

# MÖSSBAUER, THERMOMAGNETIC, AND X-RAY STUDY OF CATION ORDERING AND HIGH-TEMPERATURE DECOMPOSITION IN BIOTITE

V. I. BAGIN, T. S. GENDLER

Institute of Geophysics, Academy of Sciences, Moscow, U.S.S.R.

L. G. DAINYAK

Geological Institute, Academy of Sciences, Moscow, U.S.S.R.

R. N. KUZ'MIN

Moscow State University, Moscow, U.S.S.R.

**Abstract**—To explain the large values of the quadrupole splittings and line widths in the Mössbauer spectrum of oxybiotite, a formalized analysis of the distribution of effective charges in the anion network was conducted using an idealized model of the biotite octahedral layer. Based on this analysis, a qualitative physical model has been proposed, according to which the Mössbauer spectrum consists of a superposition of six quadrupole doublets. The proposed model explains the appearance of residual magnetization well below the biotite decomposition temperature. Annealing the biotite at 1070°K leads to the formation of nuclei of the magnetic phase in chains consisting of  $R^{3+}$  and vacancies. This phase is the decomposition product of biotite at 1370°K, i.e., a ferrispinel having  $Fe_{2-x}MgAl_xO_4$  ( $x = 0.5-0.6$ ) composition.

**Key Words**—Biotite, Ferrispinel, Mössbauer spectra, Oxybiotite, Thermal decomposition, Thermomagnetism.

## INTRODUCTION

Investigations of hydroxyl-bearing silicates and their dehydroxylated derivatives show some general features in their Mössbauer spectra. Typical features of all oxysilicates, i.e., compounds resulting from the transformation of silicates which originally contained hydroxyl groups and iron in its bivalent state, are large values of the quadrupole splitting  $\Delta$  (about 0.9–1.3 mm/sec) and line width ( $\Gamma = 0.7$  mm/sec) for  $Fe^{3+}$  ions, e.g., oxychlorite (Belov *et al.*, 1974), oxybiotite (Ivanitskiy *et al.*, 1975), and oxyamphiboles (Ernst and Wai, 1970). In contrast, silicates such as montmorillonite, illite, and glauconite, in whose structures the  $Fe^{3+}$  ion is coordinated by oxygen ions and hydroxyl groups, have visible  $\Delta$ s in the range 0.3–0.5 mm/sec (Taylor *et al.*, 1968; Weaver *et al.*, 1967; Plachinda *et al.*, 1974).

The correlations between dehydrogenation and the  $\Delta$  and  $\Gamma$  values have not yet been analyzed thoroughly. In the literature available there is only the general conclusion that an increase in degree of distortion of an iron-containing octahedron occurs on dehydrogenation (Belov *et al.*, 1974; Ivanitskiy *et al.*, 1975; Ernst and Wai, 1970; Taylor *et al.*, 1968; Weaver *et al.*, 1967; Plachinda *et al.*, 1974).

To explain the large values of quadrupole splittings and line widths in the oxybiotite Mössbauer spectrum, a formalized analysis of the distribution of effective

charges in the anion network is considered in the present paper, using the idealized model of the biotite octahedral layer. The investigation of structural peculiarities of biotite during oxidation is of significance by itself, but at the same time it is important for understanding the mechanism of the high-temperature (1370°K) decomposition processes. Also, if a reasonable solution to the biotite problem can be formulated, the same methods could be applied to other hydroxyl-bearing silicates.

## EXPERIMENTAL

A sample of biotite from a pegmatite of the Baryshevski granites (Ukrainian Shield) was used in the experiments. The chemical analysis is presented in Table 1.<sup>1</sup>

The measurements were carried out using a Mössbauer spectrometer with a constant acceleration electromechanical drive and a NTA-512M multichannel analyzer.  $Co^{57}$  in a Cr matrix was used as a source. The halfwidth of the absorption line in sodium nitroprusside (thickness = 10 mg  $Fe/cm^2$ ) was 0.29 mm/sec.

Natural polycrystalline biotite and its transformation products, obtained after annealing the original mate-

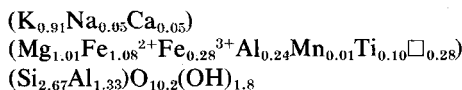
<sup>1</sup> The sample and its chemical analysis data were kindly supplied by A. V. Sukhorada. The water content was determined by V. L. Kofman using infrared spectroscopic methods.

Table 1. Chemical analysis of the biotite investigated.

Oxide	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O
Wt. %	33.92	1.74	17.36	7.54	14.36	0.22	8.63	0.62	0.35	9.10	0.10	3.70

rials at different temperatures (from 370°K to 1370°K) for various times were investigated. Biotite and its high temperature products were also analyzed by thermomagnetic and X-ray powder diffraction (XRD) methods.

A crystallochemical formula of the biotite sample was calculated from the chemical analysis on the basis of 12 (O, OH). In addition the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio was considered to be equal to 0.19 ± 0.02 (Voitkovskiy *et al.*, 1975), as obtained from the spectrum of a biotite single crystal; the dependence of hydroxyl content on the uncompensated charge in octa- and tetralayers was also taken into account (Warren, 1972). The resulting crystallochemical formula is as follows:



## RESULTS

### Natural biotite and oxybiotite

The Mössbauer spectrum (Figure 1a) of the polycrystalline biotite studied in the present work can be interpreted as a superposition of the two quadrupole doublets from Fe<sup>2+</sup> ions and one doublet from Fe<sup>3+</sup> ions (Voitkovskiy *et al.*, 1975; Bagin *et al.*, 1976). The doublet with Δ = 2.62 mm/sec is attributed to Fe<sub>cis</sub><sup>2+</sup> ions, which are situated in the more distorted cis-octahedra, and the doublet with Δ = 2.24 mm/sec to Fe<sub>tr</sub><sup>2+</sup> ions in the less distorted trans-octahedra (Pol'shin *et al.*, 1972) (see Table 2). Taking into consideration the difficulties in the determination of parameters for the part of the spectrum corresponding to the Fe<sup>3+</sup> ions, as evidenced by the spread of the data available in the literature (see Table 3), the temperature dependence of the polycrystalline spectrum was investigated in the 80°–1000°K temperature range. A sample was placed in a tightly closed container (limited access of air), and the spectra were obtained after maintaining the sample for 2 hr at each particular temperature. As

shown in Figure 1b, c, and d, with increasing temperature there is an increase in the intensity of the peak, which is the right-side component of the doublet from Fe<sup>3+</sup> ions. This indicates an oxidation of the biotite.

