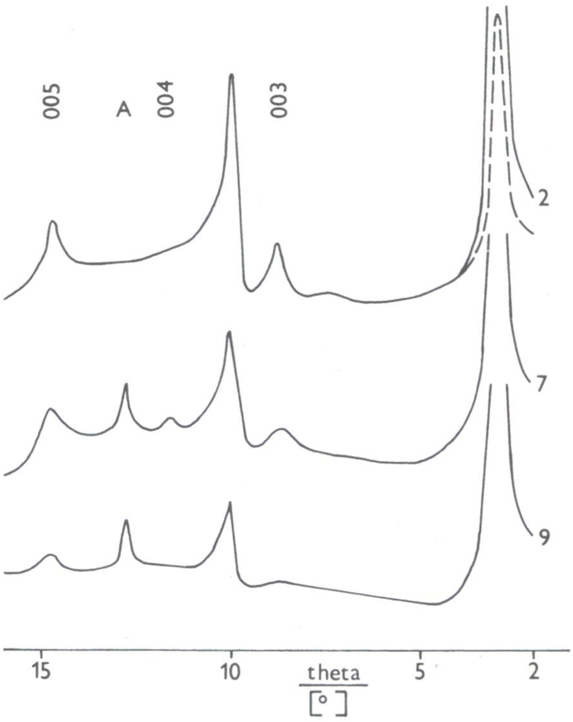

Fig. 2. X-ray diffraction patterns of randomly oriented samples Stará Kremnička - Jelšový Potok (2), Braňany 2 (7) and Střimice (9), A = anatase.

XRD: The positions of the diffraction lines were similar for all samples, but some intensity differences were noticed in the 001 diffractions of randomly oriented samples (Fig. 2) due to variations in amount of Fe in octahedral sites. The 003 diffraction was well developed in samples 1 and 2, but was suppressed in the Fe-rich samples (e.g., samples 7 and 9 in Fig. 2) as described by Wiegmann et al. (1966). The 004 diffraction became more distinct as the octahedral Fe content increased. No 004 diffraction in the pattern of sample 9 indicates lower octahedral Fe content than in sample 7 (Fig. 2).

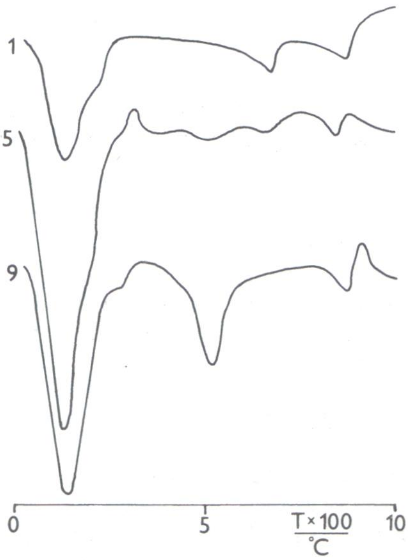

Fig. 3. DTA curves of samples Fintce (1), Blšany 1 (5) and Střimice (9).

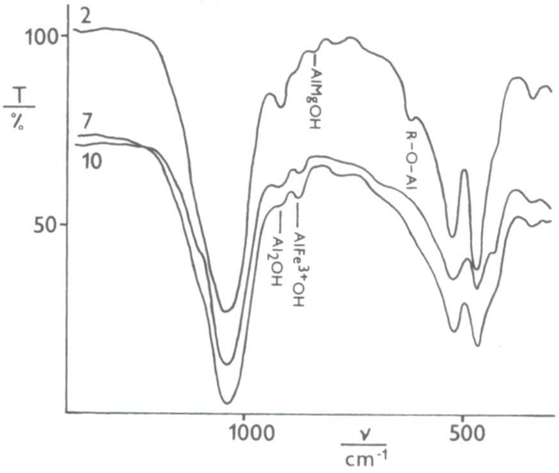

Fig. 4. Infrared spectra of samples Stará Kremnička - Jelšový Potok (2), Braňany 2 (7) and Rokle (10).

DTA: The DTA curves of samples with low Fe content (1 and 2) are characterized by one dehydroxylation peak at a temperature above 650 °*C* presented by pattern 1 in Fig. 3), whereas in the Fe-rich materials (7, 8, and 9) the peak occured in the 500 - 550 °*C* region (represented by pattern 9 in Fig. 3).

