

INFRARED SPECTROSCOPIC STUDY OF SMECTITES OCCURRING IN LOWER SILESIAN BASALT WEATHERING PRODUCTS

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Abstract: The smectites from various localities of Lower Silesian basalt weathering products were investigated in the mid-infrared range. They differ mostly in composition of the octahedral sheet. From that point of view aluminium-iron and aluminium-iron-magnesium-smectites can be distinguished. Silicon in tetrahedral sheet is partly substituted by aluminium but the extent of this substitution varies within the samples.

Key words: smectite, infrared spectroscopy, octahedral and tetrahedral sheets.

Introduction

Lower Silesian basalt weathering products are clays showing specific properties. They are practically free of quartz, strongly ferruginous (containing about 20 wt. % Fe_2O_3), very fine crystalline but displaying significant degree of aggregatization (Dyjur et al. 1991). Three mineralogical varieties of these rocks can be distinguished: smectite, kaolinite (halloysite) and smectite-kaolinite (Stoch et al. 1977). The weathering crusts in question are often cut by a network of veinlets of different thicknesses, filled with a clay substance predominantly of smectite composition, presumably precipitated from post-magmatic solutions (Kosciówko et al. 1986).

Smectites occurring in basalt weathering products are represented nearly exclusively by dioctahedral montmorillonite showing a relatively high share of charge coming from tetrahedral sheet. They contain calcium and magnesium in their interlayer spaces (Dyjur et al. 1991).

The aim of this study was to obtain more detailed data on smectites occurring in Lower Silesian basalt weathering products using infrared spectroscopy.

Materials and methods

Six samples of smectite from different regions of Lower Silesia were selected for these studies (Tab. 1). Five of them are products of hypogene weathering of basalt (samples: VII/4/27; V/5bis/28; VI/4/8; Ls II and II/2a/19) and the sixth (WG_M -8A) represents the substance precipitated from post-magmatic solutions.

For proper interpretation of results, the measurements of standards: montmorillonite of Wyoming (Wyoming SWy-1) and Cheto (Arizona SAZ-1) types as

Table 1: List of samples.

No.	Sample	Locality
1	VII/4/27	Biskupice, borehole VII/4, depth 48.0 m
2	WG_M -8A	Winna Góra (region Jawor), quarry of basalt
3	V/5bis/28	Wilczyce (region of Legnica), borehole V/5bis, depth 49.2 m
4	VI/4/8	Piotrowice (region of Jawor), borehole VI/4, depth 18.5 m
5	Ls II	Lesna (region Luban), quarry of basalt "Lesna N"
6	II/2a/19	Lesna (region of Luban), borehole II/2a, depth 36.2 m

well as Black Jack beidellite (saturated with Mg) and Fe-smectite (Manito, Wash.) were carried out under the same conditions.

The infrared spectra were measured with the Digilab FTS-60V Fourier transform infrared spectrometer. Spectra were collected after 256 scans at 4 cm^{-1} resolution in the mid-infrared range. The positions of maxima and shoulders were described in the spectra using the BIO-RADTM software.

All the samples analyzed were prepared by the potassium bromide pressed-disk technique (0.6 mg of a sample and 300 mg of KBr). The diameter of the pellets was 12 mm.

Results and discussion

Preliminary studies carried out for two grain-size fractions (2 - $0.2\text{ }\mu\text{m}$ and $< 0.2\text{ }\mu\text{m}$), separated from the samples Ls II and VII/4/27 give identical IR spectra.

Consequently, in this study each weathering crust is represented only by one grain-size fraction - 2 - 0.2 μm .

Studies in the range 3000 - 4000 cm^{-1}

Absorption spectra of standard minerals are presented in Fig. 1. Two intense bands occur in the range 3000 - 4000 cm^{-1} .

Depending on the type of smectite the first of them has a maximum between 3550 and 3700 cm^{-1} , whilst the second - in the range 3350 - 3450 cm^{-1} . Additionally, there is a shoulder between 3200 - 3250 cm^{-1} .

