INFRARED SPECTRA OF SOME CZECH AND SLOVAK SMECTITES AND THEIR CORRELATION WITH STRUCTURAL FORMULAS

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Abstract: Infrared spectra of the $<2\,\mu m$ fractions of eleven Czech and Slovak bentonites were analyzed. The sensitivity of OH vibrations to the nearest cationic environment was examined in the domain of stretching and bending vibrations. A shift of the absorption band near $3620\ cm^{-1}$, ascribed to OH stretching vibrations, to lower frequencies with increasing octahedral Fe^{3+} for Al substitution was observed. Integrated intensities of the AlAlOH (near $920\ cm^{-1}$) and Fe^{3+}AlOH (near $880\ cm^{-1}$) bands were correlated with the coefficients of octahedral cations in the structural formulas calculated from chemical analysis (SFCA) and from acid dissolution data (SFAD). Analysis of variance gave significantly better values for correlation of SFAD coefficients and confirmed that SFAD show better than SFCA the real composition of smectites. Admixtures of amorphous silica were found in all, kaolinite and cristobalite in some of the samples.

Key words: bentonite, smectite, structural formula, infrared spectroscopy, OH vibrations.

Introduction

The structural formulas of clays calculated from chemical analyses (Kelly 1955) are often distorted due to non-monomineral composition of the samples. Číčel (1981) reviewed the effect of admixtures on the structural formulas of smectites. Osthaus (1954, 1956) used acid dissolution of smectites for determination of the amount of ions in octahedral and tetrahedral coordination. Fine fractions of Czech and Slovak bentonites were studied recently by Číčel et al. (1992). Smectite was the main mineral in all of them, but only one sample was monomineralic. The structural formulas calculated from chemical analysis (SFCA) and from acid dissolution data (SFAD) differed significantly for several samples. The sensitivity of infrared spectroscopy to mineralogical and chemical differences between clay minerals is known (Stubican & Roy 1961; Farmer & Russell 1964; Farmer 1974). Craciun (1984, 1987) found the Fe^{3+} for Al octahedral substitution in montmorillonites could be identified and in some cases semiquantitatively evaluated by IR spectroscopy, using absorption bands due to OH stretching and bending vibrations.

The purpose of this study was to compare the structural formulas of Czech and Slovak smectites calculated from chemical analysis and from acid dissolution data with their infrared spectra in the region of OH vibrations, and to identify by IR spectroscopy the non-smectitic phases present in the samples.

Materials and methods

The bentonites chosen for this study, their mineralogical composition, and their structural formulas are given in Číčel et al. (1992). The octahedral coefficients from SFCA and SFAD are summarized in Tab. 1.

Table 1: Population of octahedral cations in $<2\,\mu m$ fractions of Ca-saturated bentonites, calculated per $O_{20}(OH)_4$ from chemical analysis (SFCA) and from acid dissolution data (SFAD) (Číčel et al. 1992).

No	Locality	octahedral coefficients					
		Al		Fe		Mg	
		SFCA	SFAD	SFCA	SFAD	SFCA	SFAD
1	Fintice	2.17	2.93	0.31	0.30	0.59	0.77
2	St. Krem.-JP[1]	3.02	3.29	0.34	0.27	0.59	0.44
3	Brañany 1	3.06	2.90	0.48	0.52	0.46	0.58
4	Hrochoť	3.00	3.35	0.74	0.49	0.37	0.16
5	Blšany 1	1.88	2.19	1.29	0.99	0.78	0.82
6	Blšany 2	2.07	2.50	1.35	1.14	0.57	0.36
7	Brañany 2	2.21	2.36	1.35	1.24	0.44	0.40
8	Hroznětín	1.99	2.32	1.47[a]	1.41[b]	0.65	0.27
9	Střimice	1.98	2.99	1.72[c]	0.52[d]	0.58	0.49
10	Rokle	1.53	2.01	1.93	1.64	0.59	0.35
11	Černý vrch	1.90	3.19	2.06	0.37	0.55	0.44

