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FTIR STUDY OF SOME POLISH SMECTITES

Abstract. Only selected smectites occurring on the territory of Poland were previously studied by infrared spectroscopy. Those analyses were carried out under various experimental conditions, so the results obtained are not fully comparable. The current study involved investigations of some Polish smectites by Fourier infrared spectroscopy. The method has allowed to compare the crystallochemical character of these minerals, and — first of all — to determine the composition of their tetrahedral and octahedral layers. The smectites in question represent dioctahedral varieties, including typical montmorillonites, smectites of the nontronite-montmorillonite group with a variable iron content, and also smectites of the beidellite character.

Key-words: FTIR, Polish smectites, montmorillonite, nontronite, beidellite.

INTRODUCTION

Infrared spectroscopy is one of the techniques which allows investigations of the crystallochemical character of clays, particularly providing data on the structure of the octahedral and tetrahedral layers of these silicates. Some new possibilities have been opened by the development of Fourier transform infrared spectroscopy (FTIR) as well as the computer simulation of spectra and the computer resolution of spectra into their components (Craciun 1984; Slonimskaya et al. 1986; Besson et al. 1987; Michaelian et al. 1991; Dainyak et al. 1992; Madejová et al. 1992, 1994).

Some smectites occurring on the territory of Poland were previously studied by infrared spectroscopy (Wiewióra 1973; Kłapyta 1975; Środoń 1976; Kulesza-Wiewióra 1982; Błaszczak et al. 1994). Those analyses were being carried out over a considerable time-span, using different techniques, preparation of samples and laboratory equipment. Therefore, the results obtained are not always fully comparable. The current study involved investigations of some smectites from major Polish deposits by Fourier infrared spectroscopy. The method has allowed to compare the crystallochemical character of these minerals, and — in particular —

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to determine the type of isomorphic substitutions in their tetrahedral and octahedral layers.

METHOD OF INVESTIGATIONS

The study material was represented by <2 μm clay fractions, separated out of the Chmielnik and Polany bentonites, Milowice montmorillonite clays, Poznań clays from Adamów and Bełchatów, basalt-derived weathering crusts from Męcinka, clays from Adamów and Bełchatów, basalt-derived weathering crusts from Męcinka, clays from Adamów and Bełchatów, basalt-derived weathering crusts from Męcinka,

TABLE 1
List of samples

No.	Localization	Characteristic
1.	Chmielnik	Tertiary bentonite
2.	Polany	Tertiary bentonite (within the Carpathian flysch)
3.	Milowice-1	Carboniferous
4.	Milowice-2	bentonites
5.	Adamów	Tertiary smectite clays
6.	Bełchatów	(overburden of the brown coal deposit)
7.	Machów	Tertiary smectite clay (overburden of the sulphur deposit)
8.	Krzeniów	Tertiary
9.	Męcinka	basalt-derived
10.	Leśna	clays
11.	Dylągówka	Tertiary clinoptilolite-smectite clay (within the Carpathian flysch)



Fig. 1. Localization of samples:
1 — Chmielnik, 2 — Polany, 3 — Milowice,
4 — Adamów, 5 — Bełchatów, 6 — Machów, 7 —
Krzeniów, 8 — Męcinka, 9 — Leśna, 10 — Dylągówka

Krzeniów and Leśna, and clinoptilolite-smectite clays from Dylągówka (Tab. 1, Fig. 1).

Samples were dispersed with an ultrasonic disintegrator in distilled water; then some drops of the suspension were placed on Mylar foil. After evaporation of the water at room temperature, thin layers composed of clay minerals were separated of the Mylar substratum. Another type of samples was made by drying of the suspension on a germanium plate.

Infrared spectra were recorded using a Fourier transform spectrometer (Bio-Rad Digilab Analytical Instruments, USA), model FTS 165.