Simultaneously, an increase in the resolution of the left-side component of the total biotite spectrum can be observed at temperatures above 400°K. This enables the doublet from Fe<sup>3+</sup> ions to be identified and characterized with the following parameters: δ = 0.29 ± 0.02 mm/sec<sup>2</sup> and Δ = 1.23 ± 0.03 mm/sec. This interpretation is justified by the fact that the value of the quadrupole splitting of the part of the spectrum assigned to Fe<sup>3+</sup> cations remained practically constant with increasing temperature. As should be expected, at the same time a strong temperature dependence of Δ for Fe<sup>2+</sup> ions was observed. This analysis of high-temperature spectra allows one to reach the conclusion that the left-side component of the doublet from Fe<sup>3+</sup> ions in the spectrum of the original polycrystal should be found in the negative velocity region. Analysis of the spectra also showed that the sign of the asymmetry parameter for the Fe<sup>3+</sup> components is opposite to that from the Fe<sup>2+</sup> doublets. Parameters for the Fe<sup>3+</sup> ions in this biotite sample are given in Table 2. The values of these parameters were used later for establishing the degree of oxidation of samples annealed at different temperatures.

A completely oxidized biotite was obtained by heating the polycrystal in air at 870°K for 5 hr. Its Mössbauer spectrum consists of a doublet with significantly broadened lines (Γ<sub>1/2</sub> ~ 0.7 mm/sec) from Fe<sup>3+</sup> ions and the opposite asymmetry of components compared to the spectra of the original samples (Figure 2). Δ = 1.34 ± 0.03 mm/sec, and δ = 0.55 ± 0.02 mm/sec. The formation of only one phase, i.e., the oxidized biotite, as a result of heating in air at 870°K was confirmed by

<sup>2</sup> To obtain the value δ with respect to α-Fe, a value of -0.154 mm/sec should be added to the reported values, both in the text and in the tables.

Table 2. Mössbauer parameters of natural biotite polycrystal at T = 293°K.<sup>1</sup>

Absorber	Fe <sub>cis</sub> <sup>2+</sup>			Fe <sub>tr</sub> <sup>2+</sup>			Fe <sub>oct</sub> <sup>3+</sup>			Fe <sub>cis</sub> <sup>2+</sup> /Fe <sub>tr</sub> <sup>2+</sup> ratio
	Δ mm/sec	δ mm/sec	Γ mm/sec	Δ mm/sec	δ mm/sec	Γ mm/sec	Δ mm/sec	δ mm/sec	Γ mm/sec	
Polycrystal	2.58	1.34	0.42	21.3	1.34	0.42	1.23	0.29	0.62	1.90 ± 0.02

<sup>1</sup> Δ = quadrupole splitting; δ = isomer shift; Γ = width of line at half height; the error in determining δ and Γ is ±0.02 mm/sec, Δ is ±0.03 mm/sec. δ here and elsewhere was determined with respect to Co<sup>57</sup> (Cr).

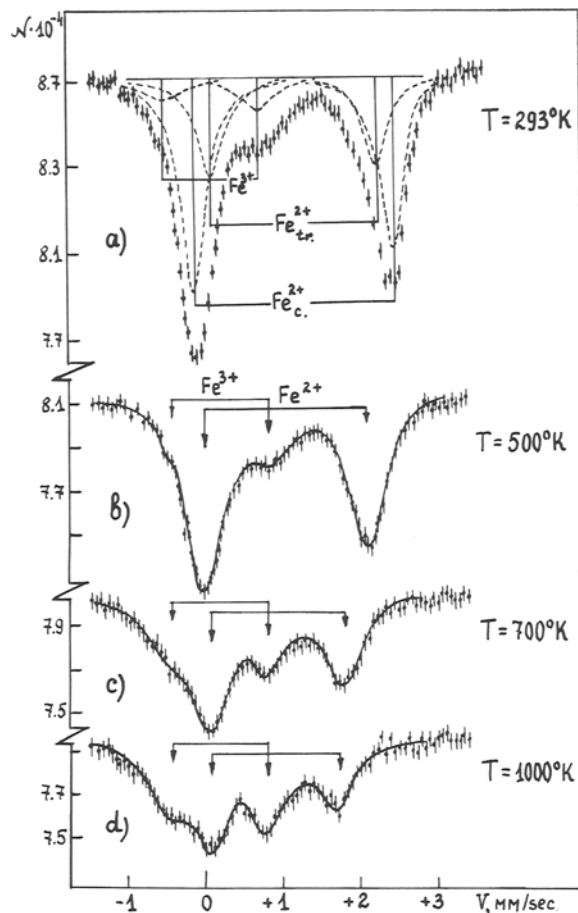
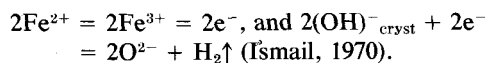


Figure 1. Mössbauer spectra of (a) biotite polycrystal at  $T = 293^\circ\text{K}$ ; (b), (c), and (d) biotite polycrystal at  $T = 500^\circ\text{K}$ ,  $700^\circ\text{K}$ , and  $1000^\circ\text{K}$ , respectively.

thermomagnetic and XRD analysis. Oxidation apparently occurs as follows:



As a result, there is a change in the environment of the iron ion, i.e., the anion composition becomes homogeneous, and a redistribution of effective charges in the immediate neighborhood of the  $\text{Fe}^{3+}$  ion takes place. Also, the isomer shift for the  $\text{Fe}^{3+}$  ions increases with an increase in the degree of oxidation of a sample (Figure 3). This reflects the increase in ionic character of the cation-anion bond as the destruction of hydroxyl groups takes place during oxidation.

