APPLICATION OF ELECTRON PARAMAGNETIC RESONANCE AND MÖSSBAUER SPECTROSCOPY IN THE INVESTIGATION OF KAOLINITE-GROUP MINERALS

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Abstract—Samples of nacrite, dickite, kaolinite, and halloysite were investigated using X-band electron paramagnetic resonance (EPR) and Mössbauer spectroscopy. Fe^{3+} gave rise to EPR signals at $g \simeq 4$ which differed with the individual polytype. Only nacrite had no resonance in this region of the spectrum, but it had one at $g \simeq 2$. Dickite had a quadruple line, kaolinite a triple line, and halloysite a single line in this region. The EPR spectra of these minerals are apparently dependent also on the orientation of adjacent layers in the structures. Other resonances were attributed to (1) clusters of ferric ions giving rise to broad resonance near $g \simeq 2$, (2) trapped holes, and (3) free radicals linked with organic matter. The Mössbauer spectroscopic results suggest that iron occurs in the ferric state (except in nacrite where Fe^{2+} is present also) as an ionic substitution (IS) in octahedral layers. This suggestion follows from the difference is the IS values between octahedral and tetrahedral symmetry sites occupied by Fe^{3+} equal to ~0.4 mm/sec. Linewidths depend mainly on the way the layers stack; for monoclinic modifications represented by nacrite and dickite, the linewidths are narrow ($\Gamma = 0.45$ mm/sec and 0.56 mm/sec, respectively); pseudomonoclinic halloysites also gave narrow linewidths ($\Gamma = 0.39$ mm/sec and 0.48 mm/sec). The widest line was observed for triclinic kaolinite ($\Gamma = 0.62$ mm/sec and 0.71 mm/sec).

Key Words—Dickite, Electron paramagnetic resonance, Halloysite, Iron, Kaolinite, Mössbauer spectroscopy, Nacrite.

INTRODUCTION

Electron paramagnetic resonance (EPR) and Mössbauer spectroscopy have been used frequently to study Fe^{3+} in kaolinite (Boesman and Schoemaker, 1961; Jones *et al.*, 1974; Meads and Malden, 1975; Jefferson *et al.*, 1975; Angel *et al.*, 1977). The present work attempts to relate the type of EPR spectrum observed to the form of iron in the kaolinite (iron in ionic substitution; adsorbed iron on the surface of kaolinite plates; separate iron minerals as impurities). Differences in the orientation of layers among kaolinite polytypes as well as differences in the degree of structural order should influence both the positions of OH groups that coordinate iron in the structure and the direction of hydrogen bonds. These differences in turn should influence the symmetry of the crystal field formed by ligands surrounding Fe^{3+} in kaolinite. Since crystal field symmetry affects the EPR signal of Fe^{3+}, the EPR method may be helpful in determining the form of iron in clays. It may also provide information about the position of iron in the kaolinite, the structural differences of polytypes of kaolinite, and the degree of order of these structures. Mössbauer spectroscopy has been applied as a complementary method to EPR to identify the oxidation state and position of iron substitution in the kaolinite structure.

MATERIALS AND METHODS

The investigated clay samples are described in Table 1. X-ray powder diffraction (XRD) patterns and chemical analysis of these minerals revealed no impurities that would produce resonance lines in EPR spectra. The chemically detected "free" iron oxides are present in an X-ray-amorphous form, possibly as poorly crystallized hematite and goethite. Structural iron in the illite and muscovite impurities had no significant influence on the EPR spectrum of kaolinite because of small amount of this mineral in the samples; however, Fe^{3+} in these phases gave rise to resonance in the $g \simeq 4$ region.

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Table 1.   Description and location of investigated samples.

