^{57}Fe Mössbauer study of stilpnomelane and associated chlorite from Polish granite pegmatites

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Abstract This paper reports the results of ^{57}Fe Mössbauer study of stilpnomelane $K_{0.6}Fe_6(Si_8Al)(O,OH)_{27} \cdot 2H_2O$ from Żółkiewka (Lower Silesia, Poland). Stilpnomelane in paragenesis with chlorite, tourmaline, claevelandite and zeolites has been found in granite pegmatites in quarries at Żółkiewka. The samples of naturally weathered stilpnomelane and chlorite from the same fragment of rock were also studied. The Mössbauer spectrum of an untreated sample could be fitted to two Fe^{2+} doublets and two Fe^{3+} doublets. The Fe^{2+} doublets have similar isomer shifts, but they distinctly differ in values of quadrupole splittings. Ferric iron, octahedrally coordinated occurs in three different environments represented by two doublets. The first of them, assigned to combined M1 + M2 positions and the second one assigned to M3 site with parameters IS = 0.36 mm/s and QS = 2.07 mm/s is visible in the spectra up to 880°C. This doublet is characteristic of stilpnomelane and can be regarded as a "fingerprint" of this mineral. After heating at 200°C, the relative content of Fe^{2+}, $\Sigma Fe^{2+}/\Sigma Fe$, decreases to 0.22 what means a 50% decrease in comparison to the initial value observed in the untreated sample. At about 1000°C, complete breakdown of the stilpnomelane structure takes place and the Mössbauer spectrum consists of two sextets and two ferric doublets. Abnormally high content of Fe^{2+} in naturally weathered stilpnomelane (0.70) comparing to the untreated sample of stilpnomelane (0.45) indicates that the sample had to be subjected to hydrothermal processes operating locally. Almost the same contents of divalent iron and hyperfine parameters of Fe^{2+} and Fe^{3+} doublets in weathered stilpnomelane and associated chlorite suggest that the process of chlorite transformation into stilpnomelane seems to be very probable.

