Structural Transformations of Northcom Transvaal and Libby Montana Vermiculite Clay Produced by Firing: Mossbauer Study

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ABSTRACT

Two samples of vermiculite clay, which are known by the names Libby Montana and Northcom Transvaal, were subjected to a firing treatment from 100 to 1000 °C. The structural transformation was monitored by observing the changes that occur in the structural iron and the change in the Mossbauer data. ^{57}Fe Mossbauer spectra indicate the presence of both Fe^{2+} and Fe^{3+} sites, and the main feature of the Mossbauer parameters of the two fired samples is that when the firing temperature is increased, the quadrupole splitting of the Fe^{3+} and to some extent Fe^{2+} doublet increases, indicating a distorted structure. There is no apparent correlation between the firing temperature and the isomer shift in both samples. The linewidth has also increased, indicating that more than one site is occupied. The complete oxidation of Fe^{2+} in the Northcom Transvaal sample occurred at 300 °C, while for the Libby Montana sample occurred at 600 °C.

INTRODUCTION

Vermiculite is a silicate mineral that belongs to the phyllosilicate subclass. Its structure corresponds to that of the 2:1 group where it consists of two tetrahedral silicate sheets interlayered by an octahedral sheet that contains aluminum and iron.[1] Vermiculite can undergo hydration-dehydration reactions due to the existence of water and OH groups, which are dependent on a variety of parameters such as temperature, pressure, particle size, relative humidity, and chemical composition.[2] Vermiculite has been studied extensively due to its unique physical and chemical features, which include low thermal conductivity and density, refractory behavior, and high cation exchange capacity, all of which lead to a wide range of commercial uses.[3-8]

Many studies on the effect of firing of clays have been carried out. It was found that between 500 and 800 °C, the clay mineral undergoes dehydroxylation. Above 800 °C, there occurs a disintegration of the clay mineral structure, followed by recrystallization in an iron-rich phase, most likely in the form of very small particles.[9] A significant increase in the volume of vermiculite is observed as a result of firing.[10] When heated to 650 – 950 °C, vermiculite can swell up to 30 times its original volume. Low thermal conductivity, low bulk density, endurance, chemical inertness, and a relatively high melting point are some of the promising qualities of expanded vermiculite. Expanded vermiculite has a wide range of uses in civil engineering, chemical industry, and agriculture.[11] Due to its outstanding thermal performance and non-combustibility, expanded vermiculite is a novel alternative to traditional fire-resistance materials.[12] The process of heat energy absorption by vermiculite was investigated, and the firing module's optical-geometric parameters were determined.[13] Under heat radiation, a method is considered for evaluating the absorption-reflection properties of a single grain of vermiculite and a dense single-layer array of intumescent vermiculite situated on a planar surface.[14]

Mossbauer spectroscopy has proved to be important in mineralogical and geochemical applications. The method has been widely applied to investigate the iron electronic environments found in clay minerals. Mossbauer study was conducted to assess the clay iron content in a variety of clay samples.[15-18] An early Mossbauer study on fired vermiculite collected from different regions of India was carried out at firing temperature up to 1100 °C.[19] The valence states and coordination behavior of iron in vermiculite were also studied by Mossbauer spectroscopy.[20] The technique used to assess the tetrahedral Fe^{3+}, octahedral Fe^{3+}, and Fe^{2+} of vermiculites.[3] In a study, it was shown that the oxidation of iron occurs mainly in octahedral sites. It was suggested that migration and oxidation of the Fe^{2+} ions from the octahedral sites to the tetrahedral sites may occur during the transformation process.[21] The heat-resistant properties of fire clay make them ideal for many industrial applications such as pottery, brick-making, and cement production.[22] The aim of the study is to characterize the iron content of the two original samples and to understand the effect of firing temperature on the two iron sites. Furthermore, adding new data related to vermiculite clay firing to temperatures from 100 to 1000 °C.