Number	Sample	Description	Origin	Impurities
1	Nacrite	Monomineral sample of hydrothermal orgin	Brand near Freiberg, Saxony, DDR	
2	Dickite	Monomineral sample	Nowa Ruda, Lower Silesia, Poland	
3	Kaolinite	Kaolin containing 76% kaolinite of a high degree of crystallinity	Maria III mine, Oldrzychów, Lower Silesia, Poland	7% dioctahedral micas, 17% quartz
4	Kaolinite	0.5–2.0 μm fraction separated from kaolinite-containing sandstones	Maria III mine, Oldrzychów, Lower Silesia, Poland	5% micas
5	Kaolinite	Kaolin filling veins in the sandstone; contains kaolinite of a high degree of crystallinity	Osiecznica mine, Osieczinica, Lower Silesia, Poland	Quartz
6	Kaolinite	<5-μm fraction of kaolinite of a high degree of crystallinity separated from sandstone	Osiecznica II mine, Osiecznica, Lower Silesia, Poland	12% quartz, 8% dioctahedral micas, ~0.2% structural Fe_2O_3
7	Kaolinite	0.5–2.0-μm fraction separated from residual kaolin	Antoni deposit, Kalno near Zarów, Lower Silesia, Poland	1% dioctahedral micas
8	Kaolinite	5.0–15.0-μm fraction separated from kaolin deposit	Roztoka, near Jawor, Lower Silesia, Poland	5% quartz
9	Kaolinite	Basalt eluvium containing kaolinite of a low degree of crystallinity	Turów brown coal mine, Turoszów, Lower Silesia, Poland	Siderite
10	Halloysite	Monomineral sample of halloysite, filling karst funnels in limestones	Łubno, near Mierzecice, Upper Silesia, Poland	
11	Halloysite	<5-μm fraction of halloysite, product of weathering of basalt	Dunino near Legnica, Lower Silesia, Poland	Hematite, iron hydroxides, siderite
12	Halloysite	<45-μm fraction	Michalovce mine, Michalovce, Slovakia	
13	Allophane	Noncrystalline material filling fissures in clay shales. $SiO_2:Al_2O_3 = 81:100$	Monasterec near Lesko, Poland	
14	Silicate glass[1]	200-μm thick layer		

[1] 72.1% SiO_2, 15.2% Na_2O, 6.5% CaO, 4.1 %MgO, 1.8% Al_2O_3, 0.3% Fe_2O_3.

The EPR spectra of the investigated samples were obtained at X-band frequency using the X-28 spectrometer constructed by the Technical University, Wroclaw, Poland. Spectra of powdered samples were obtained at room temperature using a magnetic field range of 0–5 kilogauss (kG). The purity of the samples and the degree of order of the kaolinite structure were determined by XRD, using a DRON-1.5 diffractiometer.

The total and "free" Fe_2O_3 contents of the samples are listed in Table 2. The free iron oxides were determined by the method of Mehra and Jackson (1960), i.e., by treating the samples with an aqueous solution of sodium dithionite at pH = 7.3. By this treatment, free iron oxides and hydroxides are dissolved, leaving only the iron within the structure of kaolinite.

The Mössbauer spectra of the samples were recorded

Table 2.   Iron content and crystallinity indices for kaolinite-group minerals.

Sample[1]	Total Fe$_2$O$_3$ (wt. %)	"Free" Fe$_2$O$_3$ (wt. %)	I$_{020}$/I$_{1\bar{1}0}$	I$_{020}$/I$_{11\bar{1}}$	k$_H$
1	0.34				
2	0.12	0.01			
3	0.61	0.17	0.67	0.71	1.23
4	0.40	0.14	0.62	0.55	1.39
5	0.20	0.03	0.52	0.58	1.43
6	0.49	0.14	0.67	0.67	1.23
7	1.10	0.08	0.81	0.82	0.66
8	1.11	0.03	0.82	0.88	0.69
9		0.43			
10	0.38	0.03			
11	5.15	1.06			
12	0.88	0.01			

k$_H$ = Hinckley's crystallinity index (Hinckley, 1963).
[1] See Table 1.

at room temperature using a constant-acceleration NO-KIA spectrometer with a 400-channel analyzer operating in the time mode. Monoenergetic 14.4-keV radiation was provided by a ~50-mCi source of Co^{57} dissolved in chromium. The calibration standard was α-Fe$_2$O$_3$ powder.

RESULTS

EPR spectra

Selected EPR spectra of the samples are presented in Figures 1a and 1b, arranged in order of decreasing degree of structural order. The intensity ratio of the 020 and 110 XRD peaks (Stoch, 1974) and Hinckley's index (1963) (see Table 1) were used to estimate this degree of order. All of the samples studied, except nacrite (1), showed two main resonance regions, labelled I and II, with g values near 4 and 2, respectively. These resonances are characteristic of kaolinite EPR spectra. Studies of synthetic kaolinites indicate that the resonances in region I are attributable to structural Fe^{3+} (Angel et al., 1974; Jones et al., 1974), and white region II lines may result from crystal imperfections (holes), free radicals (Friedlander et al., 1963), and Fe^{3+} ions (Boesman and Schoemaker, 1961). Tables 3 and 4 present g values, peak-to-peak linewidths, and field anisotropies of the resonances in these two regions.

The spectra of Turow kaolin (9), Kalno kaolin (7), Dunino halloysite (11), and Maria III kaolin (4) demonstrate a very wide resonance in region II, which in some cases obscures the characteristic lines in this region. This resonance has been attributed to Fe^{3+} ions (S = 5/2) in close association (Angel and Hall, 1973), and may originate at least partly from iron oxides and hydroxides on the surface of kaolinite or existing as discrete particles.

