⁵⁷Fe Mössbauer study of the oxidation state of iron in stilpnomelane from granite pegmatites in Poland

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ABSTRACT

The effects of heat treatment on stilpnomelane from granite pegmatites at Zółkiewka (Lower Silesia, Poland) were studied using 57Fe Mössbauer spectroscopy. Samples of naturally altered stilpnomelane and chlorite were also studied. The Mössbauer spectrum of an untreated sample was fitted to two Fe^{2+} doublets and two Fe^{3+} doublets. The Fe^{2+} doublets had similar isomer shifts (1.13 and 1.16 mm/s for the octahedral M1 and M2 sites), different quadrupole splitting values (QS = 2.28 and 2.66 mm/s, respectively), and an M1:M2 area ratio of nearly 1:3. For ferric iron, the first doublet was assigned to the combined M1 + M2 + M4 octahedral positions and had IS = 0.41 and QS = 1.18 mm/s. The second doublet was assigned to the M3 site, with parameters IS = 0.36 and QS = 2.07 mm/s. This is characteristic for stilpnomelane. The oxidation of Fe^{2+} is fast at low temperatures, with a maximum at 360 °C. Near 1050 °C, the stilpnomelane structure broke down completely, and the spectrum consisted of two sextets and two ferric iron doublets. The predominant phase in this new material is hematite, as represented by the two sextets. The abnormally high fractional Fe^{2+} content in the altered stilpnomelane (0.70) as compared to the untreated sample (0.45) indicates that the sample was subjected to local hydrothermal processes. Nearly identical divalent iron contents and hyperfine parameters for the Fe^{2+} and Fe^{3+} doublets (except Fe^{3+} in M3) in the altered stilpnomelane and associated chlorite strongly suggest that chlorite is transformed into stilpnomelane.

Keywords: Stilpnomelane, Mössbauer spectroscopy, iron, oxidation state, heat treated

INTRODUCTION

Stilpnomelane belongs to the group of modulated 2:1 layer silicates and is generally recognized as a group of minerals, with Fe ranging from primarily Fe²⁺ (ferrostilpnomelane) to primarily Fe³⁺ (ferristilpnomelane) (Guggenheim and Eggleton 1987). It is regarded as a metamorphic mineral and is particularly widespread in greenschist facies rocks (Winkler 1967; Chauvel 1973). Stilpnomelane frequently accompanies iron ore deposits. It is uncommon in igneous rocks and is usually the product of secondary alteration. The formula for stilpnomelane averaged from 37 literature analyses and based on the structure (Eggleton 1972) is (Ca,Na,K)4(Ti0.1Al2.3Fe35.5Mn0.8Mg9.3)(Si63Al9)(O,OH)216 nH2O.A simplified formula has been suggested (Eggleton and Chappell 1978) based on one eighth of the above structural formula. In this sense, ferrostilpnomelane can be represented as K_{0.6}Fe₆(Si₈Al) $(O,OH)_{27} \cdot 2H_2O$. The unit cell is triclinic; $a = b \approx 21.8$ Å, $\gamma =$ 120° , $d_{001} \sim 12.2$ Å. The structure of stilpnomelane as deduced from X-ray studies by Eggleton (1972) is complex. Coordination between octahedral and tetrahedral sheets is maintained over a distance of 7 linked tetrahedra, producing an "island" group of 24 tetrahedra linked together in a hexagonal array and coordinating to the octahedral sheet. The 24 tetrahedral groups are linked together by 6-membered rings of tetrahedra, with their apices pointing in the opposite direction from those of the islands. These

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rings have a more trigonal configuration, and their apices are also the apices of similar but inverted 6 member rings linking the islands coordinating to the next octahedral sheet (Eggleton 1972; Crawford et al. 1977).

Detailed studies of stilpnomelane from Zółkiewka near Strzegom (Poland) by X-ray diffraction, IR, and DTA (Sachanbiński and Janeczek 1977) have provided new data about this mineral. It is thought to be the first recorded occurrence of stilpnomelane in a granite pegmatite and was found in association with chlorite, tourmaline, microcline, cleavelandite, and zeolites. Its characteristic feature is an intense luster and glitter due to small crystal size; individual crystals are not more than 1 mm long and 1 mm thick. Chemical analysis was done by electron microprobe, and the composition was given as SiO_2 49.2%, Al₂O₃ 7.5%, FeO 29.6%, MnO 2.7%, MgO 2.5%, CaO 0.7%, Na₂O 0.5%, K₂O 2.1%. In this analysis, total Fe was determined as FeO. Additionally, the chemical analysis has revealed the presence of several trace elements (B, Be, Sn, and Li) typical of pneumatolitic and hydrothermal processes. In the same paper, the DTA curve shows an indistinct endothermic maximum at 80 °C, which corresponds to the loss of interlayer water from the sample. A marked, wide exothermic peak with a maximum at 360 °C is due to the oxidation of Fe²⁺ to Fe³⁺. The next, narrow exothermic peak has a maximum at 810 °C and was interpreted as representing the breakdown of the stilpnomelane structure. The X-ray diffractogram of the stilpnomelane sample that was heated at 600 °C shows a shift in the 001 reflection from 12.08