Before analyzing the characteristics of the effective charge distribution within the limits of the nearest neighbors of  $\text{Fe}^{3+}$  in the biotite octahedral sheet, it is necessary to note the following: (1) the interpretation of the oxybiotite Mössbauer spectrum as a superposition of the two doublets corresponding to  $\text{Fe}^{3+}$  ions in

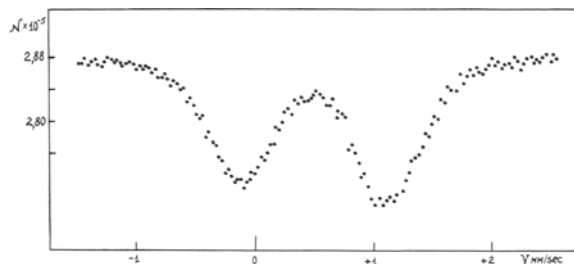


Figure 2. Mössbauer spectra of fully oxidized biotite polycrystal at  $T = 293^\circ\text{K}$ . The iron density in the sample was  $3.2 \times 10^{-3} \text{ mg/cm}^2$ . Line halfwidth is equal to  $0.68 \pm 0.02 \text{ mm/sec}$ .

cis- and trans-octahedra is inadequate because the doublet components are significantly broadened ( $0.46 \text{ mm/sec}$  compared with  $0.29 \text{ mm/sec}$  for the sodium nitroprusside standard), and (2) the  $\text{Fe}_{\text{cis}}^{3+}/\text{Fe}_{\text{tr}}$  ratio of the original biotite.

#### *Analysis of the formal effective charge distribution in the anion network of the biotite octahedral sheet*

For simplicity, the ideal biotite composition, i.e.,  $\text{K}(\text{Si}_3\text{Al})(\text{R}_{3-y}^{2+} \text{R}_{(2/3)y}^{3+} \square_{y/3})\text{O}_{10}(\text{OH})_2$ , where  $y \geq 0$ , was used for the analysis, and the octahedral sheet of biotite was considered to be composed of regular octahedra. Thus, this layer schematically could be treated as overlap of two networks, i.e., an anion network formed by regular hexagons and a cation network composed of regular triangles, with every point in the anion network located above or below the center of a triangle. Based on Pauling's electrostatic valency rule, a definite charge can be assigned to every position in the anion network.<sup>3</sup> The oxygen anion charge, which remains

<sup>3</sup> Here a formal effective charge refers to a part of the anion charge, which corresponds to each one of the surrounding cations.

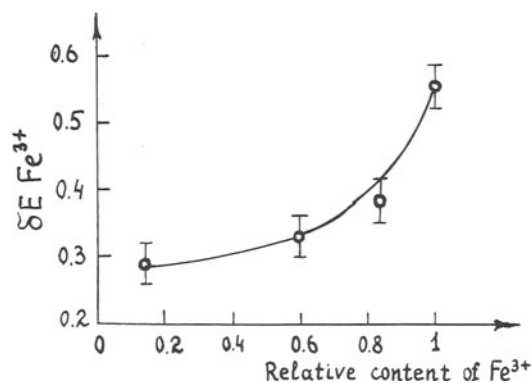


Figure 3. Dependence of  $\delta$  for  $\text{Fe}^{3+}$  ions on the relative  $\text{Fe}^{3+}$  ion content in biotite.