The resonances in region II for a halloysite (12), a poorly crystalline kaolinite (8), and a highly crystalline

Table 3.   EPR signals and g values in region II for kaolinite-group minerals.

Sample[1]	Type of line	g$_\parallel$	g$_\perp$	(H$_{an}$)[2] (G)	(ΔH)[3] (G)
1	Two-line asymmetrical	2.087	2.031	75.4	14.0
3	Two-line asymmetrical	2.079	2.035	72.0	14.7
4	Two-line asymmetrical	2.081	2.023	109.4	16.1
5	Two-line asymmetrical	2.074	2.028	74.5	13.0
6	Two-line asymmetrical	2.077	2.033	72.9	13.5
7	Two-line asymmetrical	2.075	2.030	74.0	14.5
8	Two-line asymmetrical	2.080	2.031	79.7	14.8
12	Two-line asymmetrical	2.087	2.038	79.2	15.5
2	Line consisting of four lines with the following g-factor values: 2.022, 2.071, 2.110, 1.970				
9	Broad single line: g = 2.088, ΔH = 1495.5 G				
10	Central single line with g = 2.036 and six weak lines				
11	Broad single line: g = 2.360, ΔH = 1957.5 G				

[1] See Table 1.
[2] Field anisotropy.
[3] Peak-to-peak width of the line.

kaolinite (5) are shown in Figure 2 at an expanded scale of magnetic field. The parameters characteristic of these lines are given in Table 3. The predominant resonance of kaolinite in region II has been characterized in recent EPR studies as asymmetrical, arising from a paramagnetic center with approximately axial symmetry.

The resonance in region I, appearing commonly as a triple line, has been attributed to Fe^{3+} ions substituted in the octahedral or tetrahedral sheets of the kaolinite structure. The multiple nature of this resonance is explained by assuming that the Fe^{3+} ions occupy two different sites, denoted as A and B (Angel et al., 1974;

Table 4.   EPR signals and g values in region I for kaolinite-group minerals.

Sample[1]	Number of lines	g[2]	(ΔH)[3] (G)
1	no signal		
2	4	4.48, 4.27, 3.44, 3.18	40.5, 108, 46, 59.4
3	3	4.94, 4.29, 3.57	108, 155, 140
4	3	5.68, 4.30, 3.90	95, 176, 148
5	3	4.96, 4.29, 3.56	86, 162, 135
6	3	5.02, 4.27, 3.59	101, 155, 135
7	3	4.92, 4.27, 3.56	114, 129, 216
8	3	4.94, 4.30, 3.66	95, 176, 148
9	1	4.28	175.6
10	1	4.27	171
11	1	4.30	189
12	1	4.29	189

[1] See Table 1.
[2] Error in determining g-factor = ±0.05.
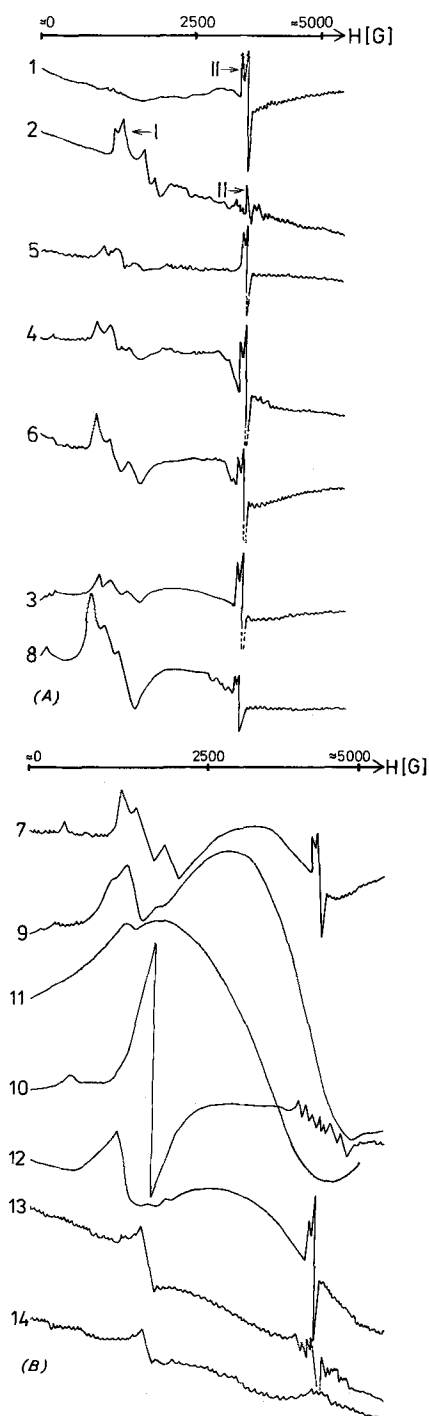[3] Error in determining peak-to-peak width = 2%.