RESULTS

The infrared spectra of the samples in question reveal within the range 3000—4000 cm^{-1} (Fig. 2—5) absorption bands typical of stretching vibrations of two types of OH groups: those linked to the cations of the octahedral layer of smectites (3500—3700 cm^{-1}) and those incorporated into interlayer water molecules (around 3400 and 3200 cm^{-1}). According to literature data (Stubičan, Roy 1961; Farmer, Russell 1967; Farmer 1971, 1974; Russell 1987), the position and shape of the first of them depend much on the chemical composition of the octahedral layer of a smectite. For a montmorillonite, a maximum around 3620 cm^{-1} attributed to OH vibrations within Al—OH groups is observed. Gradual substitution of Al^{3+} by Fe^{3+} results initially in diffusion of this band toward lower wave numbers,

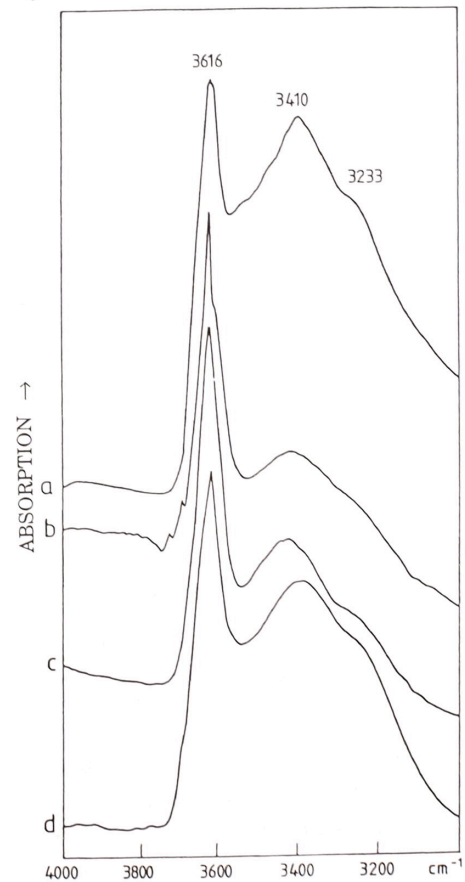


Fig. 2. Infrared spectra of samples:
a — Chmielnik, b — Milowice-1,
c — Milowice-2, d — Adamów

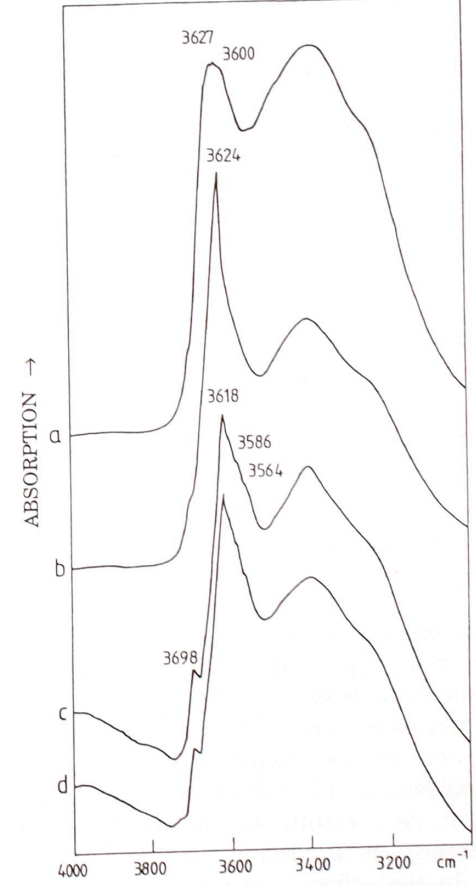


Fig. 3. Infrared spectra of samples:
a — Polany, b — Dylągówka,
c — Krzeniów, d — Męcinka