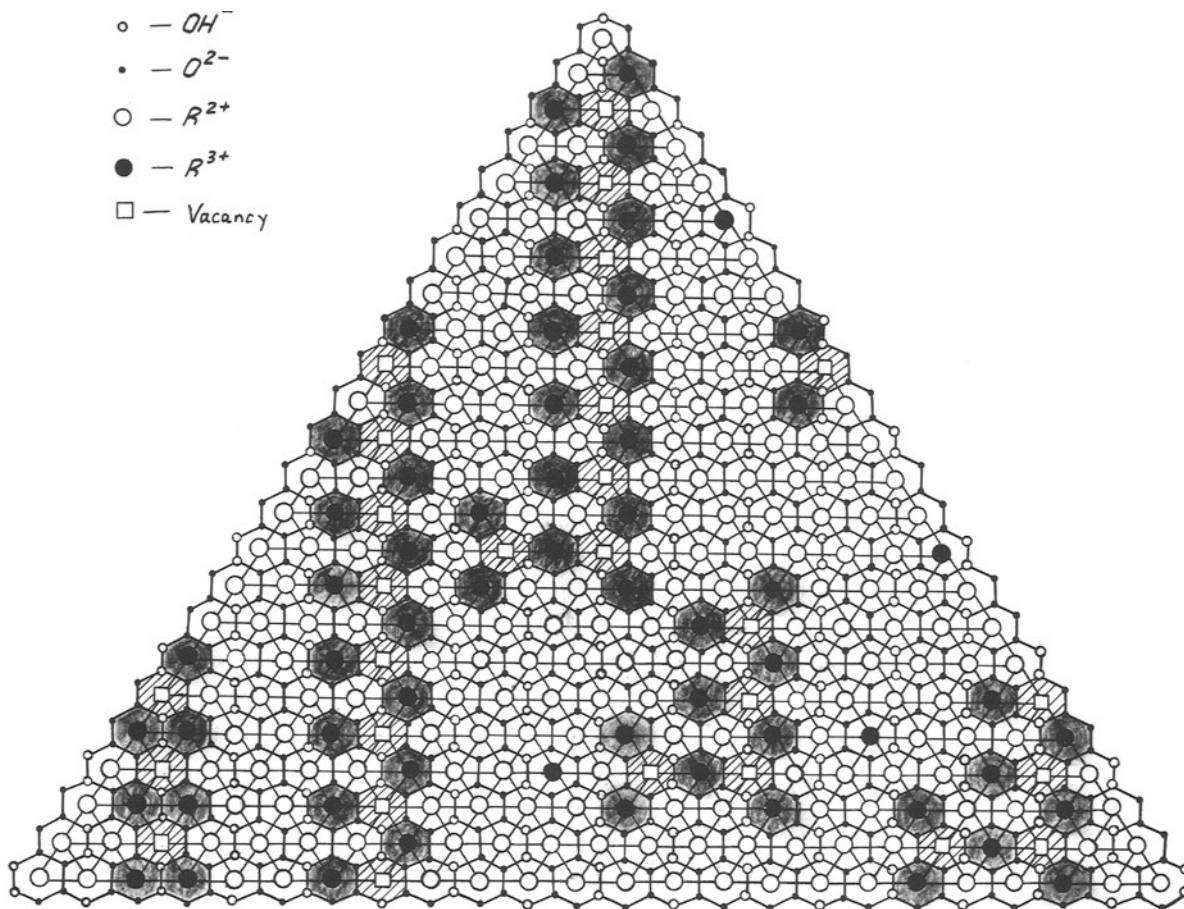


Figure 4. The model of the octahedron layer of biotite investigated at  $5 \leq V \leq 7$ ;  $\bullet = R^{3+}$ ,  $\circ = R^{2+}$ ,  $\square = \text{Vacancy}$ ,  $\bullet = O^{2-}$ ,  $\circ = OH^-$ . The octahedrons containing  $Fe^{3+}$  and  $\square$  are blackened and shaded, respectively, to underline the chain configurations.

uncompensated from O–Si linkage in the tetrahedrons, is equal to  $-1$ , and is distributed among the three cations situated in vertices of the triangle. Thus, a charge formally related to the oxygen ions in the network is equal to  $-\frac{1}{3}$ . The hydroxyl group shares its valency of  $-1$  with three cations only, i.e., a charge related to the hydroxyl group in the network is also equal to  $-\frac{1}{3}$ . If one of the points in the cation network is represented by a vacancy, the charge of the nearest anions becomes equal  $-\frac{1}{2}$ . When a “dry” oxidation of biotite takes place, the increase in the  $Fe^{3+}$  ion content is accompanied by the loss of hydroxyl groups. It follows from the kinetics of the newly-formed  $Fe^{3+}$  ions that they are surrounded by oxygen ions only. Consequently, a point which previously had a charge of  $-\frac{1}{3}$  should now be assigned a charge of  $-\frac{2}{3}$ . In the presence of OH groups and in the absence of vacancies, the arrangement of effective charges surrounding the cation is isotropic, but in the presence of vacancies and/or hydroxyl deficiency, the cation surroundings become anisotropic.

To determine for the original biotite all the possible configurations in the octahedral charge distribution and their relative concentrations, a model of a biotite octahedral sheet (Figure 4) has been constructed using the above crystallochemical formula and the methods described by Krzanowski and Newman (1972). This method is based on Pauling’s electrostatic valency rule, application of which to the structure of trioctahedral mica allows formulation of criteria, according to which the total valency of  $V$  cations in vertices of the triangle should satisfy the following relationship:  $5 \leq V \leq 7$ . Such a construction first of all excludes electrostatically prohibited combinations such as  $R^{3+}R^{3+}R^{3+}$ ,  $R^{3+}R^{3+}R^{2+}$ , or  $R\square\square$  and, secondly, it leads to combining  $Fe^{3+}$  and  $\square$  into chains having a certain configuration with ordering of  $Fe^{3+}$  and in cis- and trans-octahedra, respectively. ( $R^{3+} = Al, Ti, Fe^{3+}$ ;  $R^{2+} = Mg, Mn, Fe^{2+}$ ;  $\square = \text{vacancy}$ .)

In constructing the octahedral sheet model of the investigated biotite, the diadochy of  $R^{3+}$  or  $R^{2+}$  cations

Table 3. Mössbauer parameters of Fe<sup>3+</sup> ions in biotite (from literature).

Cation	Δ (mm/sec)	δ (mm/sec)	Reference
Fe <sup>3+</sup>	0.63–1.08	0.52–0.62	Yakovlev <i>et al.</i> , 1973
Fe <sup>3+</sup>	0.52	0.75	Haggstrom <i>et al.</i> , 1969
Fe <sup>3+</sup>	0.76	0.63	Ivanitskiy <i>et al.</i> , 1975
Fe <sub>cis</sub> <sup>3+</sup>	0.50	0.61	Manapov and Sïtdikov, 1974
Fe <sub>tr</sub> <sup>3+</sup>	0.57–0.78	0.85–0.92	
Fe <sub>tetr</sub> <sup>3+</sup>	0.36–0.50	0.32–0.36	
Fe <sub>cis</sub> <sup>3+</sup>	0.43–0.65	0.76–0.91	
Fe <sub>tr</sub> <sup>3+</sup>	0.74–1.17	0.78–0.51	
			Annersten, 1974

was not considered. Consequently, in order to determine the relative proportion of Fe<sup>3+</sup> ions in a given configuration, the crystallochemical formula and the Fe<sub>cis</sub><sup>2+</sup>/Fe<sub>tr</sub><sup>2+</sup> ratio (=1.68 ± 0.02) of original biotite (Voitkovskiy *et al.*, 1975) were used. The results of analysis for all the possible configurations of charge distribution in octahedra, which coordinate the Fe<sup>3+</sup>

cation in the original biotite, are given in the upper part of Table 4. In oxidized biotite (lower part of Table 4), the total number of such configurations is the sum of previously existing Fe<sup>3+</sup> ions and vacancies in chains, as well as from those newly formed as a result of dehydroxylation.