Figure 1. EPR spectra of kaolinite-group samples over a magnetic field range of 0–5 kG. Region I and II resonance positions are noted on the figure.
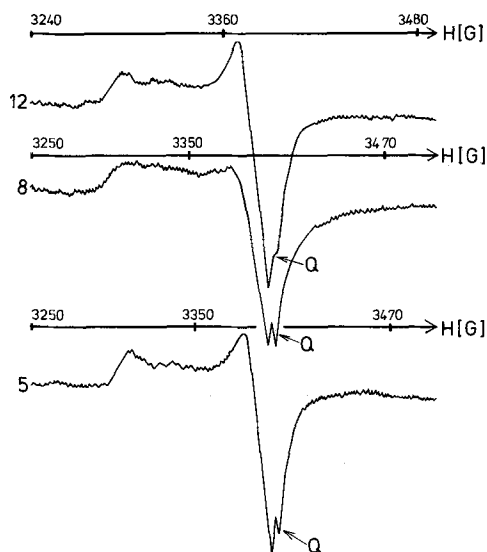

Figure 2. Region II of the EPR spectra using an expanded magnetic field scale. A resonance from the quartz sample container is denoted by Q.

Jones *et al., 1974)*. The crystal field parameters, E and D, describe respectively the rhombic and axial distortion of the Fe^{3+}. The A site has orthorhombic symmetry with crystal field parameter, λ, given by $\lambda = E/D = 1/3$.

The B site has higher symmetry with a λ value smaller than 1/3. Fe^{3+} in A sites forms a single isotropic line, and ions occupying B sites form a triple line. A correlation exists between the degree of structural order of kaolinites (measured by Hinckley's index, for example) and the relative population of the A and B sites. An increase of structural disorder produces a decrease in number of B sites and an increase in number of A sites (Jones *et al.,* 1974; Meads and Malden, 1975). Spectra of nacrite (1), dickite (2), poorly crystalline kaolinite (8), and halloysite (12) presented in Figure 3 confirm this interpretation of the EPR spectra. The spectra also indicate that the populations of A and B sites in the polytypes of kaolinite are different.

Nacrite (1) is the only mineral of the kaolinite group which does not show a strong resonance in region I, a result which suggests that there is little or no ionic substitution of Fe^{3+} in the sites responsible for this resonance. However, dickite (2) (a $2M_1$ polytype) gives a quadruple resonance in region I. Kaolinites generally have a triple resonance in region I, but halloysites (10), (11), and (12) demonstrate a single line. The fact that halloysite is the most disordered structure is consistent with the existence of only low symmetry (A) sites for Fe^{3+}.

A weak resonance at low magnetic field ($g \simeq 9$) was noted in kaolinites (6), (7), and (8). Castner *et al.* (1960) discovered a similar line in glasses containing iron impurities. This line originates from the extremely anisotropic g-tensor associated with A or B sites. The similarity of the spectra in region I to those of silicate glass and amorphous allophane (13) of chemical composition
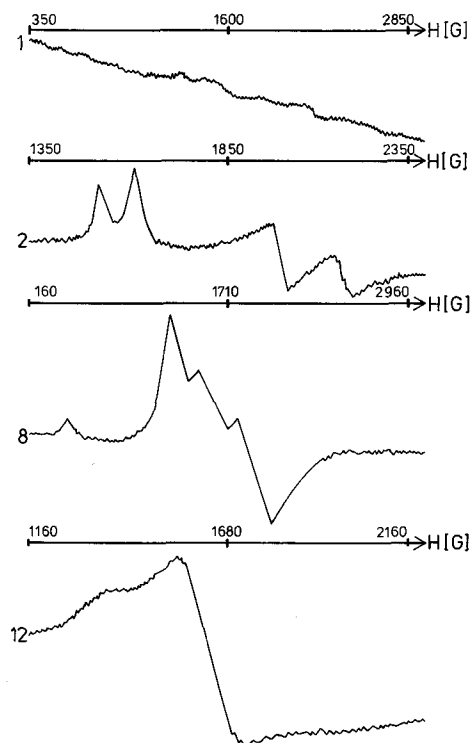
Figure 3. Region I of the EPR spectra using an expanded magnetic field scale.

Figure 4. Selected EPR spectra after treatment of samples with 9% HCl.

similar to that of kaolinite suggests that Fe^{3+} may substitute in the tetrahedral positions of kaolinites.