EXPERIMENTAL

The investigated vermiculite samples were obtained from Ward's Natural Science Establishment, namely Libby Montana and Northcom Transvaal vermiculite samples, the chemical composition shown in Table 1. Using ^{57}Co as a source, Mossbauer spectra were obtained on a Canberra Multichannel Analyzer. The source was a rhodium matrix containing 25-mCi cobalt-57 obtained from the Radiochemical Centre, Amersham.

The two vermiculite clay samples were used without any pretreatment, and when subjected to thermal treatment for 60 minutes within the range of 100 to 1000°C under air, the Libby Montana sample's small green crystalline slabs preserved their green color up to around 300 °C, after which the green slabs began to convert to a golden color and took on a spongy shape. The golden color darkened as the temperature was raised, eventually becoming a brown-gold color.

Firing the Northcom Transvaal sample, which is in the form of large brownish-green flakes, over 300 °C caused the flakes to split into several spongy layers in contact with each other. They had a golden color, the golden color getting darker on further firing. Each clay sample undergoes major physical and chemical changes and the yield after thermal process is ceramic.

Mossbauer spectra of the unfired and fired samples were taken at 77 °K.

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Table 1. The chemical composition and contents (wt%) of the two vermiculite samples.

Sample	SiO_2	MgO	Al_2O_3	Fe_2O_3	K_2O	TiO_2	CaO	Na_2O	Cr_2O_3	SO_3
Libby Montana	40.39	25.80	14.50	7.73	6.23	1.78	1.52	1.51	0.21	0.12
Northcom Transvaal	42.53	24.90	13.45	6.78	7.11	1.74	1.42	1.49	0.20	0.14

RESULTS AND DISCUSSIONS

The information that can be obtained from the data of Mossbauer spectroscopy is the characterization of the oxidation states of iron (e.g. Fe^{2+} or Fe^{3+}), the electronic configuration of the iron (e.g. low or high spin), the coordination symmetry about the iron atom (e.g. tetrahedral or octahedral) and any distortion from such tetrahedral or octahedral symmetry. The chemical composition of the two samples appears similar, with few differences in the proportions of the components that make up the composition.

Mossbauer spectra of the samples

Mossbauer spectra of the original samples are shown in Figure 1. The spectra were fitted to two doublets corresponding to high spin Fe^{3+} and Fe^{2+} sites. The isomer shift of the Fe^{3+} in the Northcom Transvaal is 0.32(1) mms^{-1} and 1.25(2) mms^{-1} for Fe^{2+}, and the quadrupole splittings are 0.78(1) mms^{-1} for Fe^{3+} and 2.80(3) mms^{-1} for Fe^{2+}. While isomer shifts of the Libby Montana vermiculite sample are 0.47(1) mms^{-1} for Fe^{3+} and 1.22(1) mms^{-1} for Fe^{2+}, and the quadrupole splittings are 0.96(1) mms^{-1} for Fe^{3+} and 2.80(1) mms^{-1} for Fe^{2+}. The parameters are close to some room temperature values reported by other researchers[23] which are 0.37(1) mms^{-1} for the Fe^{3+} isomer shift and 1.13(8) mms^{-1} for Fe^{+2}, and quadrupole splittings of 0.64(3) mms^{-1} for Fe^{3+} and 2.71(18) mms^{-1} for Fe^{2+} (Table A1). The spectra are also nearly similiar to that reported for another vermiculite samples (Table A2).[15]

The quadrupole splitting values for Fe in both vermiculite samples are larger than that found for montmorillonite, which also belongs to the 2:1 layer group, reported in previous work[24] which are 0.65(2) mms^{-1} for Fe^{3+} and 3.03(1) for Fe^{2+} (Table A3), indicating that the Fe^{3+} octahedra are distorted in the former samples. The Libby Montana vermiculite sample shows quadrupole splitting for Fe^{3+} larger than that found in the Northcom Transvaal, indicating that this site is more distorted in the former sample.