Table 4. Possible configurations of octahedral charge distributions for Fe<sup>3+</sup>.

Sample	Isomerism of octahedron in biotite	Charges surrounding (Configuration) Fe <sup>3+</sup> ion <sup>1</sup>	$ qE_{q0}  = \frac{1}{2}e^2Qq(1 + \frac{\eta^2}{3})^{1/2}$	Relative weight of configuration
Biotite	cis		$q_0 \frac{e^2Q}{L^3} \cdot \frac{1}{6}$ (2)	0.14
	cis		$q_0 \frac{e^2Q}{L^3} \cdot \frac{1}{3}$	0.02
	cis		0	0.01
Oxybiotite	cis		$q_0 \frac{e^2Q}{L^3} \cdot \frac{1}{6}$	0.10
	cis		$q_0 \frac{e^2Q}{L^3} \cdot \frac{1}{2\sqrt{3}}$	0.02
	cis		$q_0 \frac{e^2Q}{L^3} \cdot \frac{1}{3}$	0.50
	cis		$q_0 \frac{e^2Q}{L^3} \cdot \frac{1}{2}$	0.05
	cis		$q_0 \frac{e^2Q}{L^3} \cdot \frac{1}{3}$	0.04
	trans		$q_0 \frac{e^2Q}{L^3} \cdot \frac{2}{3}$	0.29

<sup>1</sup> ○ = -1/3; ● = -1/2; ⊙ = -2/3; L = distance from center to top of octahedron.

<sup>2</sup> q<sub>0</sub> is a constant that takes into account the value of the effective charge in the lattice and the real distortion of octahedra. The determination of q<sub>0</sub> in analytical form is a special problem which is why the values of ΔE<sub>Q</sub> obtained in this work cannot be used for the calculation of absolute values of the field gradient.

After revealing all possible configurations of the effective charge distribution, which coordinate the Fe<sup>3+</sup> ions both in biotite and in oxybiotite, one can utilize the additivity of the electric field gradient (EFG) and calculate Δ in a point-charge approximation (Clark, 1971; Galkin *et al.*, 1973) for each configuration: Δ = 1/2e<sup>2</sup>qQ(1 + η<sup>2</sup>/3)<sup>1/2</sup>, q = V<sub>zz</sub>, η = (V<sub>yy</sub> - V<sub>xx</sub>)/V<sub>zz</sub>, where η = asymmetry parameter of the EFG tensor, and V<sub>xx</sub>, V<sub>yy</sub>, V<sub>zz</sub> = principal components of the EFG tensor.

On calculating EFG, the octahedra were assumed to be regular with a cation-anion distance being equal to L. It is clear from Table 4 that inhomogeneous electric fields, when acting upon a Fe<sup>3+</sup> nucleus in the biotite octahedral sheet, give rise to six values of the quadrupole splitting the magnitudes of which are in the ratio 1/6:1/2√3:1/3:1/3:1/2:2/3. The line intensities of the corresponding doublet are proportional to relative weights 0.10, 0.02, 0.50, 0.01, 0.05, and 0.29, respectively. In the biotite structure, the total electric field gradient on a Fe<sup>3+</sup> nucleus is made up of a contribution from the anisotropic charge distribution plus the geometrical distortion of the coordination octahedron. A peculiarity of the doublet having a weight of 0.29 lies in its correspondence to Fe<sup>3+</sup> ions in the former biotite trans-octahedra, whereas all the other doublets correspond to Fe<sup>3+</sup> ions in configurations which were formed from cis-octahedra. Since the cis- and trans-octahedra in biotite differ somewhat in size and have different degrees of distortion (Drits, 1971), one can assume that in oxybiotite these purely geometrical differences are conserved. Thus, analyzing the data of the oxybiotite spectrum (EVM), the magnitudes of the doublets whose line intensities are proportional to 0.01, 0.02, 0.50, 0.01, and 0.05 can be put in the ratio 1/6, 1/2√3, 1/2, 1/3, and 1/2, but the Δ value with line intensities proportional to 0.29 should not be limited so strictly.

The result of analyzing the oxybiotite Mössbauer

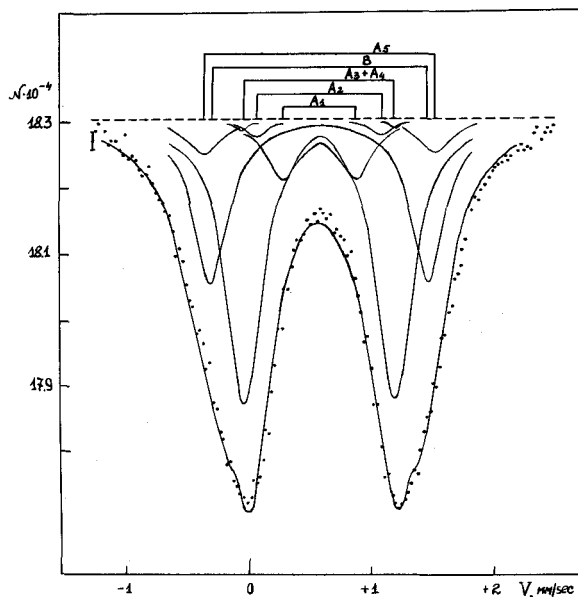


Figure 5. The result of resolution into Lorentzian curves of the experimental Mössbauer spectrum of oxybiotite within the framework of the model described in the text. Doublets  $A_1$ ,  $A_2$ ,  $A_3$ ,  $A_4$ , and  $A_5$  correspond to  $\text{Fe}^{3+}$  ions in cis-octahedra. The corresponding  $\Delta$  values (in the ratio  $1/6:1/2\sqrt{3}:1/3:1/2:2/3$ ) are equal to 0.60, 1.05, 1.24, 1.88, and 2.48 mm/sec, respectively. Doublet B corresponds to  $\text{Fe}^{3+}$  ions in trans-octahedra and its  $\Delta$  value, varied independently, is equal to 1.78 mm/sec.