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to 12.3 Å due to the oxidation of Fe^{2+} at 360 °C. The IR absorption spectrum of the stilpnomelane that was heated to 600 °C pose of the present

tion spectrum of the stilpnomelane that was heated to 600 $^{\circ}$ C lacked the band at 3450 cm⁻¹ due to stretching vibrations of the H₂O molecules. The 1140 cm⁻¹ band, which corresponds to vibrations of the Fe²⁺-O-H groups, was also absent (Sachanbiński and Janeczek 1977).

According to calculations based on the cell parameters in a study by Janeczek (1985), stilpnomelane from Zółkiewka should contain 15 Fe³⁺ ions out of 48 octahedral cations. Based on the chemical composition, there should also be at least 18 Fe²⁺ ions. Thus, the ratio Fe²⁺/ Σ Fe ≥ 0.55 . However, a classical chemical analysis was performed by Hutton (1938) on stilpnomelane samples from Zlote Hory. The samples in that study formed under the same conditions as the stilpnomelane from Zółkiewka; they were from the same geochemical province, the same stage Variscan magmatism, and showed striking similarity in chemical composition. Their composition was 14.04 wt% FeO and 20.82 wt% Fe₂O₃ (i.e., Fe²⁺/ Σ Fe = 0.43). This estimate agrees very well with the results obtained by Mössbauer spectroscopy for the untreated sample of stilpnomelane from Zółkiewka and can be assumed as the starting ratio of Fe²⁺/ Σ Fe.

PREVIOUS MÖSSBAUER STUDIES OF STILPNOMELANE

The Mössbauer data for stilpnomelane that are available in the literature are given in Table 1. The first results of Mössbauer measurements for stilpnomelane were reported by Taylor et al. (1968). In that paper, the spectrum was fitted to a large, unresolved Fe2+ doublet and two Fe3+ doublets. The Fe2+ doublet was assigned to divalent iron in Oc and Op octahedral sites according to the structure depicted by Eggleton and Bailey (1966). The Oc site was described as consisting of four hydroxyls and two adjacent O atoms at the apices of the octahedron (two O atoms in cis-arrangement). The Op site had four hydroxyls and opposed O atoms on the apices of the octahedron (two O atoms in transarrangement). The first ferric doublet had an isomer shift (IS) of 0.55 mm/s and a quadrupole splitting (QS) of 1.10 mm/s and was interpreted by the authors as representing trivalent iron in the tetrahedral site. The second ferric doublet, denoted by small quadrupole splitting (IS = 0.55 and QS = 0.60 mm/s) (Table 1), was assigned to Fe^{3+} in both *Oc* and *Op* octahedral sites.

Singh et al. (1979) described an occurrence of stilpnomelane in a thick iron ore associated with the meta-acidic intrusives of the Chamoli carbonate suite (Garhwal, Himalaya). The three ferric doublets from the top, middle, and bottom parts of the iron ore are assigned to Fe³⁺ in the octahedral position (Table 1). No Fe²⁺ components were noted. Because these measurements were done with a high velocity range (\pm 12 mm/s) and the contribution of hematite and magnetite sextets was higher than 90%, the parameters of these three Fe³⁺ doublets are uncertain. Preliminary results of a Mössbauer study of stilpnomelane from Zółkiewka (an untreated sample and samples heated at 200, 880, and 1050 °C) have been presented by Malczewski et al. (2004). The purpose of the present paper is to show that certain observed spectral features of stilpnomelane, both untreated and after heating up to ~ 900 °C, are characteristic for this mineral.

SAMPLES AND EXPERIMENTAL PROCEDURES

A sample of stilpnomelane from Zółkiewka (SZ) was collected from a fragment of granite pegmatite. The sample had dimensions ca. $10 \times 10 \times 4$ cm. The mineralogy of the rock also includes chlorite, quartz, microcline, stilbite, albite, and bavenite. The stilpnomelane crystals are dark gold-brown and are characterized by an intense luster and glitter due to their small size (no more than 1 mm in size; Fig. 1a). A sample of naturally altered stilpnomelane (ASZ) was taken from the same part of the rock. It was taken from a small fragment with dimensions about 4.5 $\times 2 \times 1.5$ cm associated mainly with stilbite and chlorite. The altered stilpnomelane is definitely lighter in color than the SZ sample and consists of a small, lusterless gray mass (Fig. 1b).