The bands between 3550 and 3700 cm^{-1} are assigned to the stretching vibrations of OH groups coordinating octahedral cations in crystal lattice of smectites. For SWy-1 and SAz-1 montmorillonites, they appear at 3635 and 3623 cm^{-1} , respectively. Black Jack beidellite is characterized by a wide band shifted towards higher wavenumbers with poorly distinguishable maxima at 3638, 3659 and 3674 (shoulder) cm^{-1} . For Manito Fe-smectite this band is also broad but shifted towards lower frequencies and the maximum appears at 3572 with a shoulder at 3595 cm^{-1} . Both the shape and position of maxima of these bands are related to the composition of octahedral sheets. The bands in the range 3620 - 3640 cm^{-1} are due to vibrations of Al-OH groups. The presence of Fe^{3+} ions in octahedral sheet results in the appearance of a band with its maximum at about 3570 cm^{-1} (Farmer 1974; Goodman et al. 1976), as observed in the spectrum of Manito Fe-smectite. Broadening of the band coming from vibration of Me-OH group and its shift towards lower frequencies with decreasing $^{[6]}\text{Al}^{3+}/^{[6]}\text{Fe}^{3+}$ ratio for fraction < 2 μm in various Czech and Slovak bentonites was reported by Madejová et al. (1992a). The substitution of $^{[6]}\text{Al}^{3+}$ by Mg^{2+} results in the appearance of a band near 3640 - 3660 cm^{-1} (Farmer 1968; Goodman et al. 1976; Craciun 1987). Čícel et al. (1992) and Madejová et al. (1992b), for different smectites, resolved the complex OH band in the range 3500 - 3700 cm^{-1} into its components. The proportionality of their integrated intensities to the number of the absorbing centers was used to calculate the contents of different cations in the octahedral sheet.

Absorption bands in the range 3350 - 3450 cm^{-1} and the shoulder at about 3200 - 3250 cm^{-1} are related to the presence of H_2O molecules in the interlayer spaces of the smectites (the band near 1640 cm^{-1} - Fig. 4 - is connected with the presence of H_2O molecules too) (Farmer & Russell 1964; Farmer 1974).

Absorption spectra of the samples studied in the range 3000 - 4000 cm^{-1} are presented in Figs. 2 and 3. In the spectra of all the examined smectite samples the band at about 3621 - 3626 cm^{-1} was observed indicating the presence of Al^{3+} ions in their octahedral positions in quantities similar to those in the Cheto-type montmorillonite. For the samples from Lesna (Fig. 3), there appear additional indistinct absorption maxima near 3565 cm^{-1} (Ls II) and

3571 and 3602 cm^{-1} (II/2a/19), indicating partial substitution of Al^{3+} by Fe^{3+} .

The shape of spectra in the range 3000 - 4000 cm^{-1} indicate that smectites studied represent the montmorillonite not the beidellite variety; in none of them a broadening of bands near 3621 - 3626 cm^{-1} and/or their shift towards higher frequencies was observed.

When considering the range in question, in the spectra of all the Lower Silesian smectites examined there appears a band of different intensity with maximum near 3696 - 3699 cm^{-1} . This indicates the presence of a small amount of kaolinite - the highest in sample VII/4/27 and the lowest in VI/4/8 (Figs. 2, 3).

Studies in the range 400 - 1800 cm^{-1}

The spectra of both the standard and examined minerals in this range are presented in Figs. 4 - 6.

In the spectra of silicates two essential ranges of strong absorption occur: near 1100 cm^{-1} related to the stretching vibrations of Si-O-Si groups and near 470 cm^{-1} connected with the bending vibrations of O-Si-O groups (Farmer & Russell 1964). The positions and widths of these bands depend distinctly on several factors, e.g. the kind of isomorphic substitutions and disorder in crystal structures, as well as on the size of crystallites (Farmer & Russell 1964; Farmer 1968). The substitutions of Al^{3+} for Si^{4+} in the tetrahedral sheet modify the vibrations of Si-O bonds and shift the band to lower frequencies, e.g. that near 1070 cm^{-1} in pyrophyllite spectrum is shifted to 1041 cm^{-1} for beidellite and to 1022 cm^{-1} for muscovite (Goodman et al. 1976). For all the examined Lower Silesian samples the maximum of the band, corresponding to the stretching vibrations of (Si, Al)-O groups, appears in the range 1032 - 1036 cm^{-1} .