spectrum according to this model using a "MIR-1" electronic computer is represented in Figure 5. The sample was positioned such that the angle between the direction of  $\gamma$ -quanta propagation and a line normal to the sample surface was  $55^\circ$  in order to eliminate texture effects (Pfannes and Gonser, 1973). The best value of  $\chi^2$  is obtained at  $\Gamma_{1/2} = 0.39$  mm/sec and when  $\Delta$  from  $\text{Fe}_{\text{tr}}^{3+}$  ions is equal to 1.78 mm/sec. As shown in Figure 5, there is a good agreement between the experimental spectrum and a theoretical curve which covers the six quadrupole doublets. Thus, the analysis of the biotite octahedral sheet structure with respect to the formal effective charges in the anion network enables one not only to explain a large value of quadrupole splitting in the oxybiotite spectrum, but also to construct a model which gives a quite satisfactory interpretation of the large line width. In addition, as shown in Table 4, even in a single crystal of biotite the majority of charge configurations in the close vicinity of  $\text{Fe}^{3+}$  ions is anisotropic; in a polycrystal their number increases because of a partial oxidation (Voitkovskiy *et al.*, 1975; Bagin *et al.*, 1976). As a result, the  $\Delta$  value for  $\text{Fe}^{3+}$  even in an unaltered polycrystal is large (1.23 mm/sec). This means that the octahedral layer of biotite contains some oxybiotite nuclei. Taking into consideration a smooth dependence of  $\delta$  for  $\text{Fe}^{3+}$  ions on their relative content in biotite, it can be concluded that transformation of

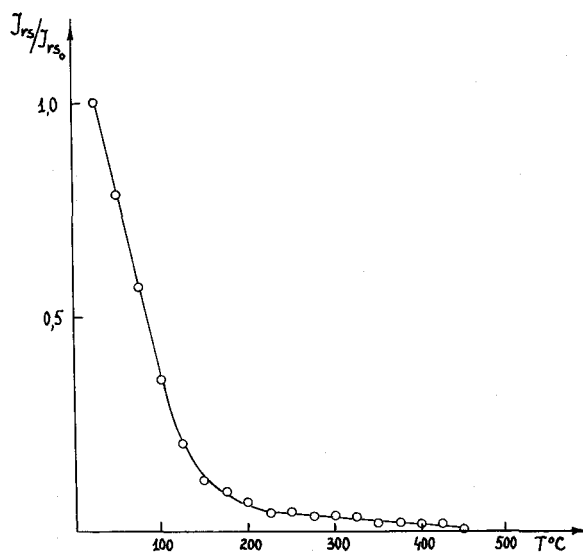


Figure 6. Dependence of residual saturation magnetization on temperature for a biotite sample heated in air at  $T = 1070^\circ\text{K}$  for 30 min.

biotite into oxybiotite (in a polycrystal) is a gradual one. (According to our preliminary results, the process of oxidation in thin (30–50  $\mu\text{m}$ ) single crystal plates of biotite occurs in steps.)

#### High-temperature decomposition of biotite

The data on the high-temperature decomposition of biotite can serve as further evidence for the model proposed, which is based on the analysis of structural characteristics of the biotite octahedral sheet.

According to Tsvetkov and Val'yashikhina (1956), an endothermic peak occurs in the 1270–1470°K temperature range in differential thermal analysis curves for a large collection of biotites. The present results prove, however, that a magnetic phase develops after a short period of heating (30 min) at 1070°K. This is evidenced by the appearance of the residual magnetization, which is absent in the original, unheated biotite. The temperature curve of the residual magnetization saturation,  $I_{\text{rs}}$ , for the newly formed phase is shown in Figure 6. Characteristically, both Mössbauer spectroscopy and XRD indicate (as in the case of a sample heated to 870°K) an oxidized biotite phase only. These results become clear in considering the fact that the mechanisms of the dehydroxylation in RRR and  $\text{RR}\square$  coordination are basically different (Vedder and Wilkins, 1969). In the first case, loss of a hydroxyl group occurs in accordance with the electron–proton exchange, which does not require destruction of the mica structure. In the second case (on considering the ordering of vacancies in trans-octahedrons), condensation of hydroxyls can occur through the vacancy with consequent removal of  $\text{H}_2\text{O}$ , which implies some destruction of the structure.

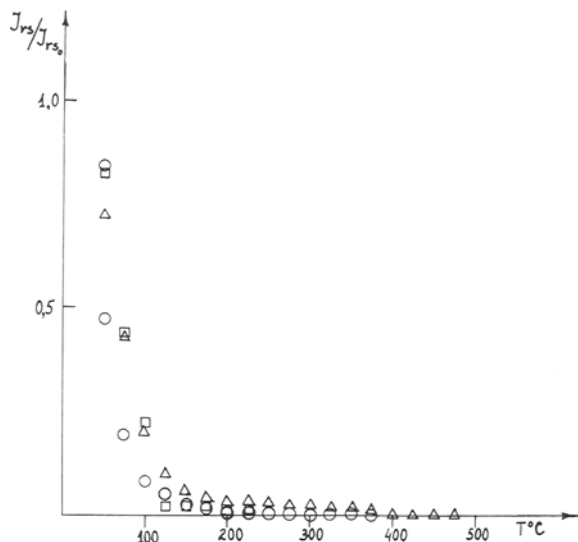


Figure 7. Dependence of residual saturation magnetization on temperature for biotite after heat-treatment in air at  $T = 1390^{\circ}\text{K}$ :  $\circ$  = for 10 min;  $\square$  = for 2 hr;  $\triangle$  = for 21 hr.