Crystals of SZ, ASZ, and associated chlorite were powdered. Eight samples of SZ were heated in a muffle furnace for 3 h at temperatures of 80, 200, 360, 450, 600, 810, 880, and 1050 °C. The temperature was stabilized at ± 4 °C and was measured with chromel-alumel thermocouples located adjacent to the samples. After quenching, the samples were prepared in the shape of a thin disk absorber (thickness 25–45 mg/cm²). 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 a linearly arranged ⁵⁷Co/Cr source (=50 mCi), absorber, and detector. The spectrometer velocity was calibrated with a high purity α -Fe foil. Values of isomer shifts for all identified subspectra are defined relative to the α -Fe standard. All Mössbauer spectra were numerically



FIGURE 1. Representative mineralization in granite pegmatites from Zolkiewka: (a) fragment with stilpnomelane and (b) fragment with altered stilpnomelane and associated chlorite. Arrows point to particular minerals.

TABLE 1. Previous ⁵⁷ Fe Mössbau	er studies of stilpnomelane
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Reference	Locality	Oxidation state	IS (mm/s)	QS (mm/s)	Intensity	Site
Taylor et al. 1968	Cuyuna Iron Range, Minnesota	Fe ²⁺	1.20	2.40	nd.	Octahedral (O_c and O_p)
		Fe ³⁺	0.55	1.10	nd.	Tetrahedral
		Fe ³⁺	0.55	0.60	nd.	Octahedral (O_c and O_p)
Singh et al. 1978	Iron ore band, Garhwal Himalaya	Fe ³⁺ (top part of the iron ore band)	0.45	0.47	0.03	Octahedral
-		Fe ³⁺ (middle part of the iron ore band)	0.35	1.04	0.03	Octahedral
		Fe ³⁺ (bottom part of the iron ore band)	0.42	0.73	0.05	Octahedral

analyzed by the fitting software MEP and all components (doublets, sextets) were considered superpositions of an appropriate number of Lorentzian lines.

RESULTS AND DISCUSSION

The Mössbauer spectra of the untreated stilpnomelane and samples heated to as high as 880 °C are shown in Figure 2. The parameters derived from the fitting procedure are summarized in Table 2. The SZ, ASZ, and heated samples did not contain Zeeman's sextets, which reflect magnetically ordered compounds. All components in the spectra were represented by characteristic doublets. Magnetic ordering did appear due to heating at ~1000 °C. The spectrum of the sample heated at 1050 °C and the spectra of the altered stilpnomelane and associated chlorite are discussed later.

Changes in Fe²⁺ distributions

Electric quadrupole interactions arising from the interaction between the nuclear quadrupole moment and the electric field in which nuclei occur produces characteristic quadrupole doublets in Mössbauer spectra. For high-spin ⁵⁷Fe²⁺ ions, these doublets are usually characterized by large isomer shifts, generally ranging from 0.7 to 1.40 mm/s with respect to α -Fe foil. The doublets also have large quadrupole splitting values, ranging from 0.7 to 3.7 mm/s (Hawthorne 1988; Murad and Cashion 2004). The isomer shift is known to be very sensitive to variations in the absorber oxidation state and coordination number. It has also been established that quadrupole splitting is generally negatively correlated with polyhedral distortion for a given site; large QS



FIGURE 2. ⁵⁷Fe Mössbauer spectra at RT for untreated stilpnomelane and for stilpnomelane samples heated for 3 h in air at the given temperature. Solid dots = experimental data; thick solid line = fitted curve; thin solid line = fitted doublets.