In the quadrupole splitting equation 1,

$$QS = \frac{1}{2} e^2 qQ (1 + \eta^2/3)^{1/2} \qquad (1)$$

the

$$q = (1 - \lambda\alpha) q_{lattice} + (1 - R) q_{valence} \qquad (2)$$

where $\lambda\alpha$ and R are empirical constants, QS is quadrupole splitting, eQ is the nuclear quadrupole moment, eq is the electrostatic field gradient and η is the symmetry parameter.
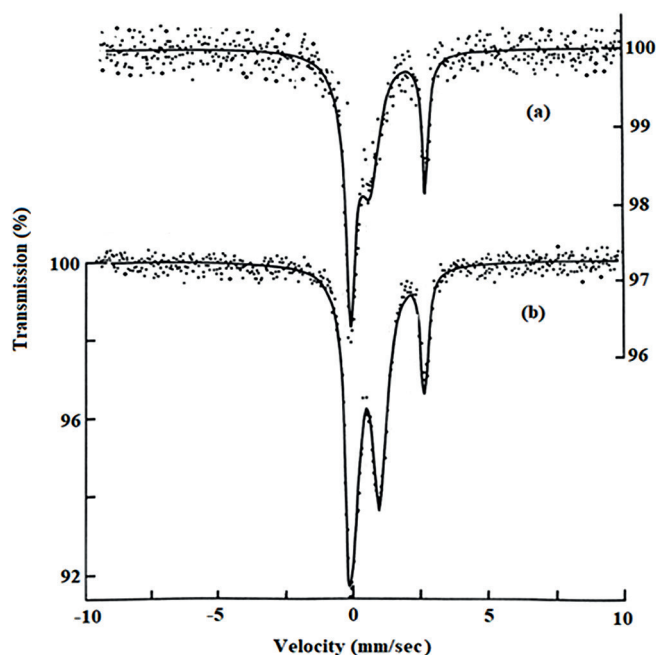

Figure 1: The ^{57}Fe Mossbauer spectra at 77 °K of the original sample of (a) Northcom Transvaal vermiculite, (b) Libby Montana vermiculite

The electronic configuration of high spin Fe^{3+} in clay minerals is spherically symmetrical, $(t_{2g})^3 (eg)^2$. $q_{valence} = 0$ in this case. As a result, the larger the quadrupole splitting value, the greater the distortion. For Fe^{2+} which is not a spherically symmetrical ion $(t_{2g})^4 (eg)^2$, the value of $q_{valence}$ term cannot be neglected. In this case the smaller the value of the quadrupole splitting, the greater the distortion.[25]

The Fe^{2+} quadrupole splitting values in vermiculite samples are smaller than those reported for montmorillonite,[24] indicating that the Fe^{2+} octahedra in vermiculite are more distorted than in montmorillonite. As a result, the electronic environment of both Fe^{2+} and Fe^{3+} are more distorted in vermiculite than in montmorillonite.

The Mossbauer parameters of the two samples fired for 60 minutes are listed in Tables 2 and 3. There is no apparent correlation between the firing temperature and the isomer shift in both samples. It was observed that decomposition of octahedral iron in vermiculite occurs before complete dihydroxylation.[26] The dioctahedral clay, like montmorillonite, dehydroxylates at lower temperatures than trioctahedral clay, like vermiculite.[27] Furthermore, the amount of

Table 2. The ^{57}Fe Mossbauer parameters at 77 °K of the Northcom Transvaal sample fired for 60 minutes under air.

Temp. °C	Fe^{2+} parameters			Fe^{3+} parameters		
	δ mms^{-1}	Δ mms^{-1}	Γ mms^{-1}	δ mms^{-1}	Δ mms^{-1}	Γ mms^{-1}
100	1.21(1)	2.76(2)	0.19(1)	0.25(2)	0.79(3)	0.42(2)
200	1.25(3)	2.80(4)	0.14(3)	0.44(2)	0.74(2)	0.41(3)
300	1.20(2)	2.78(3)	0.14(3)	0.37(1)	0.78(2)	0.44(2)
400	-	-	-	0.37(1)	0.86(2)	0.48(2)
500	-	-	-	0.43(3)	0.88(2)	0.48(2)
600	-	-	-	0.39(1)	1.02(1)	0.45(1)
700	-	-	-	0.37(1)	1.06(1)	0.46(1)
800	-	-	-	0.42(1)	1.33(1)	0.41(1)
900	-	-	-	0.40(1)	1.32(1)	0.44(1)
1000	-	-	-	0.42(1)	1.35(1)	0. 41(1)