Dehydroxylation near vacancies takes place at higher temperatures than those required for the electron-proton transformation (Vedder and Wilkins, 1969). Both temperatures, however, are sufficiently below those causing biotite decomposition. In the biotite sample investigated, dehydroxylation near vacancies apparently takes place at about  $1070^{\circ}\text{K}$ . It leads to the formation of mono- and polydomain clusters of a new phase, which possesses some residual magnetization, in long chains consisting of  $\text{R}^{3+}$  cations and vacancies. Because these dioctahedral fragments are small compared to the trioctahedral matrix of the mica, they are below the sensitivity limit for Mössbauer spectroscopy. The insensitivity of XRD to the new phase is due to its being "fixed" in a much larger (compared to the new phase) octahedral sheet of biotite, which had not experienced substantial changes during the oxidation process.

After annealing the original samples of biotite at  $1390^{\circ}\text{K}$ , the new magnetic phase is clearly observed by both Mössbauer spectroscopy and XRD, as well as by thermomagnetic analysis. The thermomagnetic analysis curve of  $I_{rs}$  for the phase which was formed after such a heat treatment (Figure 7) is very close to the  $I_{rs}$  vs. temperature curve in Figure 6. A sudden drop of  $I_{rs}$  at  $370\text{--}390^{\circ}\text{K}$  is characteristic for both curves, and there is more than a 90% decrease in  $I_{rs}$ . The shapes of the thermomagnetic analysis curves tend to be concave. Repeated thermomagnetic analysis on  $I_{rs}$  produces a curve which is practically identical to the original one. This indicates stability of the newly formed magnetic phase within the  $293\text{--}470^{\circ}\text{K}$  temperature range during the hour-long experiment. An

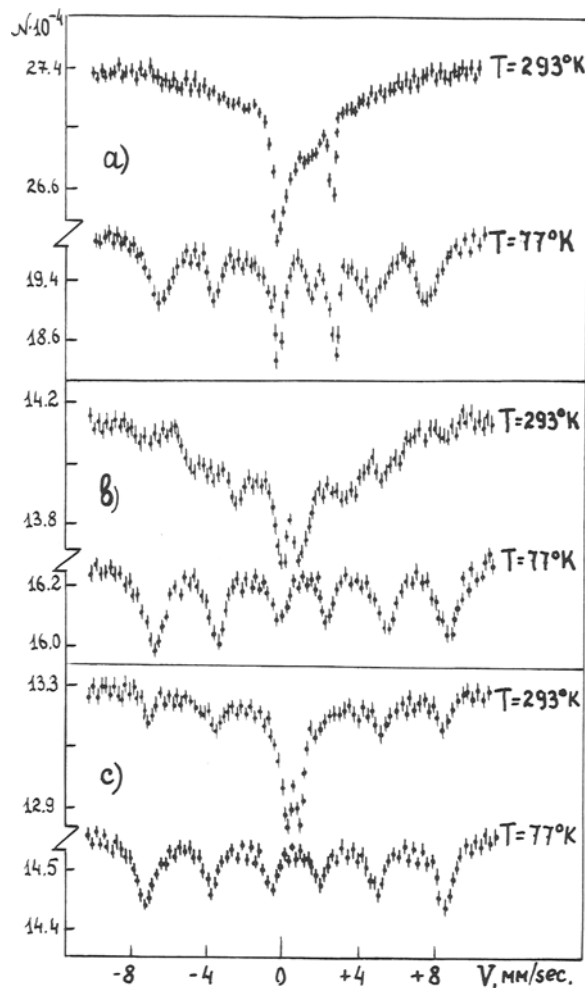


Figure 8. Biotite Mössbauer spectra at  $293^{\circ}\text{K}$  after heat-treatment in air at  $T = 1390^{\circ}\text{K}$ ; (a) for 10 min (in the middle of spectrum one can clearly observe the peaks corresponding to the preserved biotite); (b) for 2 hr; (c) for 21 hr.

increase in heating time of the original biotite at  $1390^{\circ}\text{K}$  does not change the shape of the  $I_{rs}$  thermomagnetic curves (Figure 7).

The temperature dependence of the saturation magnetization,  $I_{rs}$ , in a field of 2100 oe practically reproduces the thermomagnetic curve on  $I_{rs}$ . Thus, a temperature of  $370\text{--}395^{\circ}\text{K}$ , corresponds to an abrupt break in the curves which can be identified as the Curie temperature of the magnetic phase, formed during biotite decomposition.

Formation of the new phase can be clearly observed on examining the Mössbauer spectra. After only 10 min of heating the original biotite at  $1390^{\circ}\text{K}$ , one can observe a small depression in the background in addition to the doublet of unaltered biotite (Figure 8a). The former is characteristic of the relaxation spectra of magnetic compounds near the Curie point or for the finely dispersed superparamagnetic particles close to mono-

domain sizes. At 77°K, in addition to the biotite doublet, one can clearly observe the hyperfine magnetic splitting with an effective field  $H_{\text{eff}}$  equal to 472 Koe (Figure 8a). Heating for 2 hr at 1390°K leads to the disappearance of biotite lines and appearance of a paramagnetic doublet having  $\delta = 0.43$  mm/sec and  $\Delta = 0.69$  mm/sec (Figure 8b) on the background of the unresolved hyperfine structure. The doublet disappears when the temperature is decreased to 77°K, and a six-component spectrum having good resolution appears (Figure 8b). After 21 hr of heating biotite in air, a spectrum with a well-resolved magnetic structure and  $H_{\text{eff}} = 483$  Koe can be observed even at room temperature (Figure 8c). This indicates that a process of particle enlargement takes place. The major part of the magnetic phase of the sample is now represented by polydomain particles, whereas the central doublet corresponds to the superparamagnetic particles.

