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PROPORTION OF CENTRAL ATOMS IN OCTAHEDRA OF SMECTITES CALCULATED FROM INFRARED SPECTRA

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Abstract: Three smectites with various Fe content were chosen to study the proportion of the octahedral atoms in the region of stretching and bending OH vibrations. Complex band in OH stretching region was resolved into the components corresponding to OH groups coordinated to specific groupings of octahedral atoms. Proportionality of the integrated intensities of the OH components to the number of absorbing centres of given type was used to calculate the contents of cations in the octahedral sheet. The coefficients of the octahedral atoms thus estimated were found to be close to the values calculated from chemical analysis for sample with minor amount of non-smectitic phase.

Key words: smectite, IR spectroscopy, OH vibrations, octahedral atom contents.

Introduction

Smectites have various genetic origin and show a large compositional range within the montmorillonite-nontronite series. One of the most important questions is the occupation of octahedral sheet by different atoms. Infrared spectroscopy was found to be a useful tool in providing valuable information about mutual proportion of atoms in the octahedral sheet of clay minerals. Vibrations involving proton (hydroxyl stretching and bending) are very slightly dependent on the vibrations of silica and oxygen in the rest of the lattice but are markedly affected by the ions to which these are coordinated (Farmer & Russell 1967). Hydroxyls, thus, serve as a probe for testing the nature and the content of the octahedral cations. The OH stretching region of micaceous minerals have been studied by a number of workers (Saksena 1964; Vedder 1964; Rouxhet 1970; Farmer 1974; Rausell-Colom et al. 1978; Robert et al. 1989). Slonimskaya et al. (1986) suggested a method for quantitative analysis of IR spectra of celadonites and glauconites in the OH stretching region. Few IR studies have been devoted to characterize not only the nature but also the extent of ionic substitution along the smectite series (Farmer 1974; Craciun 1984; Grauby et al. 1991; Madejová et al. 1992).

The aim of this paper was to study the proportion of octahedral atoms in smectites with various Fe content in the region of OH stretching and bending vibrations.

Materials and methods

Ca saturated smectites from Jelšový Potok (Al-rich montmorillonite), Rokle (Fe-rich beidellite) and Nová Ves (nontronite) were studied. XRD revealed the samples contained no kaolin and/or carbonate phase (Čičel et al. 1992; Čičel & Novák 1977), which could affect analysis of octahedral cation contents from IR spectra.

KBr pressed disk technique was used for IR measurements. The diameter of the pellets was 13 *mm*. To examine the OH vibrations 2 *mg* of sample of particle size < 2 μm was added to about 200 *mg* of KBr and mixed for 3 min on vibratory grinder. A pellet obtained after pressing was heated at about 200 $^{\circ}C$ for 8 hours to remove most of the adsorbed water. IR absorption spectra were recorded with PE 983G spectrometer connected to a PE Data station 3700.

Decomposition of the OH stretching band into components was carried out with the help of a standard program, assuming a Lorentzian form of each component. The variable parameters were the location, half-width and intensity of each component. Satisfactory fitting of the spectrum required inclusion of the components near 3400 and 3650 cm^{-1} attributed to molecular water. The value of the minimization function and agreement between experimental and calculated profiles served as criteria for the quality of the decomposition.

Octahedral coefficients calculated from chemical analysis (CA) were received using the method of Kelley (1955).

Results and discussion

IR spectra of the smectites studied show an absorption band in the range 3620 - 3550 cm^{-1} (Fig. 1), which was assigned to stretching vibrations of OH groups coordinated to octahedral cations (Farmer 1974). 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 absorb near 3623 cm^{-1}. The higher content of iron broadened the band and shifted it to 3605 cm^{-1} for Rokle. Vibrations of FeFeOH group in nontronite Nová Ves absorb near 3550 cm^{-1}.

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. For smectites absorption bands situated in 950 - 800 cm^{-1} region were observed (Fig. 2). The first one, located at 918 cm^{-1} for Jelšový Potok was attributed to AlAlOH vibrations (Farmer 1974). For montmorillonite only a slight shoulder, assigned to FeAlOH vibrations, was observed near 880 cm^{-1}. Higher Fe for

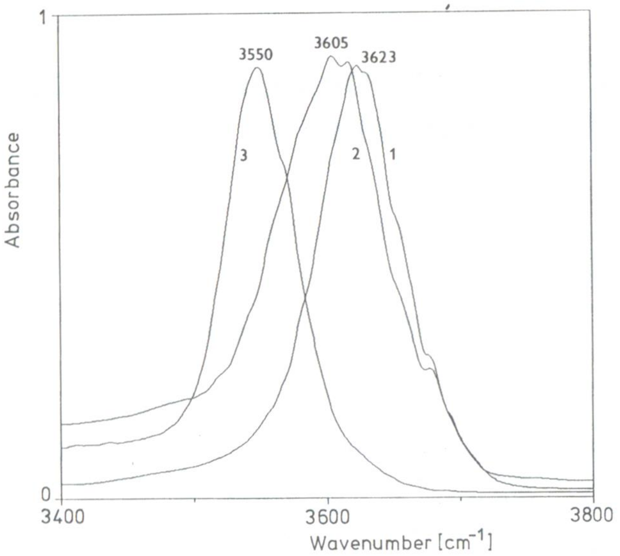

Fig. 1. OH stretching vibrations of samples.
1 - Jelšový Potok, 2 - Rokle, 3 - Nová Ves.