Sample	χ²	No.	IS* (mm/s)	QS† (mm/s)	Γ/2‡ (mm/s)	Intensity§	Site assignment
Untreated stilpnomelane (SZ)	1.29	1	1.126(4)	2.274(8)	0.167(10)	0.12	M1-Fe ²⁺
		2	1.160(2)	2.664(3)	0.175(4)	0.33	M2-Fe ²⁺
		3	0.364(1)	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+M4-Fe ³⁺
80 °C	1.06	1	1.137(10)	2.216(20)	0.150(14)	0.10	M1-Fe ²⁺
		2	1.147(5)	2.626(8)	0.156(9)	0.31	M2-Fe ²⁺
		3	0.356(3)	2.044(3)	0.121(7)	0.17	M3-Fe ³⁺
		4	0.407(10)	1.198(16)	0.308(15)	0.42	M1+M2+M4-Fe ³⁺
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)	2.006(5)	0.150(9)	0.15	M3-Fe ³⁺
		4	0.400(4)	1.252(6)	0.282(6)	0.63	M1+M2+M4-Fe ³⁺
360 °C	0.88	2	1.104(27)	2.708(27)	0.147(11)	0.05	M2-Fe ²⁺
		3	0.349(4)	2.066(7)	0.130(9)	0.28	M3-Fe ³⁺
		4	0.451(21)	1.190(23)	0.217(9)	0.35	M1+M2+M4-Fe ³⁺
		5	1.082(20)	0.760(20)	0.121(10)	0.02	M5-Fe ²⁺
		6	0.156(18)	1.472(26)	0.153(15)	0.11	M1-Fe ³⁺
		7	0.399(20)	1.672(24)	0.186(19)	0.19	M2-Fe ³⁺
450 °C	1.06	3	0.338(4)	2.002(8)	0.163(9)	0.22	M3-Fe ²⁺
		4	0.454(10)	1.094(13)	0.216(11)	0.32	M1+M2+M4-Fe ³⁺
		5	1.085(9)	0.740(10)	0.147(10)	0.06	M5-Fe ²⁺
		6	0.193(20)	1.346(13)	0.179(11)	0.16	M1-Fe ³⁺
		7	0.417(13)	1.406(10)	0.184(15)	0.24	M2-Fe ³⁺
600 °C	0.74	3	0.343(3)	2.020(7)	0.165(9)	0.24	M3-Fe ³⁺
		4	0.438(13)	1.038(18)	0.219(12)	0.33	M1+M2+M4-Fe ³⁺
		5	1.045(9)	0.840(9)	0.130(12)	0.04	M5-Fe ²⁺
		6	0.166(24)	1.282(14)	0.178(10)	0.15	M1-Fe ³⁺
		7	0.419(16)	1.408(13)	0.192(20)	0.24	M2-Fe ³⁺
810 ℃	1.03	3	0.341(4)	2.000(8)	0.154(14)	0.15	M3-Fe ³⁺
		5	1.013(24)	0.934(14)	0.131(13)	0.02	M5-Fe ²⁺
		7	0.345(5)	1.342(19)	0.230(21)	0.20	M2-Fe ³⁺
		8	0.342(2)	0.772(11)	0.256(10)	0.63	Octahedral Fe ³⁺
880 °C	0.92	3	0.356(2)	2.022(3)	0.168(5)	0.24	M3-Fe ³⁺
		8	0.324(3)	0.810(4)	0.408(8)	0.76	Octahedral Fe ³⁺

TABLE 2. Parameters for ⁵⁷Fe Mössbauer spectra for stilpnomelane from Zółkiewka (SZ) after heating for 3 h in air at the given temperatures

* Isomer shift values IS are given relative to the α -Fe standard.

‡ Half width at half maximum.

§ Estimated error $\Delta I/I \leq 12\%$.

values for Fe^{2+} are associated with regular, undistorted polyhedra, and increasingly greater distortion is reflected in decreasing QS values (Ito and Hafner 1974; Grew et al. 1999).

The stilpnomelane structure depicted by Eggleton (1972) contains four octahedral sites. Based on 48 octahedral cations, 18 of these cations share 4 O atoms with Si, another 18 share 3 O atoms with Si, 8 share 2 O atoms, and 4 share 1 or no O atoms with Si. In the following sections of this paper, these sites will be referred to as M1 (18/4), M2 (18/3), M3 (8/2), and M4 (4/1 or 0). Based on this arrangement, Fe^{2+} ions in the M1 site should have a greater barrier against oxidation than Fe^{2+} in the M2 site. This assumption will be used to differentiate between these two sites in the Mössbauer spectra.

As expected, the spectrum for the untreated SZ sample showed two doublets representing Fe^{2+} in the M1 and M2 sites (nos. 1 and 2; Fig. 2; Table 2). The first had an IS of 1.13 and a QS value of 2.27 mm/s and corresponds to Fe^{2+} in M1. The second doublet, with an IS of 1.16 and a QS of 2.66 mm/s, corresponds to Fe^{2+} in the M2 site. The relative areas of these doublets were 0.12 and 0.33, respectively, with a total relative contribution of 0.45 Fe^{2+} in the spectrum (out of a total area of 1.00 for all peaks). The area ratio M2:M1 is nearly 3:1.