Key words stilpnomelane • chlorite • Mössbauer spectroscopy

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Introduction

Stilpnomelane belongs to the group of modulated 2:1 layer silicates and is generally recognized as a group of minerals with the bulk of component Fe ranging from primarily Fe^{2+} (ferrostilpnomelane) to primarily Fe^{3+} (ferristilpnomelane). It is regarded to be a metamorphic mineral particularly widespread in the rocks of the greenschist facies [10]. Stilpnomelane frequently accompanies iron ore deposits. It is rather uncommon in igneous rocks, being usually the product of secondary alterations. The structural formula of stilpnomelane averaged from 37 literature analyses and based on the determined structure [4] is $(Ca,Na,K)_4$ $(Ti_{0.1}Al_{2.3}Fe_{35.5}Mn_{0.8}Mg_{9.3})[Si_{63}Al_9](O,OH)_{216} \cdot nH_2O$. It has been suggested [6] a simplified formula of stilpnomelane based on one-eight of the above structural formula. In this sense ferrostilpnomelane can be represented as $K_{0.6}Fe_6(Si_8Al)(O,OH)_{27} \cdot 2H_2O$. The unit cell is triclinic, $a = b \approx 21.8$ Å, $\gamma = 120°$, $d_{001} \sim 12.2$ Å. The structure of stilpnomelane deduced from X-ray studies by Eggleton is complex. In stilpnomelane coordination between octahedral and tetrahedral sheets is maintained over a distance of 7 linked tetrahedra, giving an "island" group of 24 tetrahedra linked together in a hexagonal array, and coordinating to the octahedral sheet. The 24 tetrahedra groups are linked together by 6-member rings of tetrahedra, having their
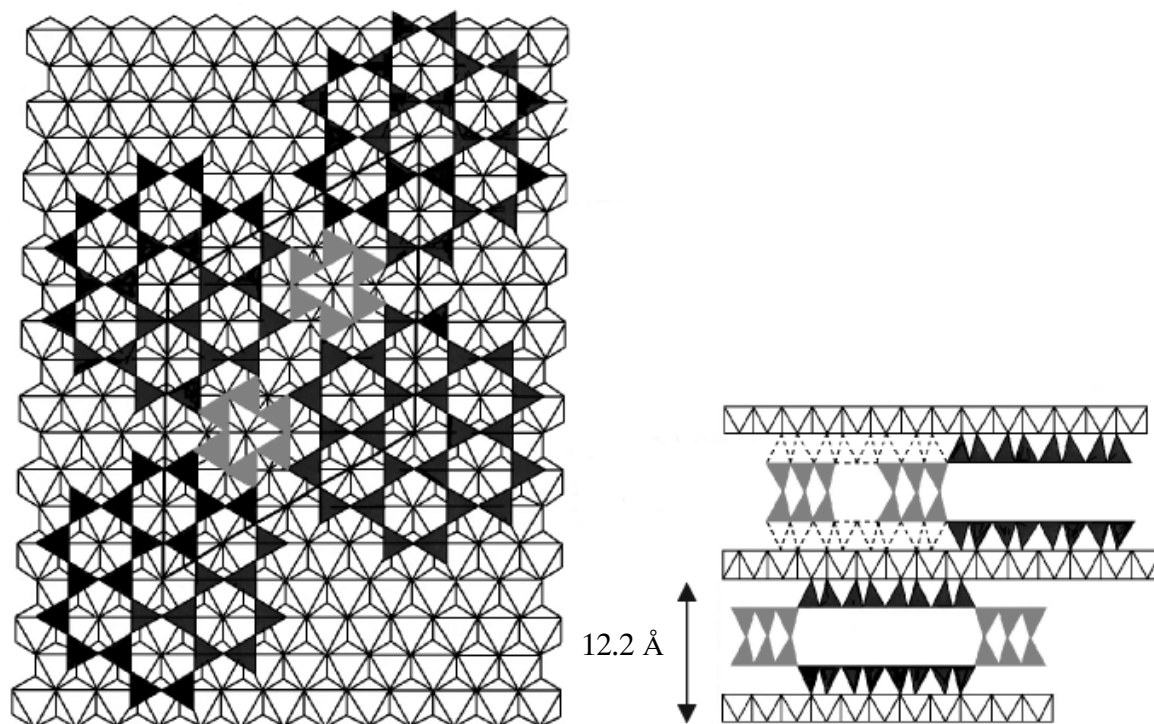
Fig. 1. The stilpnomelane structure projected on the planes (010) – left and (010) – right. Black triangles – tetrahedra composing "islands"; grey triangles – linking tetrahedra (after Crawford *et al*. [2]).

apices pointing in the opposite direction to those of the islands (Fig. 1).

In contrast to the hexagonal rings within the islands, these rings have a more trigonal configuration. The apices of the 6-member rings are also the apices of like but inverted 6-member rings, which, in turn, link the islands coordinating to the next octahedral sheet.

Detailed results of measurements for stilpnomelane from Żółkiewka near Strzegom (Poland) by X-ray, IR and DTA [10] provided new data about this mineral. It is presumably the first recorded occurrence of stilpnomelane in granite pegmatites. This mineral was in paragenesis with chlorite, tourmaline, microcline, cleavelandite and zeolites. The chemical analysis of stilpnomelane from Żółkiewka was carried out on electron microprobe and the composition of this mineral was given as: SiO_2-49.2%, Al_2O_3-7.5%, FeO-29.6%, MnO-2.7%, MgO-2.5%, CaO-0.7%, Na_2O-

0.5%, K_2O-2.1%. In these measurements, the total content of Fe was determined on electron microprobe as FeO. Additionally, the chemical analysis has revealed the presence of several trace elements (B, Be, Sn and Li) typical of the pneumatolytic and hydrothermal processes. Chlorite is a member of the group of layer silicates with the general formula [1] $Y_3[(OH)_2|Z_4O_{10}]\cdot Y_3[OH]_6$ where: Y means Mg^{2+}, Fe^{2+}, Fe^{3+} or Al^{3+} and Z means Si^{4+} partially replaced by Al^{3+}, Fe^{3+} or Cr^{3+}. Chlorite occurs in low grade metamorphic rocks of greenschist facies and as an alteration product of ferromagnesian minerals in igneous rocks.