Table 3. The ^{57}Fe Mossbauer parameters at 77 ^{o}K of the Libby Montana sample fired for 60 minutes under air.
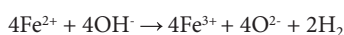
Temp. ^{o}C	Fe^{2+} parameters			Fe^{3+} parameters		
	δ mms^{-1}	Δ mms^{-1}	Γ mms^{-1}	δ mms^{-1}	Δ mms^{-1}	Γ mms^{-1}
100	1.20(1)	2.75(1)	0.16(1)	0.50(1)	0.93(1)	0.33(1)
200	1.36(1)	2.49(2)	0.22(1)	0.44(1)	1.06(1)	0.29(1)
300	1.34(1)	2.50(2)	0.22(1)	0.43(1)	1.06(1)	0.29(1)
400	1.20(1)	2.78(1)	0.19(1)	0.50(1)	1.00(1)	0.30(1)
500	1.20(1)	2.81(2)	0.19(2)	0.49(1)	1.09(1)	0.29(1)
600	1.17(1)	2.97(3)	0.11(3)	0.49(1)	1.14(1)	0.30(1)
700	-	-	-	0.49(1)	1.22(1)	0.31(1)
800	-	-	-	0.49(1)	1.27(1)	0.34(1)
900	-	-	-	0.49(1)	1.34(1)	0.36(1)
1000	-	-	-	0.48(1)	1.25(1)	0.40(1)

iron present in the matrix of the clay sample has some effect on the temperature required for the Fe^{2+} oxidation process upon firing.[28] The amount of iron in the Libby Montana sample is more than that of the Northcom Transvaal sample. This has a clear effect on the process of oxidation of Fe^{2+} to Fe^{3+}. The greater the amount of iron, the higher the temperature the sample needs to complete the oxidation process.

Two terms can explain the firing process, below 600 ^{o}C the main term is the oxidation of Fe^{2+}, and above 600 ^{o}C the main term is dehydroxylation of the lattice. The proposed mechanism[29, 30] for the oxidation of Fe^{2+} in the presence of ambient oxygen is:

$$4Fe^{2+} + 4OH^- + O_2 \rightarrow 4Fe^{3+} + 4O^{2-} + 2H_2O$$
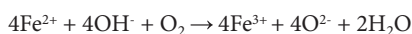
and in the absence of oxygen:

$$4Fe^{2+} + 4OH^- \rightarrow 4Fe^{3+} + 4O^{2-} + 2H_2$$

Because oxygen molecules are too big to enter the lattice at low temperatures, the second reaction dominates, even in the presence of ambient oxygen. Firing to a higher temperature causes the decomposition of the hydroxyl groups to an oxygen ion and water in the neighborhood of a vacancy.[26]