M1 and M2 populations from the two Fe²⁺ doublets were determined based on a free parameters fitting procedure. In Figure 2 (untreated sample and 80 °C sample), the high energy shoulder has a visible inflection at v = 2.16 mm/s, clearly indicating the location of one of the two doublets. Combined with precisely determined Fe³⁺ spectral parameters, this suggests an M2:M1 area ratio of 3:1. The use of quadrupole splitting distribution (QSD) analysis (Rancourt 1994; Rancourt et al. 1994) is not necessary in this case because all components are well specified and characterized by low $\Gamma/2$ values (Table 2). An M2:M1 area ratio other than 3:1 can be obtained only by arbitrarily fixing parameters for doublets 1 and 2, leading to artificial results. Changes in the relative contribution of Fe²⁺ (Σ Fe²⁺/ Σ Fe) in the Mössbauer spectra of the untreated sample and those heated up to 810 °C are given in Figure 3.

The total decrease in relative areas of the two Fe²⁺ doublets was about 0.04 in the spectrum for the sample heated at 80 °C. This indicates that the oxidation of Fe²⁺ to Fe³⁺ begins at a low temperature. Simultaneously, the Mössbauer parameters of these Fe²⁺ doublets changed slightly as compared to the unheated SZ (Table 2). This can be connected with loss of interlayer water and is consistent with the observations of Sachanbiński and Janeczek (1977), who reported an extensive endothermic peak at 80 °C on the DTA curve, corresponding to interlayer water loss.

The spectrum for the sample heated at 200 °C showed a decrease in the relative contributions from doublets 1 and 2, to a total of 0.22. Oxidation is more efficient in the M2 site, where the contribution of doublet no. 2 decreased from 0.33 (untreated sample) to 0.11. This yields an area ratio M1:M2 of 1:1. The hyperfine parameters for doublet no. 1 were noticeably different from those obtained for SZ and the 80 °C sample (Fig. 2; Table 2).

[†] Quadrupole splitting.



FIGURE 3. Relative contents of $Fe^{2+}(\Sigma Fe^{2+}/\Sigma Fe)$ vs. heating temperature. The solid straight lines represent linear fits: $(\Sigma Fe^{2+}/\Sigma Fe) = -1.1 \times 10^{-3} \times T$ (°C) + 0.46 (the first stage), and $(\Sigma Fe^{2+}/\Sigma Fe) = -1.1 \times 10^{-4} \times T$ (°C) + 0.11 (the second stage). R represents the correlation coefficient.

Two Fe²⁺ doublets (nos. 2 and 5) were identified in the spectrum for the stilpnomelane heated at 360 °C (Fig. 2; Table 2). Doublet no. 2 was assigned to Fe²⁺ in the M2 site. The second doublet (no. 5) was also present in the spectra obtained at higher temperatures and had very low quadrupole splitting values (QS = 0.76 mm/s and IS = 1.08 mm/s). The occupancy of doublet no. 2 decreased to 15% of its original value and doublet no. 1 was absent.

The Mössbauer parameters of the new Fe²⁺ doublet (no. 5) suggest an environment that is either highly distorted or very regular (Ingalls 1964). It is difficult to determine which is the case from Mössbauer data alone. It was assumed that this Fe2+ doublet represents a new M5 distorted octahedral site (IS = 1.08 mm/s). It seems reasonable to conclude from structural and Mössbauer data that this site may respond to effects from the nearest octahedral cations (Al³⁺, Mg²⁺, Mn²⁺, and Ti⁴⁺) and results from greater ditrigonal distortion of the tetrahedral layer due to intense oxidation and dehydroxylation. According to work by Eggleton (1972), this site would share four O atoms with silicon, like M1, providing a strong barrier against oxidation. Furthermore, the groups Fe²⁺Al³⁺ and Fe²⁺Ti⁴⁺ would require the highest oxidation potentials to oxidize the ferrous iron. It is worth noting that doublets with nearly the same parameters have been reported for staurolite (Dyar et al. 1991), ilmenite (Murad and Cashion 2004; MEDC 2005), [Mn_xFe_(1-x)]_vO solid solutions (Hope et al. 1982), and wustite (Manning et al. 1980).

Figure 4 shows that the spectra for the samples heated at 450, 600, and 810 °C do contain such a contribution (top right). The outermost edges of the spectra, E_L and E_H , are located at -0.60 mm/s (no influence from doublet no. 5) and +1.27 mm/s (strong influence from doublet no. 5), respectively. They are vertically shifted relative to each other due to the M5 doublet, and the displacement decreases with decreasing Fe²⁺ content at the M5 site (Fig. 4). Furthermore, in the 450, 600, and 810 °C spectra, the left side of the high energy arm is distinctly broadened by doublet no. 5 (Fig. 2). This Fe²⁺ component is also strongly supported by the fitting procedure. Good fits ($\chi^2_{red} \sim 1$) for samples heated at 360, 450, 600, and 810 °C were only obtained if doublet no. 5 was represented in these spectra. If the doublet was not represented,



FIGURE 4. Changes in the ratio $(B-E_H)/(B-E_L)$ with relative contribution of doublet no. 5. B = mean value off-resonance counting rate; $E_{Ls}E_H$ = values of the counting rate of the shoulders located at -0.60 mm/s (low-energy edge; no influence of doublet no. 5) and +1.27 mm/s (high-energy edge; strong influence of doublet no. 5).

the value of χ^2 varied between 2 and 3 and these spectra were inconsistent. The data, therefore, strongly suggest the presence of Fe²⁺ in the M5 site after heating at high temperatures.