Examining the spectra in the range 800 - 950 cm^{-1} it is possible to conclude the occupation of octahedral sheets in smectites. The bands resulting from bending vibrations of AlAlOH groups appear in the range 915 - 950 cm^{-1} , whilst those of AlFe³⁺OH near 845 - 890 cm^{-1} and resulting from AlMgOH groups near 840 cm^{-1} . The corresponding bands in the nontronite spectrum, due to Fe³⁺Fe³⁺OH groups near 815 cm^{-1} , are accompanied by a weaker one near 850 cm^{-1} (Farmer 1968; 1974). The maximum of the band assigned to AlFe³⁺OH vibrations shifts towards lower frequencies with the increase of the iron content in the lattice (Goodman et al. 1976).

The band near 915 cm^{-1} (AlAlOH) appears in the spectra of montmorillonites SWy-1 and SAz-1. In the spectrum of Manito Fe-smectite it is very poorly marked (shoulder) but there appears a distinct band at 874 cm^{-1} (AlFe³⁺OH). The latter, though weaker, is also observed in the spectra SWy-1 montmorillonite (878 cm^{-1}) and beidellite (875 cm^{-1}). On the other hand it is not visible in the spectrum of Fe-poor SAz-1 montmorillonite, in which the band near 840 cm^{-1} indicates the presence of Mg in octahedral sheet of this mineral. The considerably weaker band with

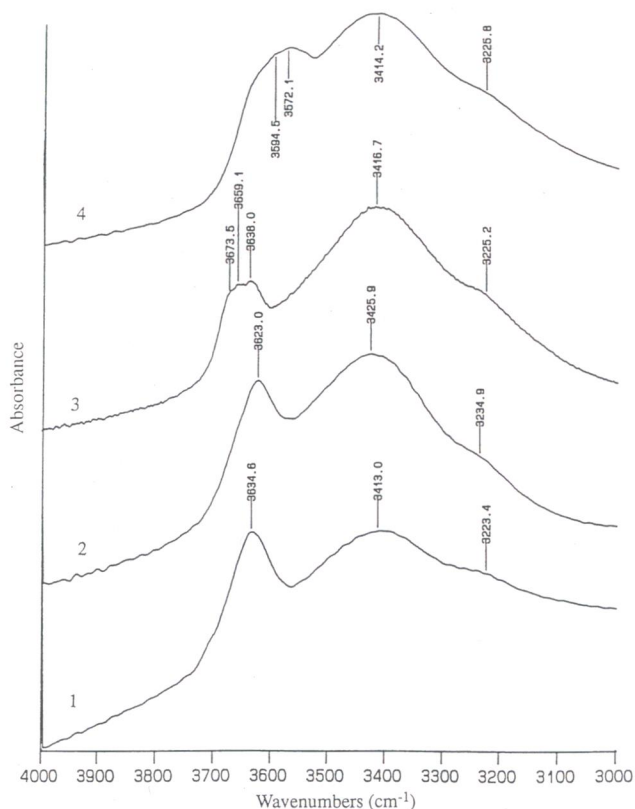


Fig. 1. Infrared spectra in the range 3000 - 4000 cm^{-1} . 1 - montmorillonite Wyoming-type (SWy-1); 2 - montmorillonite Cheto-type (SAz-1); 3 - beidellite Black Jack; 4 - Fe-smectite Manito, Wash.