$$OH^- + OH^- \rightarrow H_2O + O^{2-}$$
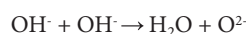
The main feature of the Mossbauer parameters of the two fired samples is the increase in the quadrupole splitting of the Fe^{3+} and to some extent Fe^{2+} doublets as the firing temperature are raised, which indicates a distorted structure. There has also been an increase in linewidth, indicating that more than one site is occupied. The temperature of Fe^{2+} oxidation is higher in both samples than in the montmorillonite clay.[24] The Libby Montana sample had complete oxidation of Fe^{2+} at 600 ^{o}C, while the Northcom Transvaal sample had complete oxidation at 300 ^{o}C. Figure 2, 3, and 4 show the Mossbauer spectra of the fired Libby Montana vermiculite sample. The behavior
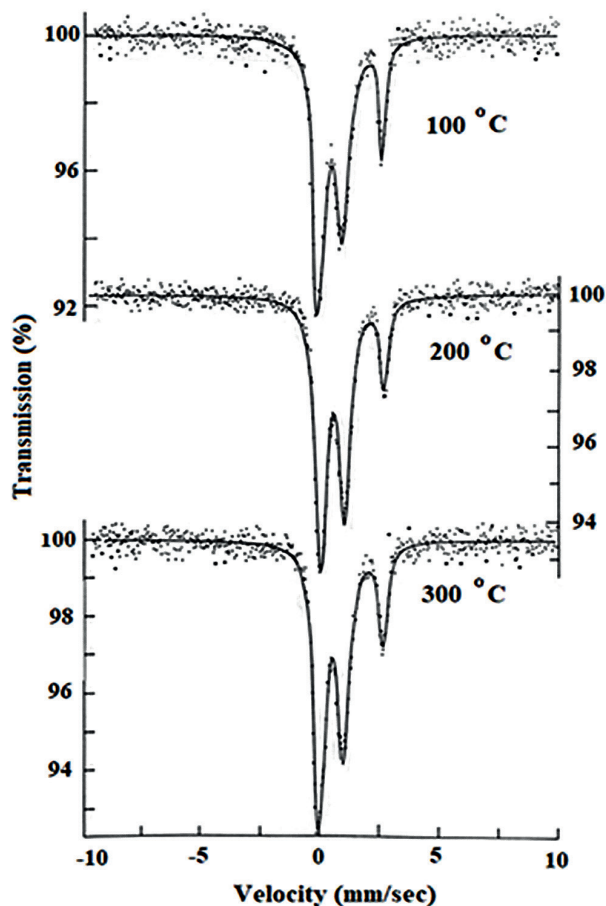
Figure 2: The ^{57}Fe Mossbauer spectra at 77 ^{o}K of Libby Montana sample fired at 100 – 300 ^{o}C for 60 minutes.
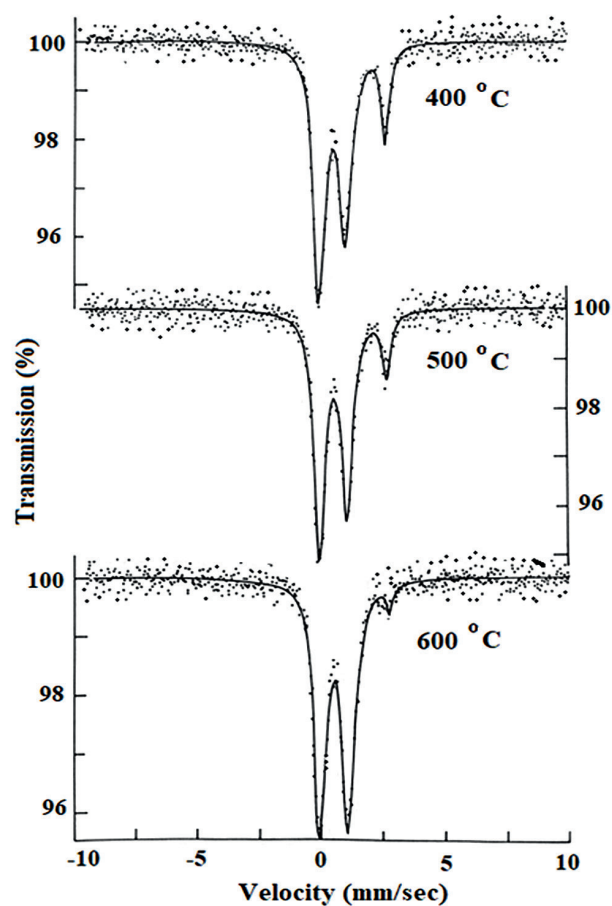
Figure 3: The ^{57}Fe Mossbauer spectra at 77 ^{o}K of Libby Montana sample fired at 400 – 600 ^{o}C for 60 minutes.
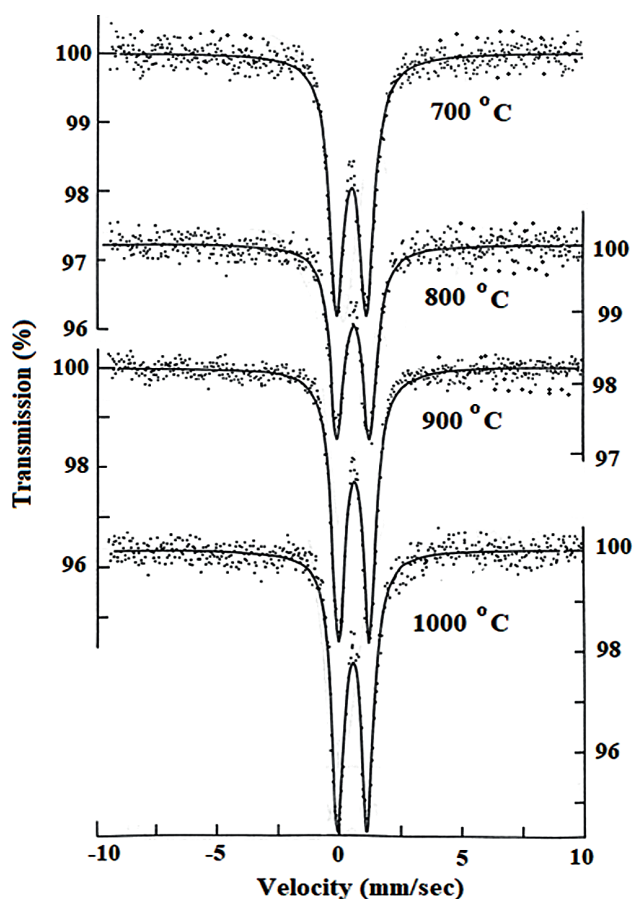
Figure 4: The ^{57}Fe Mossbauer spectra at 77 °K of Libby Montana sample fired at 700 – 1000 °C for 60 minutes.