In the 450 °C spectrum, Fe²⁺ was assigned solely to the M5 site, with a contribution of 0.06. There was no doublet representing Fe²⁺ ions in the M2 site. After heating at 600 °C, the contribution of Fe²⁺ to the entire spectrum was 0.04, and as with the previous sample, all remaining ferrous ions are located at the M5 site. After heating the stilpnomelane at 810 °C, the contribution of Fe²⁺ ions decreased to only 0.02. This characteristic Fe²⁺ doublet was absent in the spectra for the higher temperature samples.

Figure 3 shows two stages of relative Fe^{2+} content as a function of heating temperature. The oxidation of Fe^{2+} to Fe^{3+} caused an almost linear decrease in the Fe^{2+} contribution over a large temperature range (80 to 810 °C). The first stage of oxidation (80 to 360 °C) was much faster than the second stage (360 to 810 °C).

Changes in Fe³⁺ distributions

The interaction of the electric field gradient with high-spin Fe^{3+} ions in the octahedral crystalline positions is reflected in the Mössbauer spectrum by characteristic doublets with relatively small isomer shifts (0.20 to 0.60 mm/s) and quadrupole splittings from 0.20 to about 2.10 mm/s (MEDC 2005; Murad and Cashion 2004). Unlike Fe^{2+} , high quadrupole splittings for Fe^{3+} ions imply increasing distortion of the coordinated octahedra.

In the spectrum for the untreated SZ sample, two doublets were assigned to Fe³⁺ ions, with a contribution of 0.55. The first doublet (no. 3) had an IS of 0.36 mm/s and a QS of 2.07 mm/s (Fig. 2; Table 2), and its contribution to the spectrum was 0.16. It is the most characteristic and stable component. This doublet is present in all spectra up to 880 °C and its IS and QS values change very little. It can be regarded as a "fingerprint" of stilpnomelane as compared to chlorite, biotite, and other micas (Hoog and Meads 1975; Hawthorne 1988; MEDC 2005). Doublets with similar parameters have been recorded in the spectra of minerals from the epidote group (Dollase 1973), axinite (Zabiński et al. 1997), and (with greater QS) in gadolinite (Ito and Hafner; 1974; Malczewski et al. 1998). Such a doublet was also seen in the

experimental stilpnomelane spectrum presented in an extensive paper dealing with layer silicates (Taylor et al. 1968), but the doublet was not isolated in the analysis. The M3 site (Table 2) can probably be assigned to individual Fe³⁺ octahedra from the octahedral sheet, which expands laterally by thinning or compressing. This distortion is the second main structural mechanism (after tetrahedral rotation) that allows the tetrahedral and octahedral sheets to adapt (Guggenheim and Eggleton 1987).

Figure 5 shows the relative content of doublet no. 3 vs. temperature for all spectra. A significant change in the doublet area is observed after heating at 360 °C. In a paper by Sachanbiński and Janeczek (1977), the exothermic peak with a maximum at 360 °C on the DTA curve was assigned to the oxidation of Fe2+ to Fe3+ near this temperature. The Mössbauer results can also be explained as the first real rearrangement in the structure of stilpnomelane. Fe³⁺ ions have a smaller ionic radius than Fe2+ ions, and replacement of Fe²⁺ with Fe³⁺ causes contraction of the octahedral sheet, warping the tetrahedral layer into greater ditrigonal distortion to retain the mutual fit (Vedder and Wilkins 1969). The result of this adjustment is that part of the Fe2+ that is oxidized to Fe3+ at 360 °C and higher is placed into the new, strongly distorted Fe³⁺ octahedra. Contribution of this doublet to the whole spectrum differed only slightly for the samples heated at temperatures higher than 360 °C, with the exception of the spectrum for 810 °C, in which the contribution of this doublet had nearly the same value as for the untreated SZ sample (Fig. 5; Table 2). This result is difficult to explain. In part, the intensity of doublet no. 3 may be lowered by the fitting procedure as a result of a strong overlap with doublets 7 and 8. Again, this observation coincides well with the last exothermic peak observed on the DTA curve at 810 °C.