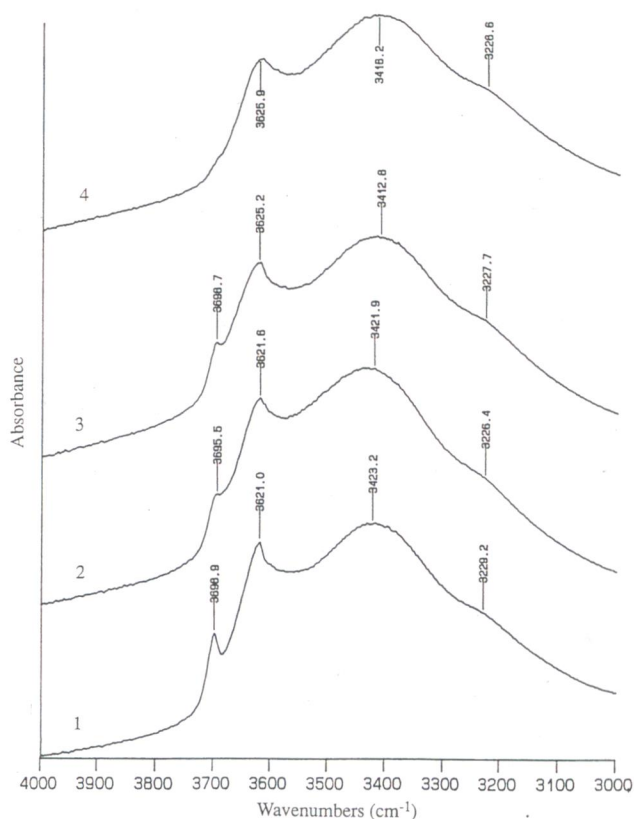


Fig. 2. Infrared spectra in the range 3000 - 4000 cm^{-1} . 1 - VII/4/27; 2 - WG_M-8A; 3 - V/5bis/28; 4 - VI/4/8.

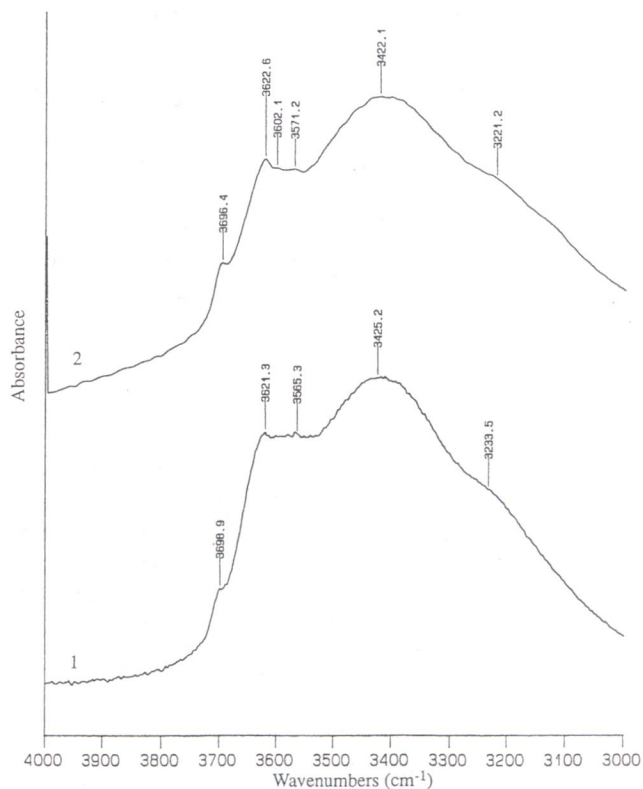


Fig. 3. Infrared spectra in the range 3000 - 4000 cm^{-1} . 1 - Ls II; 2 - II/2a/19.