Dehydroxylation of samples 3, 4, 5, 6, 10 and 11 occurred at two distinct temperatures (represented by pattern 5 in Fig.3). This is due to the changes in tetrahedral substitution and in Fe content (Johns & Jonas 1954; Čičel 1963). Smectites undergoing dehydroxylation, either in one step at about 500 - 550 °*C* or in two steps, are known as "abnormal" smectites (Greene &Kelly 1957; Mackenzie 1970). They belong to the beidellite-

Table 3: Structural formulas of smectites calculated from thechemical analyses (Tab. 2).

	interlayer	tetrahedra		octahedra			
Sample	M^+	Si	Al	Al	Fe(III)	Fe(II)	Mg
1	0.76	8.65	0.00	2.17	0.31	0.00	0.59
2	0.92	7.80	0.20	3.02	0.34	0.00	0.59
3	0.74	7.75	0.25	3.06	0.46	0.02	0.46
4	0.71	7.33	0.67	3.00	0.74	0.00	0.37
5	1.43	7.50	0.50	1.88	1.29	0.00	0.78
6	1.33	7.29	0.71	2.07	1.34	0.01	0.57
7	0.90	7.56	0.44	2.21	1.34	0.01	0.44
8	1.47	7.46	0.54	1.99	0.86	0.61	0.65
9	0.74	7.07	0.93	1.98	1.66	0.06	0.58
10	1.17	7.28	0.72	1.53	1.92	0.01	0.59
11	0.40	6.63	1.37	1.90	2.05	0.01	0.55

Table 4: Relative amount of atoms bound in smectite and amount of smectite in the $<2\mu m$ fractions of bentonites.

Sample	Si	Al	Fe	Mg	Ca	smectite
			%			
1	42	77	46	63	81	49
2	82	93	66	61	72	82
3	49	53	58	66	91	51
4	86	88	56	37	75	81
5	71	93	57	78	89	69
6	66	71	55	40	50	58
7	84	87	77	74	77	79
8	73	82	68	30	90	68
9	62	68	18	50	89	52
10	49	72	56	31	79	51
11	81	67	12	54	90	59

Table 5: Structural formulas of smectites calculated from the acid dissolution data.

	interlayer	tetrahedra		octahedra		
Sample	M^+	Si	Al	Al	Fe	Mg
1	1.26	7.51	0.49	2.93	0.30	0.77
2	0.74	7.69	0.31	3.29	0.27	0.44
3	1.10	7.48	0.52	2.90	0.52	0.58
4	0.62	7.52	0.48	3.35	0.49	0.16
5	1.62	7.20	0.80	2.19	0.99	0.82
6	0.92	7.43	0.57	2.50	1.14	0.36
7	0.80	7.60	0.40	2.36	1.24	0.40
8	1.62	7.50	0.50	2.32	1.41	0.27
9	0.86	7.74	0.26	2.99	0.52	0.49
10	1.50	6.87	1.13	2.01	1.64	0.35
11	0.50	7.95	0.05	3.19	0.37	0.44

[a] Fe(II) = 0.85, Fe(III) = 0.56
[b] Fe(II) = 0.09, Fe(III) = 0.43

nontronite group and are either ferruginous smectites or Fe-beidellites.

IR spectroscopy: A decrease in intensity of the Al_2OH_3 band at 920 cm^{-1} and an increase in the $AlFe^{3+}OH$ band at 880 cm^{-1} were observed as the Fe content in the samples increased (Fig. 4). The AlMgOH band at 840 cm^{-1} was detected only in samples 1 and 2. The band at 818 cm^{-1}, attributed to the $Fe^{3+}Fe^{3+}OH$ in nontronites (Farmer 1974), was not observed in any sample. The R-O-Al (R = Al, Mg, Li) band at 620 cm^{-1} (Farmer & Russell 1964) was present in low-Fe samples but was absent in the high-Fe members of the beidellite-nontronite series. The above mentioned bands provide approximate information about the amount of Fe bound in the smectite structure.

Structural formulas SFCA: The formal structural formulas calculated from the bulk chemical analyses are shown in Tab. 3. Sample 1 contained significant amount of free silica (cristobalite), so the calculated SFCA (Kelley 1945; Čičel 1981) was incorrect. The sum of the octahedral coefficients, f_{oct}, for samples 4, 8, 9, and 11 indicated an elevated content of Al and/or Fe. The f_{oct} for samples 2, 3, 5, 6, 7, and 10 were acceptable (Čičel 1981). However, the formal acceptability of the f_{oct} does not necessarily guarantee the correctness of the calculated SFCA.

Structural formulas SFAD: Gradual dissolution of the samples in 6 M HCl was studied to distinguish between Si, Al, Fe, Mg and Ca bound in the structure of the smectite and outside its structure (Tab. 4). The structural formulas calculated from the AD-curves (SFAD) are given in Tab. 5. Various portions of atoms bound in smectite have changed the calculated distribution of the central atoms in the octahedra. A significant difference between both SF was found for several samples (Tabs. 3 and 5). The octahedral Fe content increases in the sequence 2, 1, 11, 4, 3, 9, 5, 6, 7, 8 and 10. The AD technique provides reasonable SFAD even for samples containing free SiO_2 (e.g. sample 1) and/or hydrated hydroxides or oxyhydroxides of Al and Fe (e.g., samples 9 and 11). The portions of atoms bound in smectite varied widely (Tab. 4).