The spectra of kaolinites from which "free" iron oxides had been removed by dithionite treatment prove that this method did not remove all of the "free" iron oxides. The effect of iron removal by treatment with 9% HCl is shown for selected samples in Figure 4. Although most features of the spectra are preserved, the wide resonance at $g \simeq 2$ (obscuring region II) is completely absent or is weakened. Thus, the wide resonance is attributable to "free iron" oxides and iron mineral impurities, such as siderite or hematite. The HCl treatment does not remove all of these iron components in certain samples (e.g., Dunino halloysite (11)). Spectra obtained after dithionite treatment of samples also contain a signal originating from the sodium dithionite reagent.

In the investigated kaolins, organic matter is not present in significant quantities. However, in the Kalno kaolinite (7), free radicals attributable to organic matter were detected. Free radicals typically have g values near the "free spin" value of $g = 2.0023$, thereby overlapping region II of kaolinite. Figure 5 shows region II for a sample before (A) and after (B) a hydrogen peroxide treatment was used to oxidize the organics. The free radical signal was eliminated by this treatment.
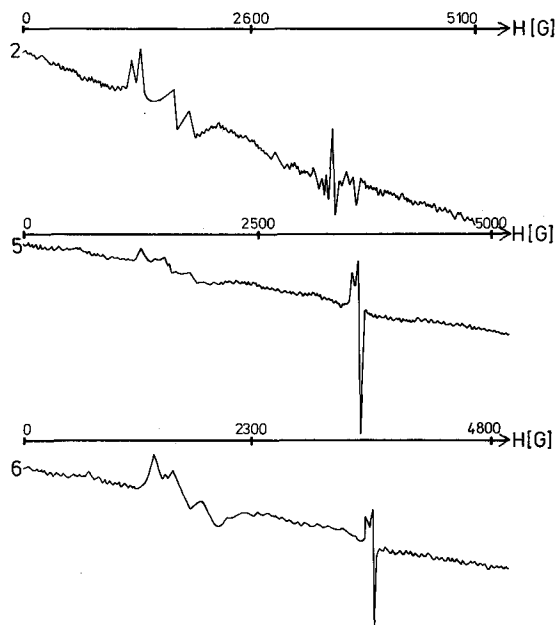
Mössbauer spectra

The Mössbauer spectra of selected minerals are shown in Figures 6a and 6b. All of the spectra were computer-fitted to yield the best values of the following parameters: isomer shifts (IS), quadrupole splittings (QS), and linewidths at half maximum (Γ). These parameters, summarized in Table 5, show that in all of the samples except nacrite, iron occurs only in the ferric state. Nacrite contains iron in both the ferric and ferrous states. Although the EPR study did not determine whether Fe^{3+} was present in the tetrahedral or octahedral layer, isomer shifts of the Mössbauer spectra prove that Fe^{3+} has octahedral symmetry in all of the samples studied, in agreement with results reported elsewhere (Malden and Meads, 1967; Meads and Malden, 1975; Angel et al., 1977). Thus, in the minerals of the kaolinite group, Fe^{3+} occurs in ionic substitution for Al^{3+} in octahedral sheets. Octahedral symmetry is readily distinguished from tetrahedral symmetry by Mössbauer spectroscopy, as shown by the spectrum of silicate glass (Figure 6b, sample (14)). Since Fe^{3+} is in tetrahedral symmetry in this glass, the value of the IS differs by about 0.4 mm/sec from the IS values of Fe^{3+} in octahedral symmetry (Table 5).

Another aspect investigated in this study was the influence of long-range order on the symmetry of the Fe^{3+} environment. The data in Table 5 indicate that the polytypic modifications of kaolinite have different linewidths. The monoclinic modifications, nacrite and dickite, have the narrowest lines of Γ = 0.45 and 0.56 mm/sec, respectively. These minerals also have the
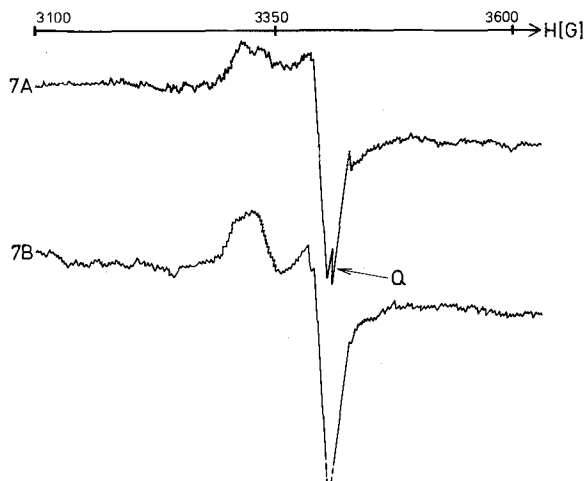
Figure 5. EPR spectra of sample (7) before (A) and after (B) treatment with peroxide.

highest degree of crystallinity among the minerals studied here. The symmetry of these polytypes depends on the relative orientation of neighboring layers. In turn, the orientation of the hydroxyl groups of octahedral sheets is determined by the layer stretching (Giese and Datta, 1973) as well as by the symmetry of the crystal field in which the Fe^{3+} is located.