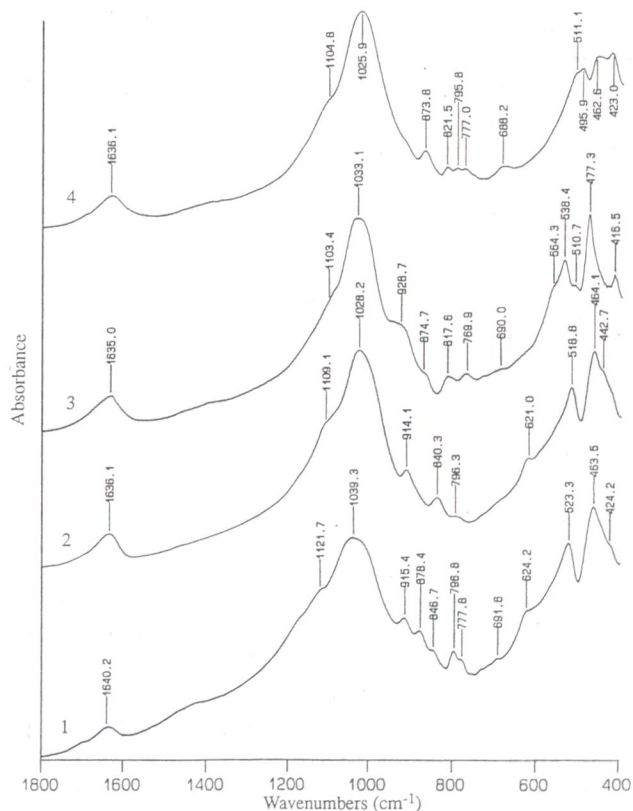


Fig. 4. Infrared spectra in the range 400 - 1800 cm^{-1} . 1 - montmorillonite Wyoming-type (SWy-1); 2 - montmorillonite Chetotype (SAZ-1); 3 - beidellite Black Jack; 4 - Fe-smectite Manito.

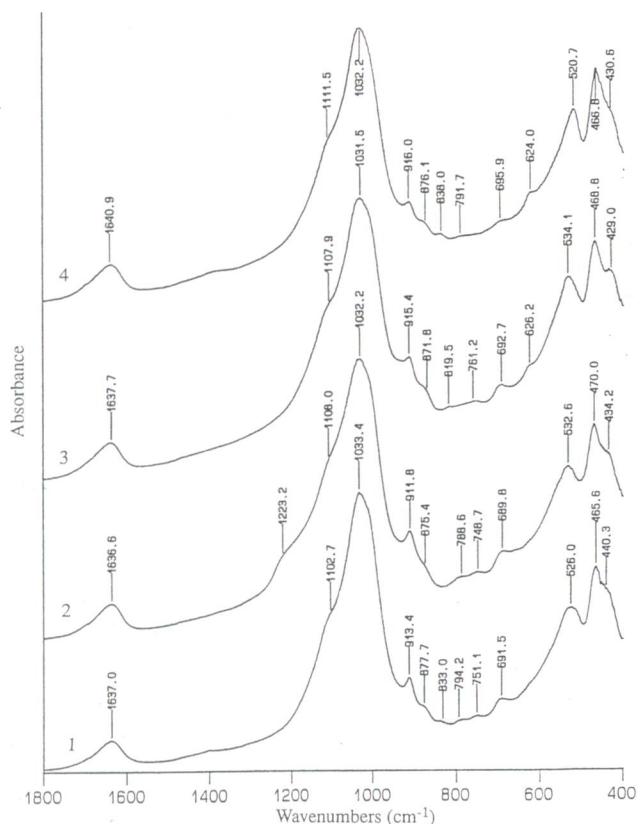


Fig. 5. Infrared spectra in the range 400 - 1800 cm^{-1} . 1 - VII/4/27; 2 - WG_M-8A; 3 - V/5bis/28; 4 - VI/4/8.

a maximum at 847 cm^{-1} , was also observed in the spectrum of SWy-1 montmorillonite.

As follows from the analysis of the bands in the range 800 - 950 cm^{-1} , the spectra of the samples studied display some differences (Figs. 5, 6). In all of them there appears a band in the range 912 - 916 cm^{-1} resulting from bending vibrations of the AlAlOH groups and more or less distinct band near 870 cm^{-1} related to the vibrations of the AlFeOH groups. In the spectra of samples VII/4/27 and VI/4/8 (Fig. 5) a band also appears with maxima at 833 and 838 cm^{-1} , assigned to vibrations of the AlMgOH groups. The weak band with a maximum at 820 and 823 cm^{-1} respectively in the spectra of V/5bis/28 and Ls II samples (Figs. 5, 6), also observed in that of Manito Fe-smectite (Fig. 4), can be explained by substitutions of Al^{3+} for Si^{4+} in tetrahedral sheet. However, in the case of high iron content it can also result from vibrations of the $\text{Fe}^{3+}\text{Fe}^{3+}\text{OH}$ groups, as in nontronite (Farmer 1974). In Russell's (1987) opinion, the bands with a maximum near 817 cm^{-1} (vibrations of $[\text{Al}]$ -O groups) and near 770 cm^{-1} (vibrations of $[\text{Al}]$ -O-Si groups) are the most characteristic for beidellite.