Distribution of the main chemical components

Silicon: The relative amount of Si bound in smectites was 42 to 86 % of total Si content. The IR absorption band at 800 cm^{-1} indicates the presence of Si bound in crystalline and/or non-crystalline phases like cristobalite, tridimite, opal, volcanic glass, etc. Crystalline SiO_2 (cristobalite) was found by XRD in sample 1 only. A part of Si is bound in kaolinite in samples 3, 4, 6 - 9 and 11. The AD data led to 8 to 43 mass % of SiO_2 bound outside the smectite structure. Some non-crystalline silica, present probably as a partly decomposed hydrated volcanic glass, was found in all samples.

Aluminium: Aluminium is present in readily soluble, octahedral, tetrahedral and insoluble forms in most samples. Of the total Al in the samples, 53 to 93 % was found in smectites (Tab. 4). Readily soluble Al, which ranged from 0 (sample 7) to 25 % (sample 6) of the total Al content, represented less than 5 % of the total Al in other seven samples. This amount can be neglected in the SF calculations. The amounts of insoluble Al varied between 0 and 44 % of total Al. Kaolinite (less than 5 % of the sample) was detected by XRD in samples 8, 9 and 11, and by IR spectroscopy also in 3, 4, 6 and 7. No other Al-bearing crystalline phases were found in any sample. Al is assumed to be bound also in the residue of the parent rock.

Iron: Readily soluble, octahedral and insoluble portions of Fe were found in all of the studied materials. Existence of at least three phases with distinct Fe populations were reported by Goodman et al. (1988) for several smectites. In none of the present samples was all of the Fe bound in the smectite structure. The amount of extraneous Fe varied from 23 % (sample 7) to 88 % (sample 11) of the total Fe content. Readily-soluble Fe(III), which ranged from 3 to 67 % of the total Fe content, is supposed to be present in hydrated Fe oxides and/or hydroxides, possibly as a fine-grained lepidocrocite and/or goethite. A Mössbauer assay is needed for better characterization of these phases. No crystalline Fe phase was identified in the samples. The amounts of Fe insoluble in 6 M HCl ranged from 10 to 28 % of the total Fe content.

Magnesium: was found in readily soluble, octahedral and insoluble form in every sample. The amount of Mg bound in octahedra were 30 - 78 % of the total Mg content. Three potential sources of readily soluble Mg are :

a - exchangeable Mg;

b - amorphous gels containing Fe, Al and Mg; and

c - a rapid liberation of Mg from the smectite structure as the first stage of its decomposition by the proton attack.

Because the samples were prepared in the Ca exchanged form, the potential amount of exchangeable Mg is low and can be neglected.

Statistical correlation between Mg(R) and the readily soluble portions of other cations present in the smectites, namely Al, Fe(III) and Al + Fe(III) were tested and gave correlation coefficients, r, of 0.27, 0.51 and 0.50, respectively. These low correlation coefficients indicate that no direct relation exists among the readily soluble components of smectites. The insoluble portion of Mg is supposed to be a part of a partly decomposed hydrated volcanic glass.

Calcium: Using the acid dissolution data, Ca can be distinguished in exchangeable and insoluble forms. The exchangeable Ca represents 50 - 91 % of the total Ca (Tab. 4). The insoluble portion is probably a part of volcanic glass.

Potassium: The basic parent rocks of the samples with the highest K_2O content (3, 6, 8, 9 and 10, Tab. 2) are poor in K. Therefore K is supposed to be bound in illitic layers of very common illite/smectite mixed-layered clays. A further assay is needed to prove this assumption.

Using the distribution of Si, Al, Fe, Mg and Ca (Tab. 3) and assuming no K, Na or Ti is bound in smectite, the relative amount of smectite in the $< 2\,\mu m$ fractions of bentonites was calculated (Tab. 4). The amount of non-smectitic phases varied between 18 and 51 mass % of the ignited sample.

Conclusions

The phase composition of the $< 2\,\mu m$ fractions separated from eleven Czech and Slovak bentonites were determined and characterized by XRD, DTA, IR and acid dissolution. Smectite was found to be the dominant mineral in all samples, but only one of them contained no other crystalline phase.

Readily soluble and insoluble components were found by AD in all of the samples. The amount of each of these extraneous phases was in the range of 18 - 51 mass % of the sample.

The distribution of principal atoms (Si, Al, Fe, Mg and Ca) was determined from the AD data. The results were then used for structural formula (SFAD) calculations. The SFAD were found to be suitable even for samples containing free silica and/or other extraneous components.