The results of XRD investigations of biotite samples annealed at 1370°K are in agreement with those obtained from the Mössbauer measurements. After only 10 min of heating, one can observe a set of diffraction maxima which may be indexed according to the *fcc* lattice of spinel, in addition to a diffraction pattern due to biotite. An increase in heating time results in a gradual disappearance of the diffraction pattern of biotite and the appearance, in conjunction with the reflections from the same spinel phase, of leucite reflections. The lattice constant *a* of the spinel is 8.26 Å.

On analyzing the results of the present investigation on the formation of the magnetic phase during high-temperature decomposition of biotite and the results of other investigators (Sharma *et al.*, 1973; Blyasse, 1968), one can determine the composition of this spinel:  $\text{Fe}_{2-x}\text{MgAl}_x\text{O}_4$  ( $x = 0.5-0.6$ ). This was discussed in detail by Bagin *et al.* (1976).

The present work, therefore, enables one to follow a process of the formation of magnetic ferrispinel during the high-temperature biotite decomposition, stage by stage. Its formation begins at 1070°K in dioctahedral fragments of the biotite octahedral sheet, as evidenced by the appearance of the residual magnetization in the samples annealed at this temperature. The newly formed particles of this phase have a domain structure, but their quantity is small. At 1390°K, the number of particles increases dramatically with their size distribution depending on the duration of the heat treatment. In addition to the presence of the polydomain particles, a considerable quantity of finely dispersed particles of a superparamagnetic size or having a size close to that of monodomain particles is present.

## CONCLUSIONS

The analysis of structural characteristics of a mica, intermediate between di- and trioctahedral varieties, that was carried out on a theoretically synthesized bio-

tite octahedral layer, proved to be valuable in interpreting the results of investigations of the process of high-temperature biotite transformations. Based on this analysis, a physical model has been proposed, which enables satisfactory interpretation of the large line widths and quadrupole splitting in the Mössbauer spectrum of oxybiotite. The approach described here can be used to explain the appearance of the residual magnetization long before the biotite decomposition temperature is reached. Annealing biotite at 1070°K leads to the formation of magnetic phase nuclei in chains consisting of  $\text{Fe}^{3+}$  ions and vacancies. This phase, which is a product of biotite decomposition at 1370°K, is a ferrispinel having the following composition:  $\text{Fe}_{2-x}\text{MgAl}_x\text{O}_4$ , where ( $x = 0.5-0.6$ ).

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**Резюме**—Для объяснения больших значений квадрупольного расщепления и полуширины линии в Мессбауэровском спектре оксибиотита, в данной работе проводится анализ распределения формальных эффективных зарядов в узлах анионной сетки для идеализированной модели октаэдрического слоя биотита. На основе этого анализа предлагается физическая модель, согласно которой мессбауэровский спектр оксибиотита представляет собой суперпозицию шести дублетов квадрупольного расщепления. Предложенная модель позволяет объяснить возникновение остаточной намагниченности задолго до температуры распада биотита. Отжиг биотита при 1070°K приводит к образованию зародышей магнитной фазы в цепочках, состоящих из  $R^{3+}$  и вакансий, являющейся продуктом распада биотита при 1370°K.

**Resümee**—Um die großen Werte der Quadrupol-Aufspaltung und der Linienbreiten im Mössbauerspektrum von Oxybiotit zu erklären, wurde unter Verwendung eines idealisierten Modells der Biotit-Oktäederschicht eine formalisierte Analyse der Verteilung der effektiven Ladungen im Anionen-Netzwerk durchgeführt. Aufgrund dieser Analyse wurde ein qualitatives physikalisches Modell vorgeschlagen, nach dem das Mössbauerspektrum aus einer Überlagerung von 6 Quadrupol Dubletten besteht. Das vorgeschlagene Modell erklärt das Auftreten von Restmagnetisierung weit unter der Zersetzungstemperatur des Biotits. Glüht man den Biotit bei 1070°K, so führt das zur Bildung von Keimen der magnetischen Phase in Ketten, die aus  $R^{3+}$  und Leerstellen bestehen. Diese Phase ist das Zersetzungsprodukt von Biotit bei 1370°K, d.h. einem Ferrispinel mit der Zusammensetzung  $Fe_{2-x}MgAl_xO_4$  ( $x = 0,5-0,6$ ). [U.W.]

**Résumé**—Pour expliquer les valeurs élevées des scissions quadrupolaires et des largeurs des droites dans le spectre de Mössbauer de l'oxybiotite, une analyse formalisée de la distribution de charges effectives dans le circuit des anions a été faite, utilisant un modèle idéalisé de la couche octaédrique de la biotite. Sur la base de cette analyse, un modèle physique qualitatif a été proposé, selon lequel le spectre de Mössbauer consiste en une superposition de six doublets quadrupolaires. Le modèle proposé explique l'apparition de magnétisation résiduelle bien en dessous de la température de décomposition de la biotite. Si on tempère la biotite à 1070°K, on obtient la formation de noyaux de la phase magnétique en chaînes consistant de  $R^{3+}$  et de vides. Cette phase est le produit de décomposition de la biotite à 1370°K, c.à.d., un ferrispinel de composition  $Fe_{2-x}MgAl_xO_4$  ( $x = 0.5-0.6$ ). [D.J.]