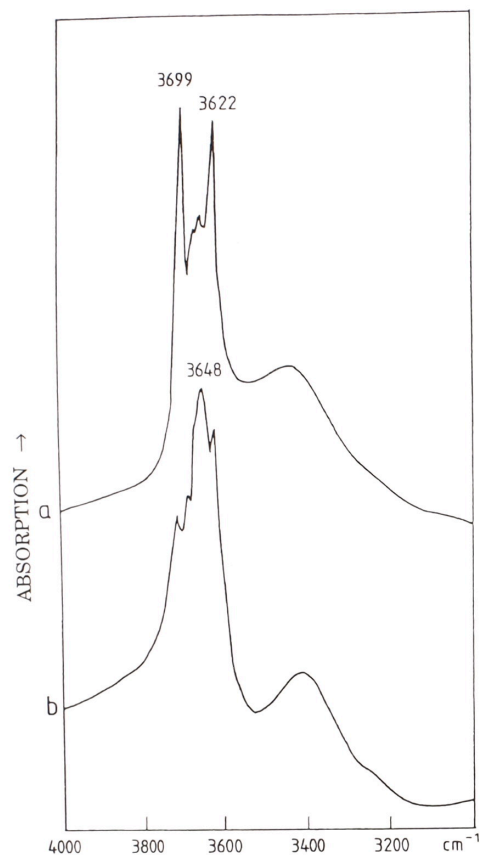
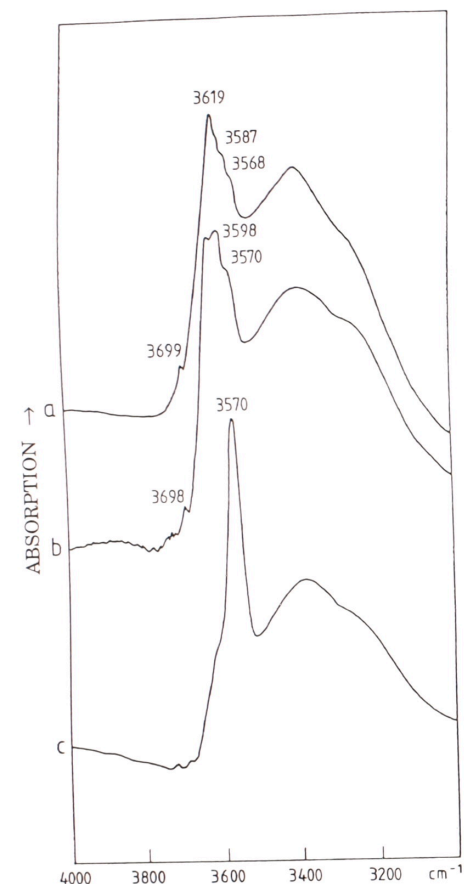


Fig. 4. Infrared spectra of samples:
a — Machów, b — Leśna, c — nontronite
(Pfaffenreuth, Germany)

Fig. 5. Infrared spectra of sample from
Bełchatów: a — before, b — after
subtraction of kaolinite bands

and then in shifting the band in the same direction down to around 3560 cm⁻¹, the value typical of Fe—OH vibrations of nontronite (Farmer, Russell 1967; Goodman et al. 1976).

The stretching vibrations within the Me—OH groups of the octahedral smectite layers are also modified by more distant neighbours of these groups, being considerably affected by isomorphic substitution of Si by Al in the tetrahedral layer. As a result, the absorption band for beidellite shifts toward higher wave numbers, i.e. to around 3660 cm⁻¹.

In the infrared spectra of smectite samples from Chmielnik, Milowice and Adamów (Fig. 2), the absorption band attributed to vibration of the OH groups belonging to octahedral layers is situated in the range 3616—3625 cm⁻¹, proving the presence of montmorillonite. In the spectrum of the Milowice-1 sample (Fig. 2b),