The band with a maximum near 690 cm^{-1} is considered by numerous authors to be due to stretching vibrations of the Al-O group in AlO_4 tetrahedral (Handke & Mozgawa 1993).

The presence of Al in octahedral sheets of the smectites studied was evidenced, apart from the band near 915 cm^{-1} , by another one near 530 cm^{-1} , corresponding

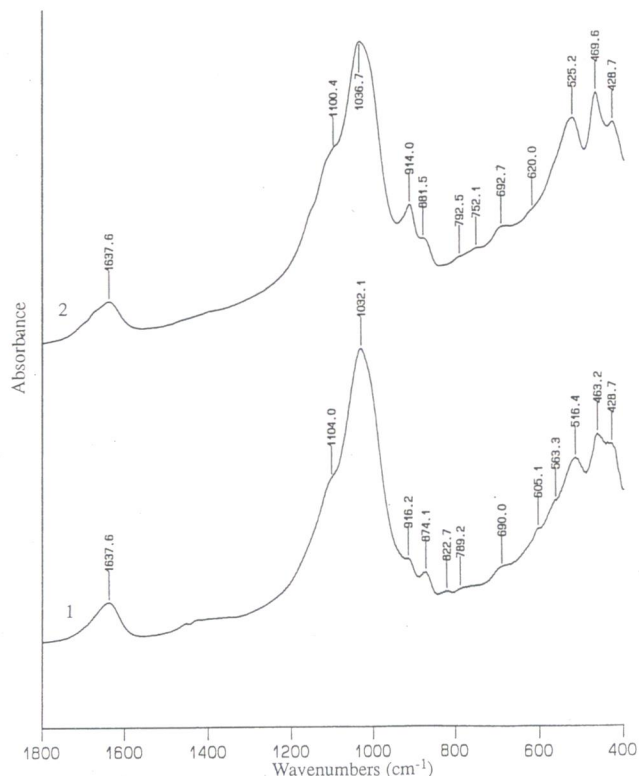


Fig. 6. Infrared spectra in the range 400 - 1800 cm^{-1} . 1 - Ls II; 2 - II/2a/19.

to bending vibrations of the Si-O-Al groups (Craciun 1987). With increasing substitution of Al^{3+} by Fe^{3+} in montmorillonites this band shifts towards lower frequencies (Stoch 1974). Stubičan & Roy (1961) have found that the difference between the intensity of the band near 473 cm^{-1} , assigned to bending vibrations of the O-Si-O groups, and near 535 cm^{-1} may indicate the substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet of beidellites. This difference diminishes with an increase of this substitution. In the case of the Lower Silesian samples studied (Figs. 5, 6) it is of the same order for the smectite samples VII/4/27, V/5bis/28, VI/4/8 and WG_M-8A whereas it is distinctly lower for the samples from Lesna (Ls II and II/2a/19), suggesting that in the two latter the tetrahedral sheet is enriched in Al.

In the spectra of all the examined smectite samples and standards, in the range 430 - 440 cm^{-1} a band appears which is related to the presence of iron in the smectite lattice (Craciun 1987). In the analyzed spectra, the intensity of this band is different and varies in a similar way to the intensity of the band with a maximum near 870 - 880 cm^{-1} .

Conclusions

Infrared spectroscopic studies have shown that the smectites occurring in Lower Silesian basaltic weathering products are montmorillonites containing in the octahedral

sheets predominantly aluminium, partly substituted by iron and/or magnesium. Some differences in the composition of the samples examined were found. It is concluded that the iron content in the octahedral sheet increases in the following sequence:



The spectra of samples VII/4/27 and VI/4/8 indicate the presence of magnesium in the octahedral sheet.

In the tetrahedral sheet silica is substituted partly by aluminium. The content of $^{[4]}\text{Al}$ in smectites from Lesna is higher than that in smectites from other localities.

The spectrum of $\text{WG}_M\text{-8A}$ sample, formed under different conditions and being the product of precipitation from post-magmatic solutions, does not differ essentially from the spectra of the remaining samples.

The smectite samples studied are not fully monomineral since they all contain small amounts of kaolinite.

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