The linewidths of the halloysites are also very narrow: $\Gamma = 0.39$ mm/sec for the Dunino sample, and $\Gamma = 0.48$ mm/sec for the Michalovce sample. The layers are stacked almost at random in these minerals, causing the symmetry of the unit cell to be pseudo-monoclinic (Zvyagin, 1967). This may create a crystal field having a symmetry similar to the nacrite or dickite, which is reflected in narrow linewidths. The widest linewidths are observed for a triclinic kaolinite. However, the linewidth of this mineral depends on the sample and varies from $\Gamma = 0.62$ to $\Gamma = 0.71$ mm/sec.

The EPR results showed that Fe^{3+} can occupy two

Table 5. The values of the best-fit parameters.

Sample[1]	Ion	A[2] (%)	IS[3] (mm/sec)	QS (mm/sec)	(mm/sec)
1	Fe^{2+}	53 (7)	−0.73 (3)	2.50 (9)	0.47 (9)
1	Fe^{3+}	47 (9)	−0.06 (4)	0.54 (3)	0.45 (11)
2	Fe^{3+}	100	0.25 (1)	0.56 (1)	0.56 (3)
4	Fe^{3+}	100	−0.03 (2)	0.67 (2)	0.62 (4)
7	Fe^{3+}	100	−0.11 (1)	0.56 (1)	0.71 (6)
8	Fe^{3+}	100	0.03 (1)	0.54 (1)	0.65 (5)
11	Fe^{3+}	100	0.01 (1)	0.60 (1)	0.39 (1)
12	Fe^{3+}	100	−0.03 (1)	0.54 (1)	0.48 (2)
14	Fe^{3+}	100	−0.37 (2)	0.38 (2)	0.25 (4)

[1] See Table 1.

[2] A = abundance. The meaning of the other symbols is given in the text.
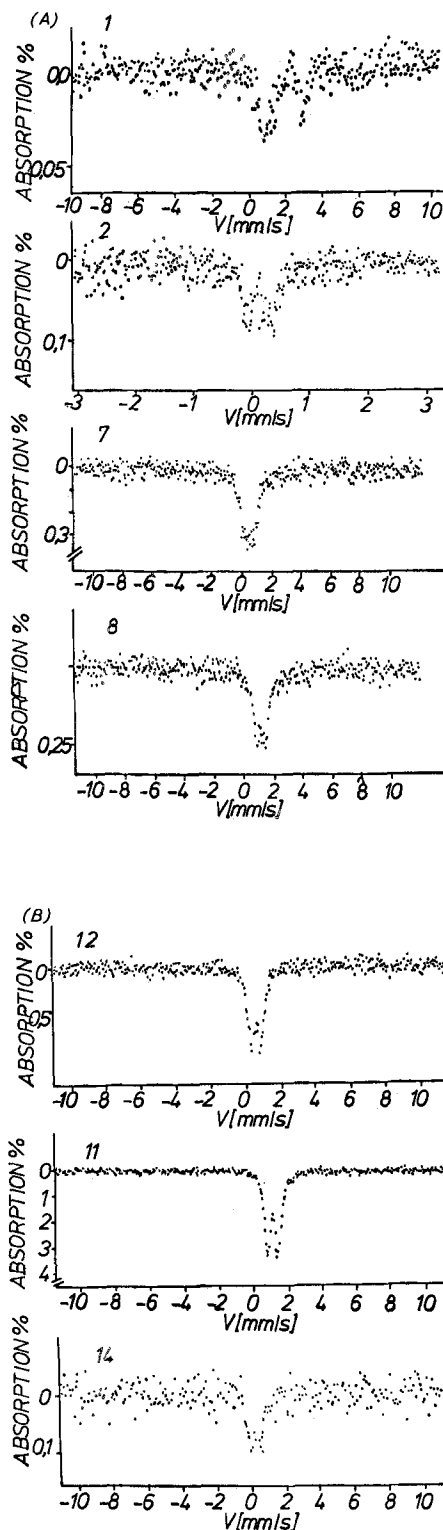
[3] Relative to α-Fe_2O_3 standard.