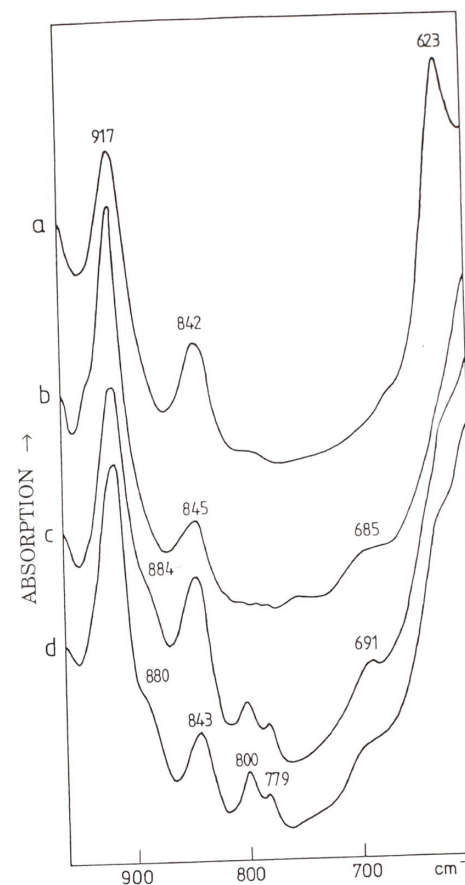


Fig. 6. Infrared spectra of samples:
a — Chmielnik, b — Milowice-1,
c — Milowice-2, d — Adamów

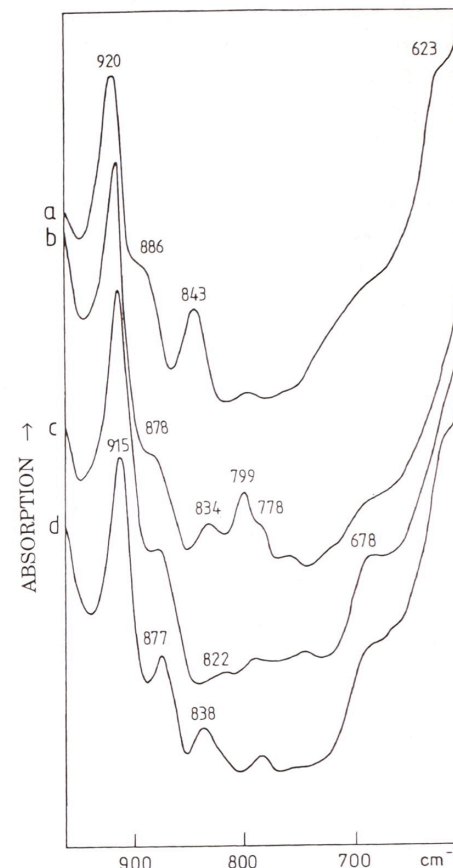


Fig. 7. Infrared spectra of samples:
a — Polany, b — Dylągówka,
c — Krzeniów, d — Męcinka

this band is of a complex character. It has been formed by superposition of two bands — a sharp one and a more diffused one. This fact is probably connected with the presence of two types of unit layers, the smectite and illite ones, in the structure of the mineral in question. This assumption has been confirmed in X-ray investigations which revealed that the sample contains a mixed-layer mineral of the smectite/illite type. Almost identical position of absorption bands of these two components indicates that their chemical composition is similar.

In the infrared spectrum of the Polany smectite (Fig. 3a), beside the band at 3627 cm⁻¹ there is another one, at 3600 cm⁻¹, characteristic of a partial substitution of Al³⁺ by Fe³⁺.

In the spectra of samples from Dylągówka, Krzeniów, Męcinka (Fig. 3b—d), Machów and Leśna (Fig. 4a, b), the band of Me—OH vibrations is clearly asym-