The second doublet assigned to Fe³⁺ ions (no. 4; Fig. 2; Table 2) in the SZ spectrum had an area of 0.33. This doublet had the greatest content for all samples up through the 600 °C sample. The high Γ value and its intensity at 200 °C suggest that this doublet represents all overlapped components of ferric iron from the M1, M2, and M4 sites. The intensity of this doublet increased to 0.63 due to the intense oxidation of Fe²⁺ to Fe³⁺ in the M2 site at 200 °C. This result is in good agreement with the reduced Fe²⁺ content in the M2 (0.21) and M1 (0.02) sites after the oxidation at 200 °C. The relative area changed only slightly (from 0.33 to 0.35) as the temperature increased from 360 to 600 °C.



FIGURE 5. Variation in the relative contents of doublet no. 3 vs. heating temperature. Solid line = average contribution of the doublet.

values are close to that for SZ (0.39). Isomer shifts for this doublet at these temperature ranges changed slightly from 0.42 to 0.45 mm/s, and quadrupole splittings decreased systematically from 1.24 mm/s at 200 °C to 1.04 mm/s at 600 °C. This suggests a more regular arrangement of these ferric positions. This doublet was not observed after heating at 810 and 880 °C.

Two new doublets (nos. 6 and 7; Fig. 2; Table 2) were separated when fitting the spectrum for the sample heated at 360 °C. The IS values were 0.16 and 0.40 mm/s, and the QS values were 1.47 and 1.67 mm/s, respectively. These data allowed the assignment of these doublets to Fe^{3+} positions. As might be expected, the first (no. 6) can be assigned to Fe^{3+} in the M1 site (after the oxidation of Fe^{2+} in M1). Doublet no. 7 was assigned to Fe^{3+} in the M2 site (after oxidation of Fe^{2+} in M2). These doublets can be clearly separated from doublet no. 4 after heating at 360, 450, and 600 °C. The high QS values suggest strong distortion in the Fe^{3+} M1 and M2 sites.

The less intense doublet (no. 6) had a low isomer shift value, indicating that most of the ferric iron was formed in a very asymmetric environment. This can be explained by dehydroxylation (Vedder and Wilkins 1969; Hoog and Meads 1975). Dehydroxylation is easier for OH ions bonded to two divalent ions and a vacancy than for those bonded to two trivalent ions and vacancy (Vedder and Wilkins 1969). An O^{2-} ion left over due to the condensation of hydroxyls can be connected to these two divalent octahedral ions and lead to some distortion of the octahedral layer. In other words, this site will tend to have a coordination lower than six. The isomer shift remains nearly constant with temperature, but quadrupole splittings for this doublet gradually decrease from 1.47 (360 °C sample) to 1.28 mm/s (600 °C sample). Doublet no. 6 has not been identified in the sample heated at 810 °C.

Similarly, doublet no. 7 represents a highly distorted M2 octahedral Fe³⁺ position and is characterized by practically unchanged isomer shifts for the 360, 450, and 600 °C samples (0.40 to 0.42 mm/s). Quadrupole splitting was greatest (1.67 mm/s) after heating at 360 °C, whereas the values were equal (1.41 mm/s) for the 450 and 600 °C samples (Table 2). For the 810 °C sample, doublet no. 7 is characterized by lower IS and QS values due to the formation of a more uniform structure. In the spectra for 810 and 880 °C, a new quadrupole doublet with broad peaks (no. 8; Fig. 2; Table 2) was visible. This doublet results from the superposition of a large number of somewhat different quadrupole doublets assigned to Fe³⁺ in octahedral positions. The only doublet the 880 °C sample has in common with both the original structure and the 810 °C sample is doublet no. 3.

The spectrum of the sample heated at 1050 °C is shown in Figure 6, and the spectrum parameters are given in Table 3. At about this temperature, a complete breakdown of the stilpnomelane structure takes place, and the spectrum consists of two ferric doublets (D1 and D2) and two sextets (S1 and S2). The predominant iron phase in this new material is hematite. It is represented by the two sextets, with a contribution of 0.71 in the spectrum. The parameters allowed the assignment of the doublets to Fe³⁺ in octahedral positions. The hyperfine parameters of the S2 sextet are not quite typical for pure bulk hematite. This results primarily from the influence of Al³⁺ substitution, which lowers both the magnetic ordering and the saturation hyperfine

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Sample	χ²	No.	IS* (mm/s)	H† (T)	QS (mm/s)	Γ/2 (mm/s)	Intensity§
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)	50.9(1)	0.204(6)‡	0.339(33)	0.32
		S2	0.331(15)	47.6(2)	0.066(1)‡	0.166(13)	0.39

TABLE 3. Parameters of ⁵⁷Fe Mössbauer spectrum for stilpnomelane after heating for 3 h in air at 1050 °C

* Isomer shift values are given relative to the lpha-Fe standard.