[1]Stará Kremnička - Jelšový Potok
[a]Fe(II) =0.61, Fe(III) = 0.86 [b]Fe(II) = 0.85, Fe(III) =0.56
[c]Fe(II) = 0.06, Fe(III) = 1.66 [d]Fe(II) = 0.09, Fe(III) = 0.43
Other samples: Fe(II) $\leq$ 0.02

Infrared spectroscopy

The potassium bromide pressed-disk technique (0.3 mg of a sample and 200 mg of KBr) was used. The diameter of the pellets

was 13 *mm*. IR spectra (4000 - 300 cm^{-1}) were recorded with a Perkin - Elmer 983 G double-beam infrared spectrophotometer, connected to a Perkin - Elmer Data Station 3700. The integrated absorption intensities of the OH bands, measured by the base-line method, were obtained using the Application Program of the Data Station .

Results and discussion

Spectra - structure relationships

Vibrations involving protons, especially OH stretching vibrations are directly affected by the nearest cationic environment and provide information on the nature and content of these cations. All samples showed an absorption band in the range 3620 - 3600 cm^{-1}, which was assigned to stretching vibrations of OH groups coordinated to octahedral cations. Both the position and the shape of the band was affected by the composition of the octahedral layer. The OH vibrations of montmorillonite Jelšový Potok absorbed near 3623 cm^{-1}. The higher content of iron broadened the band and shifted it to lower values - e.g. 3618 cm^{-1} for Hroznětín and 3605 cm^{-1} for Rokle (Fig.1). Vibrations of FeFeOH group in nontronites were reported to absorb near 3550 cm^{-1} (Farmer 1974).
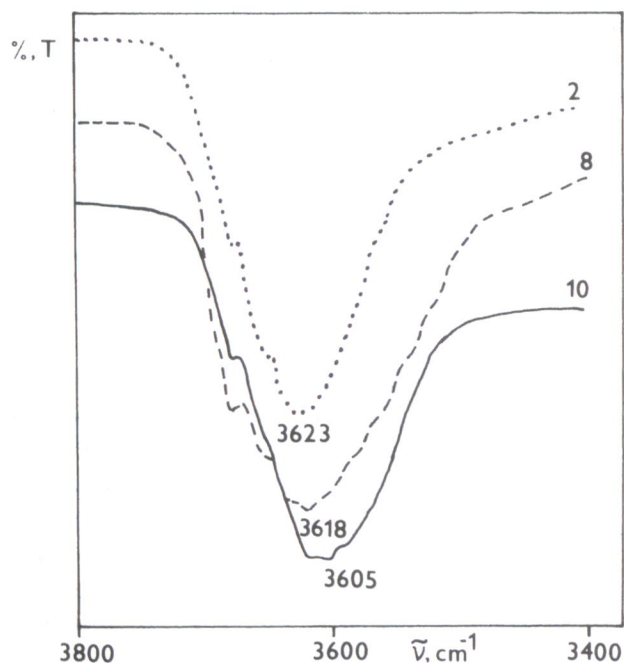

Fig. 1. OH stretching vibrations of samples Stará Kremnička - JP (2), Hroznětín (8) and Rokle (10), dehydrated at 200 °C for 6 hours.