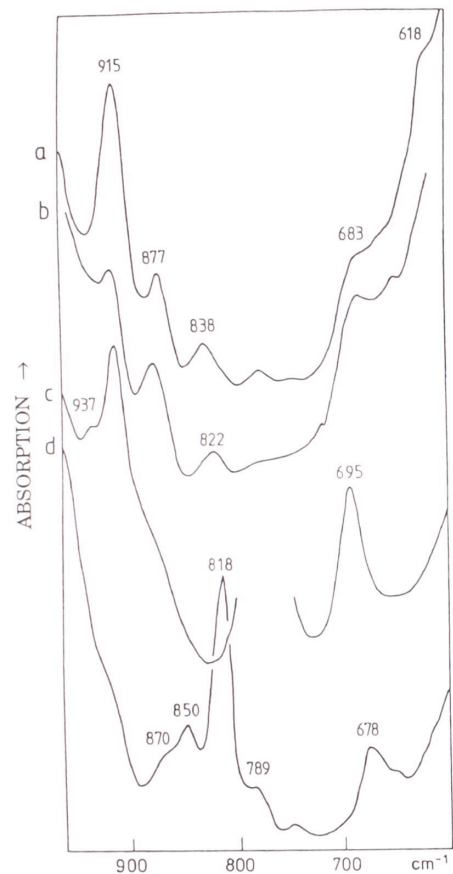


Fig. 8. Infrared spectra of samples:
a — Machów, b — Leśna, c — Bełchatów,
d — nontronite (Pfaffenreuth, Germany)

the chemical composition of the sample are required.

Within the range 600–950 cm^{-1} , the spectra of samples in question (Fig. 6–8) show — first of all — absorption bands attributed to the bending vibrations of the Me–OH groups. The position of these bands depends on the chemical composition of the octahedral layer of a smectite. For dioctahedral smectites, the bending vibrations of the AlAlOH , $\text{AlFe}^{3+}\text{OH}$ and AlMgOH groups occur at around 920, 845–890 and 840 cm^{-1} respectively. When groups $\text{Fe}^{3+}\text{Fe}^{3+}\text{OH}$ are formed in nontronite, the maximum of absorption is shifted to around 815 cm^{-1} (Farmer, Russell 1967; Russell 1987).

The spectrum of the Chmielnik smectite (Fig. 6a) has the character typical of montmorillonite, with intensive bands at 917 and 842 cm^{-1} attributed to the bending vibrations of AlAlOH and AlMgOH groups. The positions of these bands

metrical. Beside a major maximum at 3624–3618 cm^{-1} , characteristic of montmorillonite, its widening toward lower wave numbers is observed. Such a character proves the increasing presence of Fe^{3+} in the octahedral layer of these clays. Within the samples in question, this substitution is the highest for the basalt-derived clay from Leśna, for which the absorption maxima at 3598 and 3570 cm^{-1} are markedly strong, the latter band being typical of nontronite (Fig. 4c). An additional band around 3698 cm^{-1} in the spectra of clays from Krzeniów, Męcinka, Machów and Leśna is caused by the admixture of kaolinite.

Figure 5a presents the spectrum of the Poznań clay from Bełchatów, revealing first of all intensive bands at 3699 and 3622 cm^{-1} and a weaker one at 3648 cm^{-1} . The former two are caused exclusively by kaolinite, the latter one may be a result of coincidence of bands of kaolinite and other clay minerals. After subtraction of kaolinite bands, the remaining spectrum (Fig. 5b) shows the major maximum at 3648 cm^{-1} , suggesting that the Bełchatów smectite is of the beidellitic character. However, the computer-generated subtraction spectrum cannot be here a decisive proof of identification and further studies on

in samples from Milowice, Adamów, Polany, Dylągówka, Męcinka and Machów (Fig. 6–8) vary in the ranges 915–920 cm^{-1} and 834–845 cm^{-1} . The relative ratio of the intensities of the AlAlOH and AlMgOH bands also varies and indicates that the highest amount of Mg^{2+} ions occurs in the octahedral layers of the smectites from Chmielnik, Milowice-2 and Polany, while the lowest in the Dylągówka sample.

The AlMgOH bands have not been revealed in the spectra of samples from Krzeniów and Leśna (Fig. 7c, 8b). In both there is, however, a weak band at 822 cm^{-1} , whose position is close to that of the 818 cm^{-1} band of nontronite (Fig. 8d). The band is connected with the bending vibrations of the $\text{Fe}^{3+}\text{Fe}^{3+}\text{OH}$ groups.

In the spectra of most samples, except for those from Chmielnik (Fig. 6a) and Milowice-1 (Fig. 6b), there is an absorption band between 876 and 886 cm^{-1} , indicating the presence of $\text{AlFe}^{3+}\text{OH}$ groups. The band is the weakest in the spectra of the Milowice-2, Adamów and Bełchatów samples (Fig. 6c, d, 8c; respectively), and the strongest in the spectra of the Krzeniów, Męcinka, Machów and Leśna samples (Fig. 7c, d, 8a, b; respectively).