Samples and experiment

A sample of stilpnomelane from Żółkiewka (SZ) was collected from the rocky fragment of granite-pegmatite

Table 1. Parameters of ^{57}Fe Mössbauer spectra (Fig. 2) of untreated stilpnomelane from Żółkiewka (SZ) and samples after 3 h heating at 200°C and 880°C in air. Isomer shift values IS are given relative to the α-Fe standard.

Sample	χ^2	No.	IS [mm/s]	QS [mm/s]	Γ/2	Intensity[*]	Site assignement
Untreated	1.89	1	1.126(4)	2.274(8)	0.167(10)	0.12	M1 – Fe^{2+}
stilpnomelane		2	1.160(2)	2.664(3)	0.175(4)	0.33	M2 – Fe^{2+}
(SZ)		3	0.364(2)	2.066(2)	0.133(4)	0.16	M3 – Fe^{3+}
		4	0.410(6)	1.176(9)	0.341(7)	0.39	M1 + M2 – Fe^{3+}
3 h × 200 C	0.89	1	1.143(9)	2.324(9)	0.219(14)	0.10	M1 – Fe^{2+}
		2	1.152(6)	2.620(14)	0.132(13)	0.12	M2 – Fe^{2+}
		3	0.353(4)	2.010(5)	0.150(9)	0.15	M3 – Fe^{3+}
		4	0.400(4)	1.252(6)	0.282(6)	0.63	M1 + M2 – Fe^{3+}
3 h × 880 C	0.92	3	0.356(2)	2.022(3)	0.168(5)	0.24	M3 – Fe^{3+}
		5	0.324(3)	0.810(4)	0.408(8)	0.76	Octahedral Fe^{3+}

[*] Estimated error $\Delta I/I \leq 12\%$.

with dimensions ~(10 × 10 × 4) cm, associated with chlorite, quartz, albite, microcline, stilbite and epidote. Its characteristic feature is an intense lustre and glitter due to a small size of dark gold-brown crystals, which are not more than 1 mm long and 0.1 mm thick. The associated chlorite formed soft and black irregular assemblage with size of about several cm. The sample of naturally weathered stilpnomelane from Żółkiewka (WSZ) was taken from the same part of rock from a small fragment with dimensions about 6 × 2 × 2 cm associated mainly with stilbite and chlorite. The naturally weathered stilpnomelane definitely lighter than the SZ sample, formed small lustreless gray brown concentrations.

The crystals of untreated stilpnomelane (SZ) weathered stilpnomelane (WSZ) and chlorite were powdered and prepared in the shape of a thin disc absorber (thickness 25÷45 mg cm^{-2}). The powdered samples of SZ were also heated in a muffle furnace at 200°C, 880°C and 1050°C for 3 h for each sample. Temperature was stabilized with an accuracy of ±4°C and was measured with chromel-alumel thermocouples located adjacent to the sample. After quenching, the samples were prepared in the same manner as the untreated ones. The Mössbauer transmission spectra were recorded at room temperature using a constant acceleration spectrometer with triangular velocity shape, a multichannel analyzer with 1024 channels, and linear arrangement of the [57]Co/Cr source (= 50 mCi), absorber and detector. The spectrometer velocity was calibrated with a high purity α-Fe foil. Values of isomer shifts (IS) for all identified subspectra were determined relatively to the α-Fe standard. The spectra were numerically analyzed by fitting code MEP in which all components (doublets, sextets) were considered as superpositions of appropriate number of Lorentzian lines.

Results and discussion

The Mössbauer spectra of the untreated stilpnomelane sample SZ and the samples heated at 200°C and 880°C are shown in Fig. 2. The parameters derived from fitting procedure are summarized in Table 2. The structure depicted by Eggleton and Bailey [5] would contain two Oc and Op octahedral sites [11]. The octahedral site Oc, consists of four hydroxyls and two adjacent oxygens at the apexes of the octahedron (two oxygens in *cis*-arrangement). The Op site consists of four hydroxyls and opposed oxygens on the apexes of the octahedron (two oxygens in *trans*-arrangement). In this paper, these sites will be renamed as M1 (Op) and M2 (Oc). These sites would have analogous topology to M(1) and M(2) sites in micas when replacing OH with O. In the spectrum of untreated sample SZ two expected doublets from Fe^{2+} in M1 and M2 sites are clearly visible (no. 1 and 2, Fig. 2, Table 1). The first of them, with parameters IS = 1.13 and QS = 2.27 mm/s corresponds to Fe^{2+} in M1. The second one with IS = 1.16 and QS = 2.66 mm/s corresponds to Fe^{2+} in M2 site. Relative areas of these doublets are 0.12 and 0.33, respectively, with total contribution of 0.45 Fe^{2+} in the spectrum. The area ratio M2:M1 is nearly equal to 3:1 and it differs from these reported in micas, where ideal value M(2):M(1) is 2:1. In the spectrum of SZ sample, two doublets assigned to Fe^{3+} ions with contribution of 0.55 have been identified. The