The bending vibrations of OH groups often give a clearer indication of octahedral composition than do the stretching vibrations, as the former give separate bands for different species of hydroxyl. In dioctahedral smectites, AlAlOH, Fe^{3+}AlOH and AlMgOH absorb near 920, 880 cm^{-1} and 840 cm^{-1}, respectively, (Farmer 1974). The IR spectra of smectites with different composition of octahedral layers showed different intensities of the bands in the range 920 - 800 cm^{-1} (Fig. 2). Rising Fe^{3+} for Al substitution caused an increase of absorption band intensity near 880 cm^{-1} and its decrease near 920 cm^{-1} . The band of Al MgOH vibrations was observed only in samples 1, 2, 3 and 5.
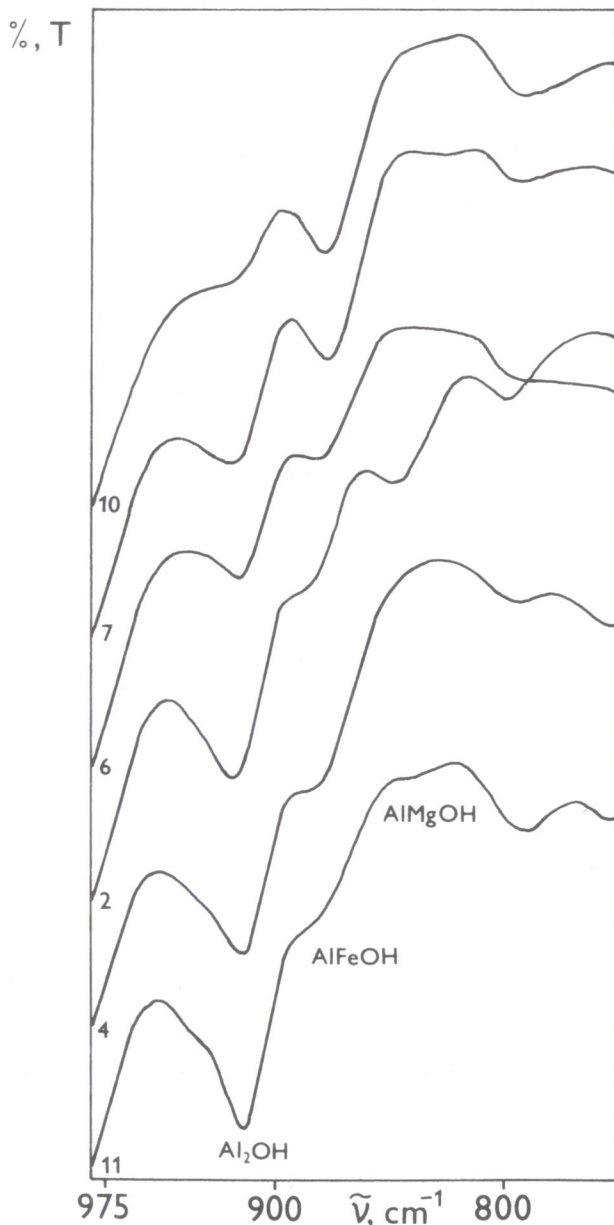

Fig. 2. OH bending vibrations of samples Stará Kremnička - JP (2), Hrochoť (4), Blšany 2 (6), Braňany 2 (7), Rokle (10) and Černý vrch (11).