No crystalline readily soluble phase was found in the samples. The readily soluble portions of Al, Fe and Mg are supposed to be bound in poorly crystallized, hydrated oxides and/or hydroxides. The presence of Mg in these gels is still questionable.

The portions of atoms which are insoluble likely are bound either in crystalline phases (kaolinite, cristobalite) and/or in a partly weathered volcanic glass.

Correct determination of structural formulas of smectites is of importance also in the technical use of bentonites. Their technological suitability is strongly affected by the composition of the smectite layers, and by some admixtures, e.g. iron oxides.

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References

Číčel B., 1963: On the problem of bond strength of OH groups in layer silicates. *Geol. Práce, Spr.* (Bratislava), 30, 249 - 272.

Číčel B., 1981: The influence of mineral impurities on the calculated statistical distribution of atoms in UCF of smectites. In: Konta J. (Ed.): Proc. 8th Conf. *Clay Miner. Petrol.*, Teplice 1979, Charles Univ., Prague, 35 - 40.

Číčel B. & Novák I., 1977: Dissolution of smectites in hydrochloric acid. I. Half-time of dissolution as a measure of reaction rate. In: Konta J. (Ed.): Proc. 7th Conf. *Clay Miner. Petrol.*, Karlovy Vary 1976, Charles Univ., Prague, 163 - 171.

Farmer V. C. & Russell J. D., 1964: The infra-red spectra of layer silicates. *Spectrochim. Acta*, 20, 1149 - 1173.

Farmer V. C., 1974: Layer silicates. In: Farmer V. C. (Ed.): Infrared spectra of minerals. *Mineralog. Soc.*, London, 331 - 363.

Franče J., 1983: Bentonites. In: Kužvart M. (Ed.): *Deposits of industrial materials of Czechoslovakia. Charles Univ.*, Prague, 189 - 200 (in Czech).

Goodman B. A., Nadeau P. H. & Chadwick J., 1988: Evidence for the multiphase nature of bentonites from Mösbauer and EPR spectroscopy. *Clay Miner.*, 23, 147 - 159.

Greene-Kelly R., 1957: The montmorillonite minerals (smectites). In: Mackenzie R. C. (Eed.): Differential thermal investigation of clays. *Mineral. Soc.*, London, 140 - 164.

Horváth I., 1966: Crystallochemical structure of montmorillonitonites from East Slovakia - possibility of its determination and significance. *Silikaty* (Prague) 10, 152 - 16 (in Slovak).

Johns W. D. & Jonas E. C., 1954: Some observations on the relation between isomorphism and properties of clays. *J. Geol.*, 62, 163 - 171.

Kelley W. P., 1945: Calculating formulas for the fine grained minerals on the basis of chemical analysis. *Amer. Miner.*, 30, 1 - 26.

Kelley W .P., 1955: Interpretation of chemical analysis of clays. *Clays and Clay Miner.*, 1, 92 - 94.

Konta J., 1957: *Clay minerals of Czechoslovakia. Academia*, Prague, 1 - 319 (in Czech).

Konta J., 1986: Textural variation and composition of bentonite derived from basaltic ash. *Clays and Clay Miner.*, 34, 257 - 265.

Kraus I., Hroncová Z., Horský S. & Mihalič A., 1989: Deposits and occurrences of bentonites in Slovakia. *Miner. slovaca* (Bratislava), 21, 525 - 531 (in Slovak).

Kraus I. & Kužvart M., 1987: Deposits of industrial materials. *SNTL & ALFA*, Prague, 103 - 109 (in Czech).

Mackenzie R. C., 1970: Simple phyllosilicates based on gibbsite- and brucite-like sheets. In: Mackenzie R. C. (Ed.): Differential thermal analysis. *Academic Press*, London, 1, 497 - 551.

Osthaus B. B., 1954: Chemical determination of tetrahedral ions in nontronite and montmorillonite. *Clays and Clay Miner.,* 2, 404 - 417.

Shrbená B. & Vaněk J., 1981: Scanning electron microscope investigation of the Braňany bentonite. In: Konta J. (Ed.): *Proc. 7th Conf. Clay Miner. Petrol.*, Teplice 1979, Charles Univ., Prague, 119 - 128.

Šindelář J., 1984: Bentonite from the Cerny vrch deposit (NW Bohemia). In: Konta J. (Ed.): *Proc. 8th Conf. Clay Miner. Petrol.,* Zvolen 1982, Charles Univ., Prague, 93 - 100.

Wiegmann J., Horte C.H. & Kranz G., 1966: Mineralanalytische Untersuchungen an Gliedern der Montmorillonitgruppe. Ber. deutsch. *Ges. geol.* Wiss. B *Miner. Lagerstättenf.* (Berlin), 11, 317 - 342.