Figure 6. Room temperature Mössbauer spectra of (a) Nacrite (1), dickite (2), Kalno kaolin (7), Roztoka kaolin (8). (b) Dunino halloysite (11), Michalovce halloysite (12), silicate glass (14). (IS scale is *not* relative to Fe_2O_3.)

sites of different crystal field symmetry, A and B, in kaolinite. However, the values of the IS and the QS attributable to the Fe^{3+} occupying these two sites must be so similar that the Mössbauer spectrum consists of one broadened doublet instead of two resolved doublets. Therefore, the apparent linewidth of this composite spectrum should depend on the relative abundance of the two sites.

No correlation between the Mössbauer linewidth and the degree of layer stacking order (measured, for example, by Hinckley's index), has been revealed. One merely observes that the linewidth tends to decrease with increasing crystallinity (samples (7), (8), (4)). The linewidth may also be affected by various lattice imperfections (Kvashnina and Krivoglaz, 1967), which become less abundant with increasing crystallinity. The measured linewidth is the resultant of all of these effects, i.e., the perfection of the lattice, the way the layers stack, and the degree of layer stacking.

CONCLUSIONS

The EPR spectra of kaolinites of different origin and degree of structural order are similar to the spectra of synthetic kaolinites obtained by other workers. Two resonance regions are present in the spectra of all kaolinites. In region I, resonances of Fe^{3+} in A sites (single line) and B sites (triple line) are differentiated. The relative number of high symmetry B sites increases according to the following sequence: halloysite < kaolinite < dickite. Thus, the number of these sites decreases with an increasing degree of disorder in layer stacking.

Resonance region II is produced by defects in the kaolinite structure, and some evidence exists that Fe^{3+} in nacrite contributes to the resonance absorption in this region. One nacrite sample contains iron, but the complete absence of lines in resonance region I of the EPR spectrum suggests that the iron may produce a signal in region II. The shape of the asymmetrical line in region II is typical of a paramagnetic center with approximately axial symmetry (Searl et al., 1959), and it may indicate the occurrence of Fe^{3+} in a crystal field of distorted octahedral symmetry as was suggested by Boesman and Schoemaker (1961).

The similarity of the spectra of a nacrite and a dickite sample suggests certain structural similarities of the minerals. The single line observed in region I for halloysites suggests the absence of Fe^{3+} in B positions, resulting from a lack of order in the arrangement of layers in the structure. The quadruple line of dickite in region I provides evidence for a ligand symmetry of structural Fe^{3+} that is different from that observed in kaolinite. Nacrite does not give a resonance in region I, suggesting that Fe^{3+} substitution in sites responsible for the resonance is not allowed in the nacrite structure. A different configuration of the OH groups in the nacrite polytype has been hypothesized (Giese and Datta,

1973). This structural alteration would change the crystal field symmetry of Fe^{3+}, thereby affecting the region I resonance.

Although the EPR method could not determine the position of ferric ions in the structure, it detected the presence of structural iron in polytypes of kaolinite, as well as "free" iron oxides and organic matter.

The results of the Mössbauer spectroscopy study can be summarized as follows: (1) Iron occurred in the ferric state in all kaolinite-group minerals except nacrite, which had about 43% of its iron in the ferrous state. (2) Fe^{3+} occupies sites of octahedral symmetry in the kaolinite-group minerals. (3) Polytypic modifications of kaolinite have different linewidths, with nacrite, dickite, and halloysite having narrow lines and kaolinite having the widest lines. The broadened lines may result from a superposition of two lines ascribed to the two sites (A and B) with slightly different symmetry. (4) Linewidths depend mainly on the way the layers stack and are influenced by differences in layer stacking of polytypes and the degree of layer stacking order.

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Резюме—Образцы накрита, диккита, каолинита, и галлоизита были исследованы при помощи рентгеновских полос электронного парамагнитного резонанса (ЭПР) и спектроскопии Мессбауэра. При g ≃ 4, Fe^{3+} вызывали появление ЭПР, разного для индивидуальных политипов. Только накрит не давал резонанса в этой области спектра, но резонанс появлялся при g ≃ 2. Диккит имел четырехкратную, каолинит—тройную, а галлоизит—одиночную линию в этой области. Для этих минералов спектры ЭПР, очевидно, зависят от ориентации соседних слоев в структуре. Другие резонансы были приписаны к: (1) группам ферритовых ионов, вызывающим широкий резонанс в поблизости g ≃ 2, (2) захватанным дырком, и (3) свободным радикалам, связанным с органической материей. Результаты спектроскопии Мессбауэра указывают на то, что железо встречается в виде феррита (исключая накрит, в котором Fe^{2+} также присутствует) как ионное замещение (IS) в октаэдрических слоях. Это предположение следует из наличия разницы (равной ≃ 0,4 мм/сек) между величинами IS для октаэдрического и тетраэдрического мест симметрии, занятых ионами Fe^{3+}. Ширина линии зависит, в основном, от расположения слоев; моноклинная форма накрита и диккита дает узкие линии (Г = 0,45 мм/сек и 0,56 мм/сек, соответственно); псевдомоноклинный галлоизит также дает узкие линии (Г = 0,39 мм/сек и 0,48 мм/сек). Более широкие линии наблюдались для триклинного каолинита (Г = 0,62 мм/сек и 0,71 мм/сек). [Е.С.]