The integrated band intensities of OH vibrations were assumed to be proportional to the number of OH groups associated with the certain pair of octahedral cations (Craciun 1984; Slonimskaya et al. 1986). Integrated intensities of the AlAlOH (near 920 cm^{-1}) and Fe^{3+}AlOH (near 880 cm^{-1}) bands were correlated with the coefficients of octahedral cations in the structural formulas SFCA and SFAD (Tab. 1). The slope and intercept values for the calculated straight lines are given in the captions of Figs. 3 and 4. Analyses of variance gave significantly better values for correlation of SFAD coefficients ($R^2 = 90$ % for Al and 83 % for Fe) than for SFCA coefficients ($R^2 = 71$ % for Al and 22 % for Fe). R is the multiple correlation coefficient, R^2 denotes the percentage of the total variation in the data about the average $\bar{y}$. These results suggest the SFAD show better than SFCA the real composition of smectites. This is reasonable considering the effect of non-smectitic phases on SFCA and their minor effect on SFAD calculation (Číčel et al. 1992).
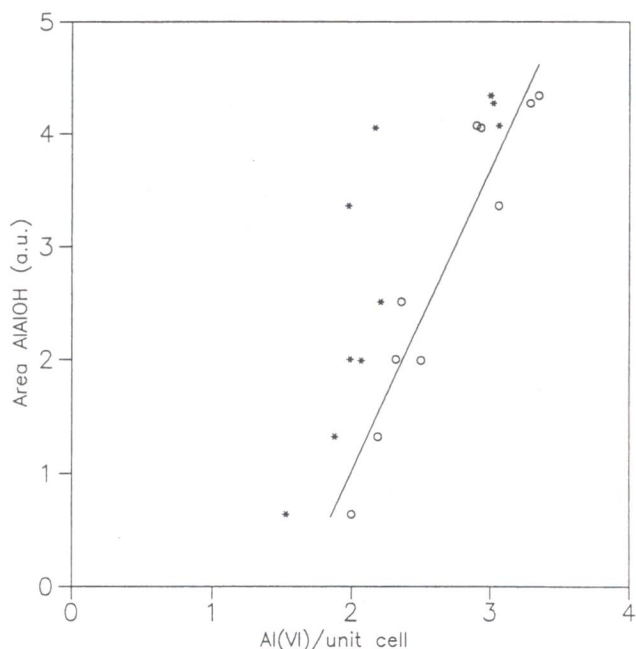
Fig. 3. Relationships between the integrated intensity of the AlAlOH absorption band near $920\,cm^{-1}$ and octahedral Al coefficients in SFCA (*) and SFAD (o). The solid line (y = 2.72x - 4.45, x = 2.01 - 3.35, R^2 = 0.90) is calculated for the SFAD values, the line for SFCA (y = 2.09x - 1.94, x = 1.53 - 3.06, R^2 = 0.71) is not shown. (a.u.) = area unit
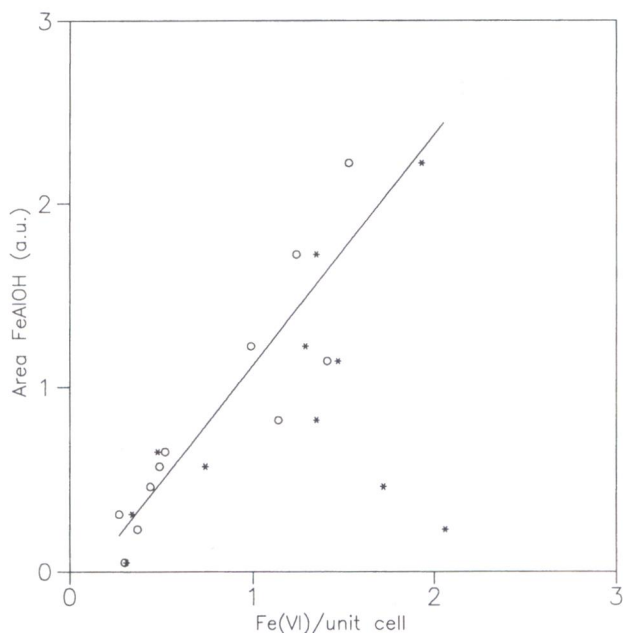

Fig. 5. OH stretching vibrations of samples with kaolinite (Hrochoť (4), Černý vrch (11)) and without kaolinite (Stará Kremnička - JP (2)) admixture.

Fig. 4. Relationships between the integrated intensity of the Al Fe^{3+}OH absorption band near $880\,cm^{-1}$ and octahedral Fe^{3+} coefficients in SFCA (*) and SFAD (o). The solid line (y = 1.25x - 0.16, x = 0.27 - 1.64, R^2 = 0.83) is calculated for the SFAD values, the line for SFCA (y = 0.50x + 0.27, x = 0.31 - 2.06, R^2 = 0.22) is not shown. (a.u.) = area unit

Fig. 6. IR spectra of samples Fintice (1) and Stará Kremnička - JP (2).