first of them IS = 0.36 mm/s and QS = 2.07 mm/s (no. 3, Fig. 2, Table 1) whose contribution to the whole spectrum is equal to 0.16, is the most characteristic and stable component among others and can be assigned to highly distorted M3 octahedral Fe^{3+} site. This doublet is present in all spectra up to the sample heated at 880°C and its IS and QS values practically do not change. It can be regarded
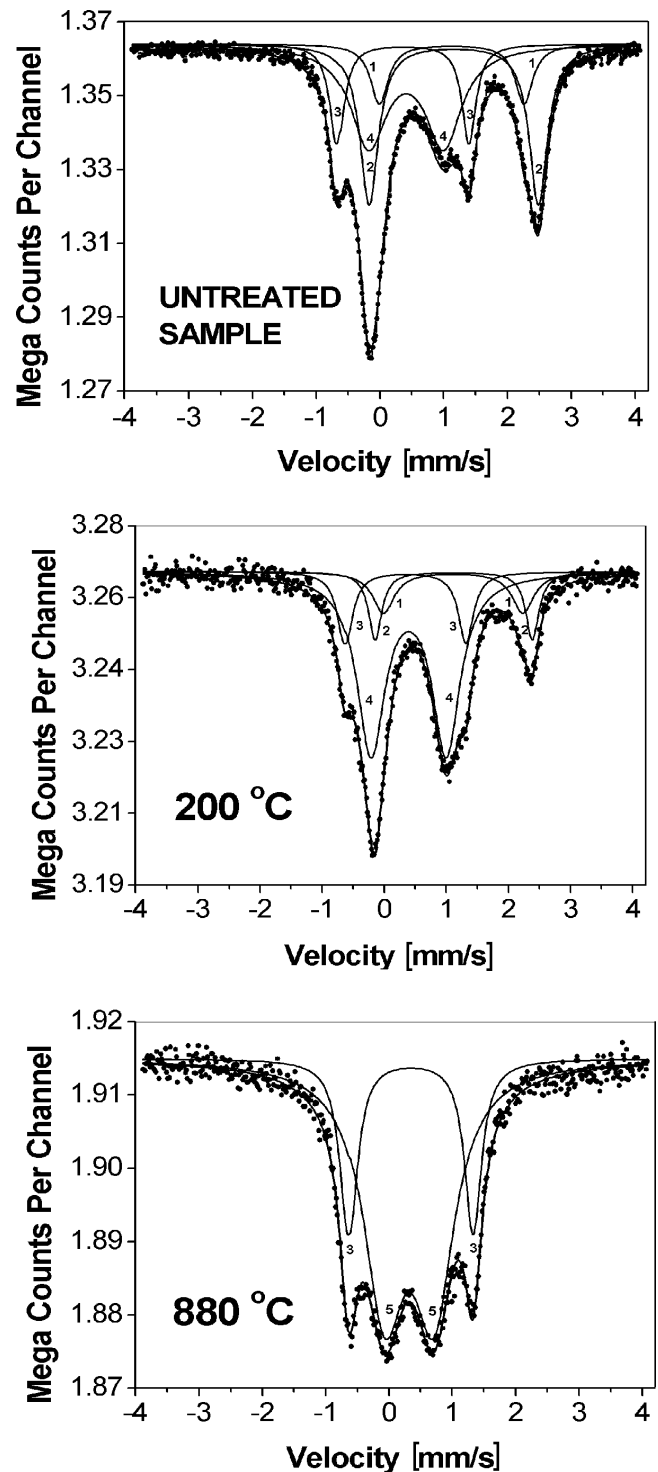

Fig. 2. [57]Fe Mössbauer spectra of untreated stilpnomelane from Żółkiewka (SZ) and samples after 3 h heating at 200°C and 880°C in air. Solid dots – experimental data; thick solid line – fitted curve; thin solid line – fitted doublets. All spectra were recorded at room temperature.