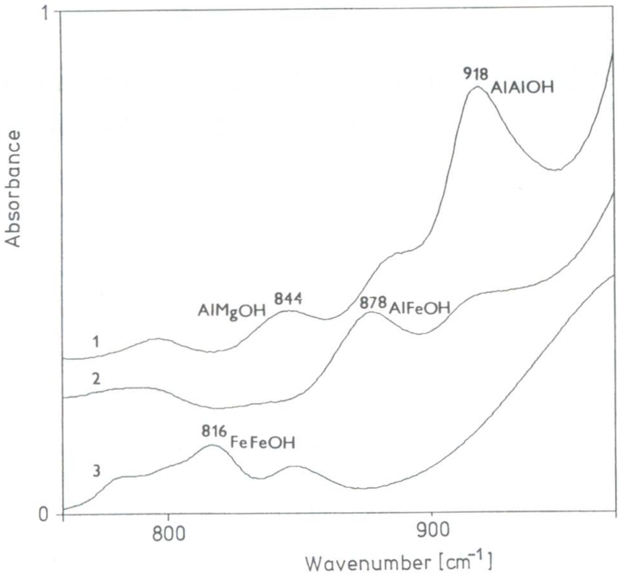

Fig. 2. OH bending vibrations of samples.
1 - Jelšový Potok, 2 - Rokle, 3 - Nová Ves.

Al substitution in beidellite Rokle (Čičel et al. 1992) caused an increase of absorption band intensity near 880 *cm*$^{-1}$ and its decrease near 920 *cm*$^{-1}$. The 840 *cm*$^{-1}$ band is usually attributed to AlMgOH vibrations in smectites. For nontronite Nová Ves the FeFeOH vibrations absorb at 816 *cm*$^{-1}$.

OH stretching vibrations

The IR spectra of smectites show in the OH stretching region a broad complex band which reflects the diversity of environments of the hydroxyl groups. Studies of OH stretching region of micas of known composition have shown, that the band could be resolved into the components corresponding to OH groups coordinated to specific groupings of octahedral atoms. An assumption of approximately equal absorption coefficients for different types of absorbing OH centres (Rouxhet 1970) make possible the use of quantitative IR determinations to short range ordering of octahedral cations around the OH groups .

A method for quantitative analysis of IR spectra in the OH stretching region suggested by Slonimskaya et al. (1986) for celadonites and glauconites was applied to three smectites with different Fe content. The method involves the assignment of the individual OH stretching vibrations to a certain pair of octahedral cations, decomposition of OH band and calculation of octahedral cation content. The wavenumbers of individual OH components, taken from Slonimskaya et al. (1986) and Farmer (1974) were used as the basis for our decomposition. Figs. 3 - 5 present IR spectra of smectites and their resolution into the OH components. The respective wavenumbers are given in Tab. 1. The most intensive bands for Jelšový Potok (Fig. 3) are the bands related to aluminium (AlAlOH, AlMgOH, AlFeOH). The bands due to iron show higher contribution to spectrum for sample Rokle (Fig. 4). The IR spectrum of nontronite Nová Ves contains only the bands of FeFeOH and AlFeOH vibrations (Fig. 5).

The integrated intensities of component bands are proportional to the concentration of OH groups with the given cationic environment. The content of each cation was obtained as a sum of contributions of this cation to the integrated intensities of the bands of those OH groups, which contain the given cation in their coordinational sphere. The population of the octahedral layer was calculated from three independent IR spectra. The contents of Al, Mg and Fe thus estimated were compared with those obtained from chemical analysis (Tab. 2).

The coefficients of octahedral atoms calculated from IR spectra were found to be close to the values from chemical analysis for sample Jelšový Potok. Octahedral Al and Fe contents estimated from IR spectra do not coincide with those from chemical analysis for Rokle. Iron bound in non-smectitic phases - goethite (Čičel et al. 1992), covered in the CA calculation, increases a portion of Fe in octahedral positions. Correctness of the coefficient calculations from chemical data is not sufficient in this case. The IR spectrum of Nová Ves (Fig. 5) contains a band at 3580 cm-1 attributed to AlFeOH vibrations, while according to the chemical analysis calculation the octahedra contain no aluminium. This discrepancy may be due to the fact, that Al and Fe distribution between tetrahedral and octahedral sites used in conventional CA calculation need not to be correct. The higher content of Fe in tetrahedral sites implies the some Al should be placed in octahedral positions. The distribution of iron needs to be confirmed by Mössbauer spectroscopy.

Table 1: Wavenumbers of components of the OH stretching band of montmorillonite Jelšový Potok, beidellite Rokle and nontronite Nová Ves.