Admixtures

The IR spectra were used to identify the non-smectitic phases present in the $<2\,\mu m$ fractions of bentonites. Vibrations of crystalline (kaolinite, cristobalite) and amorphous (volcanic glass) admixtures were found in the spectra.
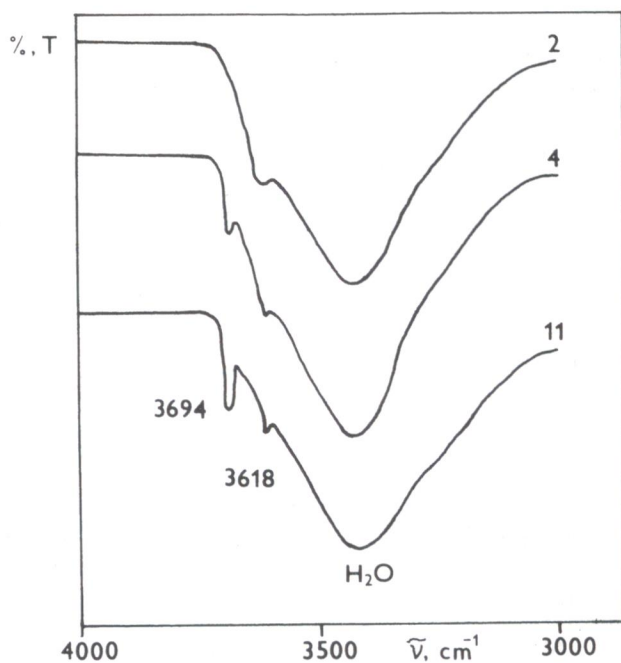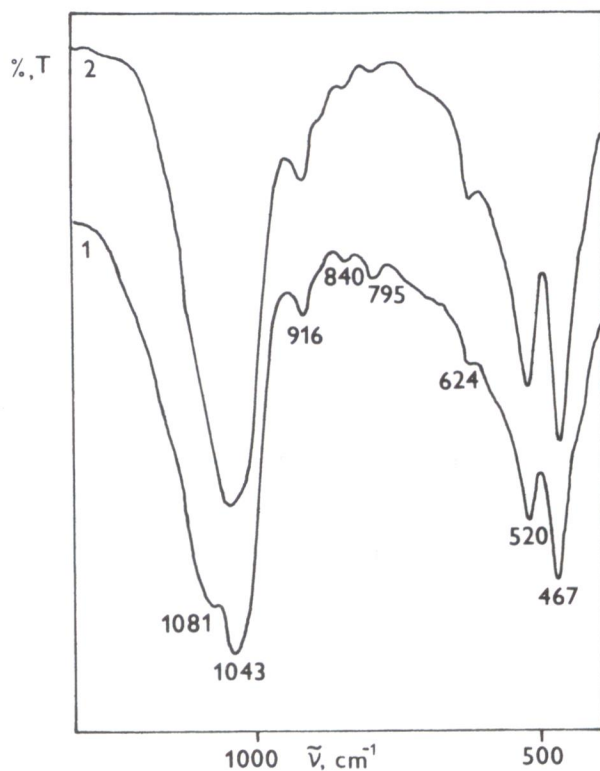
The high frequency OH stretching band at $3694\,cm^{-1}$ indicates minor amounts of kaolinite in the samples 3, 4, 6, 7, 8, 9 and a bigger amount in sample 11 (Fig. 5). Bending OH vibrations of kaolinite absorb near $915\,cm^{-1}$ (Farmer 1974). Thus the high value of integrated intensity of the band near $913\,cm^{-1}$ in sample 11 was associated not only with AlAlOH vibrations of smectite,

but also with the vibrations of kaolinite. Therefore sample 11 was not included into the correlation of spectral data with the Al content (Fig. 3). Kaolinite was identified by XRD only in samples 8, 9 and 11.

A very strong band near 1040 cm^{-1} assigned to stretching Si-O vibrations of smectites, and a weak band of Si-O groups of amorphous silica near 790 cm^{-1} (Farmer 1974) were present in all spectra. The absorption bands at 1081, 795 and 624 cm^{-1} indicate presence of cristobalite (van der Marel & Beutelspacher 1976; Craciun 1987) in sample 1 Fintice (Fig. 6). Cristobalite was identified in this sample also by XRD (Číčel et al. 1992).

Conclusions

1 - Better correlation was found for integrated intensities of AlAlOH and AlFe^{3+}OH bands and the coefficients of octahedral cation in the SFAD, compared to that in the SFCA. The results suggest the structural formulas calculated from acid dissolution data are closer to the real composition of eleven smectites than the structural formulas calculated from chemical analyses.

2 - Kaolinite was present in samples 3, 4, 6, 7, 8, 9 and 11, cristobalite in sample 1, amorphous silica in all samples.

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