Table 2. Parameters of ^{57}Fe Mössbauer spectra (Fig. 3) of the stilpnomelane SZ sample after heating at 1050°C in air. Isomer shift values IS are given relative to the α-Fe standard.

Sample	χ^2	No.	IS [mm/s]	H [kOe]	QS [mm/s]	$\Gamma/2$	Intensity$^{(*)}$
3 h × 1050°C	0.95	D1	0.304(15)	–	1.316(27)	0.229(19)	0.15
		D2	0.367(17)	–	0.670(30)	0.232(21)	0.14
		S1	0.373(6)	509(1)	0.204(6)	0.339(33)	0.32
		S2	0.331(15)	476(2)	0.066(1)	0.166(13)	0.39

$^{(*)}$ Estimated error $\Delta I/I \leq 12\%$.

as a "fingerprint" of stilpnomelane comparing to chlorite, biotite and other micas. Doublets with similar parameters were recorded in the spectra of minerals from epidote group [3], axinities [13] and (with greater QS) in gadolinite [7, 8]. This site is also visible in experimental spectrum of stilpnomelane presented in an extensive paper referred to layer silicates [11], but this doublet was not isolated in the analysis. The second doublet assigned to Fe^{3+} ions (no. 4, Fig. 2, Table 1) in the SZ spectrum with area 0.33 is characterized by the greatest contribution amongst all other doublets. The highest Γ value and the rapid growth of its intensity at 200°C suggest that this doublet represents unresolved components of ferric iron from both M1 and M2 positions. Due to intense oxidation of $Fe^{2+} \rightarrow Fe^{3+}$ in M2 site at 200°C, the intensity of this doublet increases to 0.63. This result is in good agreement with decreasing Fe^{2+} content in M2 (0.21) and M1 (0.02) site after oxidizing process at 200°C.

The Mössbauer spectrum of the sample heated at 200°C shows a considerable decrease of relative contribution from Fe^{2+} doublets i.e., no. 1 and 2 to the value 0.22. Oxidation process is preferentially more efficient in M2 site where the contribution of doublet no. 2 decreased from 0.33 (untreated sample) to 0.11 and the area ratio M1:M2 is 1:1. In the spectrum 3 h × 880°C a new wide quadrupole doublet (no. 5, Fig. 2, Table 1) is visible. This doublet results from a superposition of a large number of somewhat different quadrupole doublets due to Fe^{3+} in predominantly octahedral positions. In comparison with original structure after heating at 880°C only doublet no. 3 is still observed in
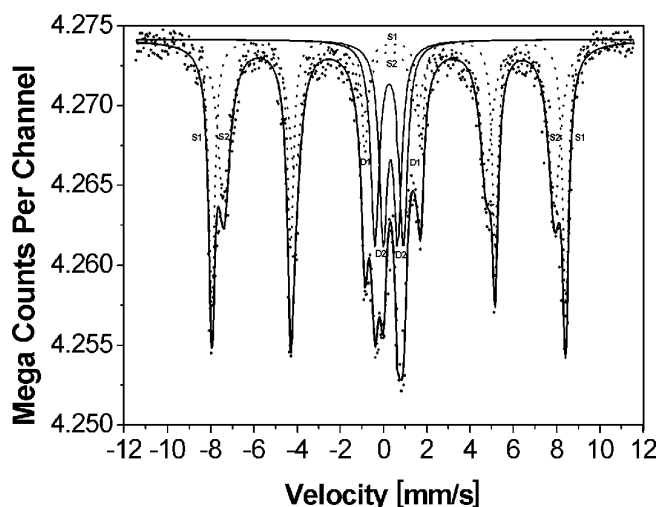
the spectrum. None of the Fe^{2+} components were noted after heating at this temperature.

At 1050°C, complete breakdown (Fig. 3, Table 2) of the structure takes place and the spectrum consists of two ferric doublets (D1 and D2) and two sextets (S1 and S2). Predominant iron phase in this new material is a hematite-like phase represented by the two sextets involving 0.71 contribution in the spectrum. Parameters of both doublets allowed to assign these doublets to Fe^{3+} in octahedral positions.