† Hyperfine magnetic field.

‡ Suggested reference e.g., McCammon (1995).

§ Estimated error $\Delta l/l \leq 12\%$.



FIGURE 6. ⁵⁷Fe Mössbauer spectrum of stilpnomelane after heating at 1050 °C. Solid dots = experimental data; thick solid line = fitted curve; thin solid line = fitted doublets (D1 = outer, D2 = inner); doted line = fitted sextets (S1 = outer, S2 = inner).

field (Murad and Cashion 2004). For hematite, room-temperature hyperfine fields noticeably below 51 T can usually be taken to indicate deviations from ideal chemistry.

No ferric iron in a pure tetrahedral site was identified in any of the samples analyzed in this study. Based on work by Rancourt et al. (1992), the spectral components of Fe³⁺ in tetrahedral positions should be characterized by an IS ≈ 0.17 mm/s and QS \approx 0.50 mm/s with respect to an α -Fe standard. However, doublets with such spectral components were not observed in this study. After heating at 360, 450, and 600 °C, doublet no. 6 exhibited IS values similar to that listed (Table 2), but the quadrupole splittings were much higher than 0.50 mm/s. Furthermore, this doublet originates from the deformation of the octahedral layer in M1 positions caused by dehydroxylation and oxidation processes. Thus, unlike the previous interpretation (Taylor et al. 1968), the data presented here indicate that ferric iron does not occupy tetrahedral sites in stilpnomelane.

Altered stilpnomelane and associated chlorite

Unexpected results were obtained for the sample of altered stilpnomelane (ASZ). As previously noted, this sample has many features of chemical alteration. Fitted doublets and calculated parameters for the spectra of the altered stilpnomelane and associated chlorite are shown in Figure 7 and Table 4. The Mössbauer results are as follows: (1) the relative content of Fe²⁺ was distinctly higher (0.70) than for the SZ sample (0.45). Two ferrous doublets (nos. 1 and 2; Table 4; Fig. 7) in M1 and M2 sites had nearly the same parameters as analogous doublets in the SZ spectrum, with an area ratio of 1:3; and (2) the relative content of Fe³⁺ in ASZ was much lower (0.23) than for the SZ



FIGURE 7. Mössbauer spectra of (a) altered stilpnomelane from Zółkiewka (ASZ), and (b) associated chlorite. Solid dots = experimental data; thick solid line = fitted curve; thin solid line = fitted doublets.

sample (0.55). The characteristic Fe^{3+} doublet no. 3 was less intense (0.10) in WSZ than SZ (0.16). The high content of Fe^{2+} in ASZ, and the simultaneously low content of Fe^{3+} in the M3 site suggest that this sample might have been subject to hydrothermal processes operating locally.

Stilpnomelane can be regarded as an intermediate mineral between chlorite and micas and is most likely formed by the transformation of Fe-rich chlorite. The specimen from the Polish pegmatites is probably a secondary mineral arising from Fe-rich chlorite (Sachanbiński and Janeczek 1977), which forms layers up to 7 cm thick. This conclusion is supported by direct comparison of the ASZ Mössbauer spectrum with that for associated chlorite from the same rock fragment (Fig. 7; Table 4). The ferrous doublets in both octahedral sites (M1 and M2) showed strikingly similar parameters, with isomer shifts of 1.12–1.13 and 1.14 mm/s, and quadrupole splittings of 2.35–2.33 and 2.68–2.70 mm/s in altered stilpnomelane and chlorite,

Sample	χ²	No.	IS*	QS (mm/s)	Γ/2 (mm/s)	Intensity†	Site assignment
			(mm/s)				5
Altered stilpnomelane (ASZ)	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	1.51	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⁺
* Isomer shift values are given r	elative to the	α-Fe standar	d.				

TABLE 4. Parameters of ⁵⁷Fe Mössbauer spectra for the altered stilpnomelane from Zółkiewka (ASZ) and associated chlorite

respectively. A characteristic ferric doublet (no. 3) was seen in the ASZ and SZ samples, but is absent in the chlorite spectrum (Fig. 7). In addition, the area ratio of M1:M2 was 1:3 for ASZ and 1:2 for the chlorite.

The reduction of Fe^{3+} intensity in M3 is connected with the rehydroxylation process. As a result of rehydroxylation, hydroxyl anions re-occupy the original sites in the original orientation. It has been reported (Vedder and Wilkins 1969) that the OH⁻ content in micas after rehydroxylation was restored to about 84%. 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 has taken place in the ASZ sample. Consequently, the ASZ sample could be representative of the early stage of stilpnomelane formation. If so, it can be assumed that pegmatite ferristilpnomelane forms by oxidation of earlier ferrostilpnomelane.

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