Resümee—Proben von Nakrit, Dickit, Kaolinit, und Halloysit wurden mit Hilfe von elektronenparamagnetischer Resonanz (EPR) und Mössbauerspektroskopie untersucht. Fe^{3+} verursacht g-Werte von etwa 4, die bei den einzelnen Polytypen verschieden waren. Nur Nakrit hatte keine Resonanz in diesem Bereich des Spektrums dafür aber eine bei g etwa 2. Dickit zeigte in diesem Bereich eine Vierfachlinie, Kaolinit eine Tripellinie, und Halloysit eine einfache Linie. Die EPR-Spektren dieser Minerale hängen offensichtlich auch von der Orientierung der benachbarten Lagen in der Struktur ab. Andere Resonanzen können folgenden Faktoren zugeschrieben werden: (1) Cluster von Fe^{3+}-Ionen verursachen eine breite Resonanz nahe g etwa 2, (2) Haftleerstellen, und (3) freie Radikale, die an organischem Material gebunden sind. Die Ergebnisse der Mössbauerspektroskopie deuten darauf hin, daß das Eisen in 3-wertigem Zustand auftritt (mit Ausnahme von Nakrit, bei dem auch Fe^{2+} vorhanden ist) und in ionischer Form in den Oktaederlagen substituiert. Diese Schlußfolgerung ergibt sich aus dem Unterschied von etwa 0,4 mm/sek bei den IS-Werten zwischen den von Fe^{3+}-besetzten Oktaeder- und Tetraederplätzen. Die Linienbreiten hängen hauptsächlich von der Art der Schichtfolge ab; bei monoklinen Modifikationen wie Nakrit und Dickit sind die Linienbreiten klein (Г = 0,45 mm/sek bzw. 0,56 mm/sek); pseudomonokline Halloysite haben auch eine schmale Linienbreite (Г = 0,39 mm/sek und 0,48 mm/sek). Die breiteste Linie wurde bei triklinem Kaolinit beobachtet (Г = 0,62 mm/sek und 0,71 mm/sek). [U.W.]

Résumé—Des échantillons de nacrite, de dickite, de kaolinite, et d'halloysite ont été investigués employant la résonnance paramagnétique à électrons bande-X (EPR) et la spectroscopie de Mössbauer. Fe^{3+} a donné lieu à des phénomènes EPR à g ≃ 4, différant avec chaque polytype individuel. Seule la nacrite n'avait pas de résonnance dans cette région du spectre, mais elle en avait à g ≃ 2. La dickite avait une ligne quadruple, la kaolinite, une triple ligne, et l'halloysite, une seule ligne dans cette région. Les spectres EPR de ces minéraux sont apparemment aussi dépendants de l'orientation de couches adjacentes dans les structures. D'autres résonnances ont été attribuées à (1) des ensembles d'ions ferriques donnant lieu à une large résonnance près de g ≃ 2, (2) des trous pris au piège, et (3) des radicaux libres liés à de la matière organique. Les résultats de la spectroscopie de Mössbauer suggèrent que le fer apparait a l'état ferrique (sauf dans la nacrite ou Fe^{2+} est aussi présent) comme substitution ionique (IS) dans les couches octaèdres. Ces suggestions sont déduites de la différence dans les valeurs IS entre les sites de symmétrie octaèdres et tetraèdres occupés par Fe^{3+} égal à ≃0,4 mm/sec. Les largeurs des lignes dépendaient surtout de la manière dont s'empilaient les couches; pour les modifications monocliniques representées par la nacrite et la dickite, les lignes étaient étroites (Г = 0,45 mm/sec et 0,56 mm/sec, respectivement); les halloysites pseudomonocliniques donnaient aussi des lignes étroites (Г = 0,39 mm/sec et 0,48 mm/sec). La ligne la plus large était observée pour la kaolinite triclinique (Г = 0,62 mm/sec et 0,71 mm/sec). [D.J.]