Rather unexpected results have been obtained for the sample of naturally weathered stilpnomelane WSZ. As previously noted, this sample has all features of weathering.
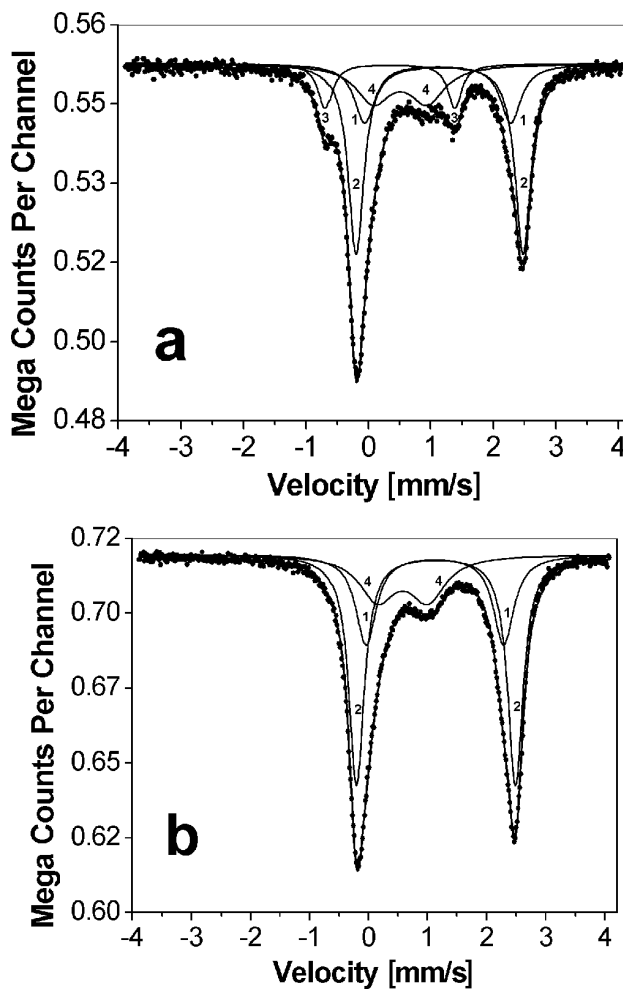

Fig. 3. ^{57}Fe Mössbauer spectrum of stilpnomelane sample after heating at 1050°C. Solid dots – experimental data; thick solid line – fitted curve; thin solid line – fitted doublets (D1 – outer, D2 – inner); dotted line – fitted sextets (S1 – outer, S2 – inner).

Fig. 4. Mössbauer spectra of: (a) naturally weathered stilpnomelane from Żółkiewka (WSZ) and (b) associated chlorite. Solid dots – experimental data; thick solid line – fitted curve; thin solid line – fitted doublets.

Table 3. Parameters of ^{57}Fe Mössbauer spectra (Fig. 4) of the weathered stilpnomelane from Żółkiewka (WSZ) and associated chlorite. Isomer shift values IS are given relative to the α-Fe standard.

Sample	χ^2	No.	IS [mm/s]	QS [mm/s]	Γ/2	Intensity[*]	Site assignment
Weathered stilpnomelane (WSZ)	1.31	1	1.116(10)	2.346(13)	0.199(9)	0.17	M1 – Fe^{2+}
		2	1.144(1)	2.682(4)	0.152(4)	0.53	M2 – Fe^{2+}
		3	0.353(3)	2.066(4)	0.135(7)	0.10	M3 – Fe^{3+}
		4	0.512(16)	0.864(17)	0.336(17)	0.20	M1+M2 – Fe^{3+}
Associated chlorite	1.91	1	1.127(2)	2.334(8)	0.209(6)	0.26	M1 – Fe^{2+}
		2	1.145(1)	2.696(7)	0.158(2)	0.51	M2 – Fe^{2+}
		3	–	–	–	–	–
		4	0.581(6)	0.854(4)	0.363(8)	0.23	M1+M2 – Fe^{3+}

[*] Estimated error $\Delta I / I \leq 8\%$.