The comparison of the relative intensities of bands at around 920, 876–886 and 835–845 cm^{-1} indicates that the Leśna smectite has the highest substitution of Fe^{3+} for Al^{3+} in the octahedral layer among the smectites in question.

In the spectrum of the Bełchatów sample (Fig. 8c) there are bands at 937 and 915 cm^{-1} , attributed to the AlAlOH bending vibrations in kaolinite and smectite. There is no band at around 840 cm^{-1} , which would indicate the presence of AlMgOH groups. Their lack confirms indirectly the beidellitic character of this smectite.

Some spectra have absorption bands at around 800 and 780 cm^{-1} , characteristic of a quartz admixture.

The band at around 690 cm^{-1} is attributable to the stretching vibrations of the Al–O groups in tetrahedra (Handke, Mozgawa 1993). Such a band occurs in the spectra of most samples under study but it may also be connected with the presence of kaolinite. If kaolinite does occur, the band in question is of little use in the determination of the crystallochemical character of smectites.

In the spectrum of the Chmielnik smectite (Fig. 6a), there is an intense band at 623 cm^{-1} . According to some authors (Farmer, Russell 1964), this band is caused by vibrations within R–O–Al groups (where R = Al, Mg, Li), while its intensity decreases with the increasing content of Fe^{3+} in the crystal structure of a smectite. In the spectra of remaining samples this band is either significantly weaker or disappear completely. It has not been possible, however, to correlate its intensity with the iron content in some samples under study.

CONCLUSIONS

The results of current investigations indicate that the Chmielnik smectite represents a typical, Al-rich montmorillonite with isomorphic substitutions Mg–Al in the octahedral layer. No iron has been found in the crystal structure of this mineral.

The similar crystallochemical character has been found to occur in the smectite unit layers in the mixed-layer smectite-illite clay of the Milowice-1 sample.

The smectites of the Milowice-2, Adamów, Polany, Dylągówka, Męcinka and Machów samples are typical ferrous montmorillonites of the montmorillonite-nontronite range. They still show the presence of isomorphic substitutions Mg-Al in the octahedral layer. The iron content in the crystal structure is low in the Milowice-2 and Adamów smectites; in the remaining samples the content of $\text{AlFe}^{3+}\text{OH}$ groups gradually increases (Polany → Dylągówka → Męcinka → Machów).

The smectites from Krzeniów and Leśna do not have Mg-Al substitutions in their octahedra. In the structure of both minerals there are $\text{AlFe}^{3+}\text{OH}$ groups, but the Leśna smectite has considerably higher its iron content. Among the samples in question this smectite is the closest to nontronite. Despite the lack of direct spectroscopic proofs, the isomorphic substitutions Al-Si in the tetrahedral layer are the source of cation exchange capacity of the Krzeniów and Leśna smectites. These two varieties belong thus to the beidellite-nontronite range.

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BADANIA NIEKTÓRYCH POLSKICH SMEKTYTÓW METODĄ SPEKTROSKOPII W PODCZERWIENI (FTIR)

Streszczenie

Smektyty występujące na obszarze Polski były badane wyrywkowo metodą spektroskopii w podczerwieni. Analizy te wykonano w różnych warunkach eksperymentalnych, dlatego porównanie wyników nie jest w pełni możliwe. W pracy przedstawiono wyniki badań smektytów z różnych rejonów Polski, przeprowadzone przy zastosowaniu fourierowskiej spektroskopii w podczerwieni. Pozwoliły one na porównanie charakteru krystalochemicznego tych minerałów, a przede wszystkim określenie budowy warstw oktaedrycznych i tetraedrycznych. Stwierdzono, że badane próbki reprezentują różne rodzaje smektytów dioktaedrycznych. Występują wśród nich typowe montmorillonity, smektyty o zmiennej zawartości żelaza z szeregu montmorillonit-nontronit, a także smektyty o charakterze beidellitowym.