of the two samples upon firing appears similar to the behavior of another vermiculite sample studied in the same field.[19] There was an increase in quadrupole splitting (Table A4).

CONCLUSIONS

Firing the Northcom Transvaal and Libby Montana vermiculite clay causes a change in their color as well as their physical appearance. A significant increase in the volume is observed as a result of firing. The main characteristic of the Mossbauer parameters of the two fired samples is that as the firing temperature rises, the quadrupole splitting of the Fe^{3+} and, to a lesser extent, Fe^{2+} doublet increases, indicating a distorted structure. In both samples, there appears to be no link between the firing temperature and the isomer shift. The linewidth has also increased, indicating that more than one site is occupied. The entire oxidation of Fe^{2+} in the Northcom Transvaal sample occures at 300 °C, while in the Libby Montana sample it occures at 600 °C.

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APPENDICES

Table A1. The ^{57}Fe Mossbauer parameters at R. T. of vermiculite clay sample.

	Fe^{2+} parameters		Fe^{3+} parameters		
Sample	δ mms^{-1}	Δ mms^{-1}	δ mms^{-1}	Δ mms^{-1}	Ref.
Vermiculite	1.13(8)	2.71(18)	0.37(1)	0.64(3)	23

Table A2. The ^{57}Fe Mossbauer parameters at 95 ^{o}K of montmorillonite clay sample.

	Fe^{2+} parameters		Fe^{3+} parameters		
Sample	δ mms^{-1}	Δ mms^{-1}	δ mms^{-1}	Δ mms^{-1}	Ref.
Vermiculite	1.206	2.88	0.431	0.88	15

Table A3. The ^{57}Fe Mossbauer parameters at 77 ^{o}K of montmorillonite clay sample.

	Fe^{2+} parameters		Fe^{3+} parameters		
Sample	δ mms^{-1}	Δ mms^{-1}	δ mms^{-1}	Δ mms^{-1}	Ref.
Montmorillonite	1.25(1)	3.03(1)	0.43(2)	0.65(2)	24

Table A4. The ^{57}Fe Mossbauer parameters at R. T. of vermiculite clay sample fired to different temperatures.

Firing temp. ^{o}C	δ mms^{-1}	Δ mms^{-1}	Ref.
25	0.60(0.03)	1.05(0.03)	19
400	0.55(0.03)	1.05(0.03)	
550	0.75(0.03)	1.45(0.03)	
800	0.75(0.03)	1.05(0.03)	
1000	0.55(0.03)	0.75(0.03)	
1100	0.60(0.03)	0.60(0.03)	