Cationpair	Wavenumber [*cm*$^{-1}$]		
	Jelšový Potok	Rokle	Nová Ves
AlMg	3681	3681	–
AlAl	3637	3637	–
AlAl	3620	3619	–
AlMg	3602	3601	–
AlFe^{3+}	3585	3584	3580
Fe^{3+}Mg	3558	3567	–
Fe^{3+}Fe^{3+}	–	3546	3550
Fe^{3+}Fe^{3+}	–	3532	3534

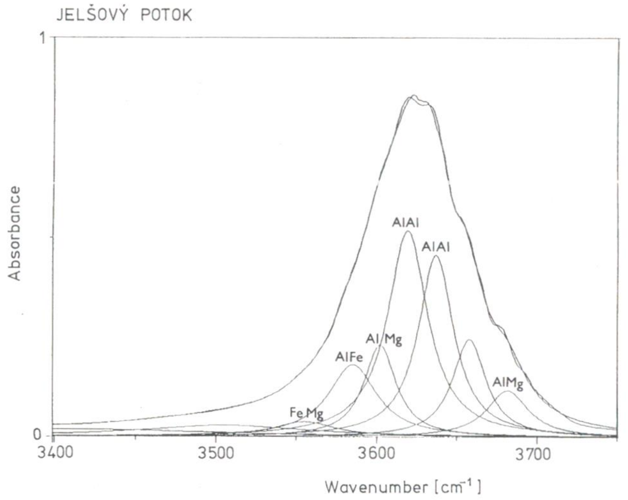

Fig. 3. IR spectrum of montmorillonite Jelšový Potok; experimental and calculated curves and the OH components.

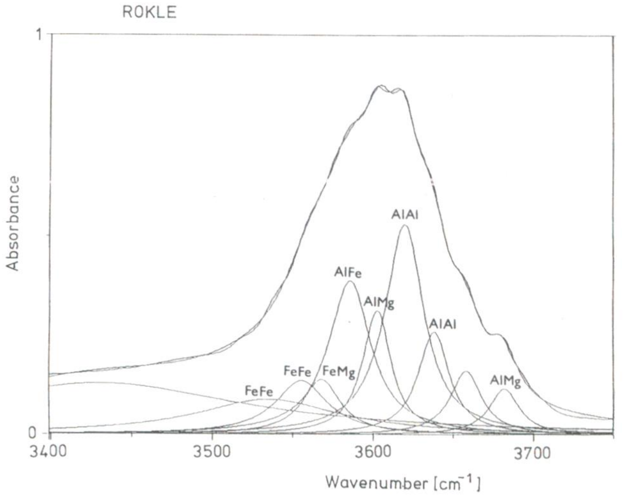

Fig. 4. IR spectrum of beidelitte Rokle; experimental and calculated curves and the OH components.

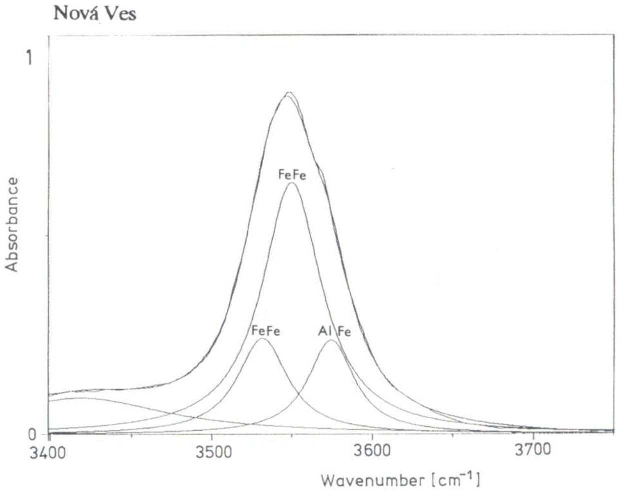

Fig. 5. IR spectrum of nontronite Nová Ves; experimental and calculated curves and the OH components.

Table 2: Population of octahedral cations calculated for Jelšový Potok, Rokle and Nová Ves from chemical analysis (CA) and IR spectra, based on $O_{20}(OH)_4$.

Sample		octahedra		
		Al	Mg	Fe
Jelšový Potok	CA	3.00	0.63	0.38
	IR-1	3.02	0.56	0.42
	IR-2	3.07	0.57	0.36
	IR-3	3.05	0.55	0.40
Rokle	CA	1.53	0.59	1.93
	IR-1	2.05	0.58	1.37
	IR-2	2.06	0.52	1.42
	IR-3	2.03	0.50	1.47
Nová Ves	CA	–	–	3.91
	IR-1	0.31	–	3.69
	IR-2	0.38	–	3.62
	IR-3	0.39	–	3.61

Conclusions

The results show the method of spectral decomposition and correlation of octahedral atoms contents with areas of the corresponding OH bands provides reasonable results for dioctahedral smectites.

The coefficients of octahedral atoms calculated from IR spectra were found to be close to the values received from the chemical analyses for samples containing minor amount of non-smectitic phases. High amount of iron bound in goethite (52 % of total Fe for Rokle), increases the difference between corresponding coefficients significantly. The decomposition of the IR spectrum of nontronite Nová Ves show some Al in the octahedral positions of this clay.

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