The Mössbauer results are the some kind of unexpected:

1. Relative content of Fe^{2+} is distinctly higher (0.70) than for the SZ sample (0.45). Two ferrous doublets (no. 1 and 2, Fig. 4a, Table 3) in M1 and M2 sites have nearly the same parameters as analogous doublets in the spectrum of SZ sample, with the areas ratio 1:3.

2. Relative content of Fe^{3+} in WSZ is much lower (0.23) than for the SZ sample (0.55). The characteristic doublet of Fe^{3+} no. 3, is less intense (0.09) in WSZ than in SZ (0.16).

The high content of Fe^{2+} in WSZ and the low content of Fe^{3+} in M3 site suggests that this sample had to be subject to hydrothermal processes operating locally.

Stilpnomelane can be regarded as an intermediate mineral between chlorite and micas and, consequently, the most frequent and probable is the process of transformation of chlorites (those reach in iron) into stilpnomelane. The specimen from the Polish pegmatites is probably a secondary mineral arising from iron chlorite [10] that forms layers reaching a thickness of 7 cm. This conclusion could be supported by a direct comparison of the WSZ Mössbauer spectrum with the spectrum of associated chlorite from the same rocky fragment (Fig. 4b, Table 3). The ferrous doublets in both M1 and M2 octahedral sites have a striking similarity in parameters with isomer shifts 1.12–1.13 mm/s (M1), 1.14–1.14 mm/s (M2) and quadrupole splittings 2.35–2.33 mm/s (M1), 2.68–2.70 mm/s (M2) in weathered stilpnomelane and chlorite, respectively. The distinctive feature of these Mössbauer spectra is the presence of the characteristic ferric doublet (no. 3 in WSZ and SZ samples), while it is absent in the spectrum of chlorite (Fig. 4b). The reduced intensity of Fe^{3+} in M3 can be connected with rehydroxylation process. It is supported by the fact that the increase of the intensity of doublet no. 3 after heating SZ at 880°C is joined with rapid oxidation involving directly dehydroxylation. As a result of rehydroxylation, hydroxyls anions re-occupy the original sites in the original orientation. As it has been reported [12], the OH$^-$ content in micas after rehydroxylation was restored to about 84% and along with the reconstitution of the OH content the distortion of the SiO network is repaired. It seems reasonable to assume that a similar process takes place in the WSZ sample. On the other hand, the WSZ sample could be representative for the early stage of stilpnomelane formation. If so, it can be assumed that pegmatite ferristilpnomelane forms by oxidation of earlier ferrostilpnomelane.

In all examined samples no ferric iron in pure tetrahedral site was identified. Based on the work by Rancourt *et al*. [9], spectral components of Fe^{3+} in tetrahedral positions should be characterized by IS ~ 0.17 mm/s and QS ~ 0.50 mm/s with respect to α-Fe standard. However, doublet with such spectral components has not been observed in any spectrum of our stilpnomelane. Thus, opposite to previous interpretation [11], we conclude that ferric iron does not occupy tetrahedral site in pegmatite stilpnomelane from Żółkiewka.

Conclusions

Results of Mössbauer measurements showed that stilpnomelane from Żółkiewka, the first recorded occurrence of stilpnomelane in granite pegmatites, very easy undergone the oxidation process. In accordance with the Eggleton and Bailey's model of stilpnomelane, there are two divalent iron octahedral sites M1 and M2 with initial Fe^{2+} contribution ratio 1:3, respectively. After heating stilpnomelane at 200°C, the total contribution of Fe^{2+} doublets, $\Sigma Fe^{2+}/\Sigma Fe$, from M1 and M2 sites decreases to 50% of its initial value. The most characteristic Fe^{3+} doublet with the average spectral parameters IS ~ 0.35 mm/s and QS ~ 2.03 mm/s can be regarded as a "fingerprint" of stilpnomelane comparing to chlorite, biotite and other micas. It is characteristic of spectra of SZ, WSZ and the samples heated up to 880°C that they do not contain Zeeman's sextets reflecting magnetically-ordered compounds. Characteristic doublets represent all components in the spectra of these samples. Magnetically ordered stage appears not before heating at ~1000°C. The Mössbauer spectrum of the weathered (or rehydroxylated) stilpnomelane showed a striking similarity to the spectrum of the associated chlorite supporting earlier hypothesis of chlorite transformation into stilpnomelane.

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