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EPR STUDY OF PARAMAGNETIC DEFECTS IN CLAY MINERALS

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Abstract. Radiation induced defects (RID-s) and transition metal ion impurities were revealed by EPR (Electron Paramagnetic Resonance) spectroscopy in kaolinites from a number of Polish deposits. A relationship between the intensity of the EPR signals of the RID-s and quantity of radioactive elements was defined in these minerals. In one of the deposits of kaolinites (Wyszonowice) the EPR signal intensity depends on grain size. Other clay minerals studied (illites, montmorillonites) only show weak signals of the RID type.

Key-words: EPR, clay minerals, radiation induced defects

INTRODUCTION

First reports on the nature and localization of iron centers in kaolinites appeared in the 1960s and 1970s (Friedlander et al. 1963; Angel, Hall 1973; Angel et al. 1974; Meads, Malden 1975; Herbillon et al. 1976). The effectiveness of chemical methods in removing extra-framework iron, and the ordering of the kaolinite structure on the basis of the intensity ratio of particular Fe^{3+} EPR signals, were also investigated then and later (Angel, Hall 1973; Gaite et al. 1993; Gaite et al. 1997). Polish mineralogists contributed involved research data on the catalytic properties of smectites (Bahranowski et al. 1996) and on the purification of clay raw materials contaminated with iron (Komusiński et al. 1981; Komusiński, Stoch 1984; Bahranowski et al. 1993).

By the end of the 20th century, the research was focused on point defects of the O^- type generated in clay minerals by ionizing radiation. The minerals most susceptible to irradiation, and thus the most investigated, were kaolinites in which paramagnetic hole centers were formed according to the reaction:

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$$O^{2-} \rightarrow O^{-} + e^{-} \quad (1)$$

Three types of centers – A, A′ and B – were identified (Angel et al. 1974; Meads, Malden 1975; Ildefonse et al. 1991). Two of these (center A of rhombic symmetry and center A′ of axial symmetry) are located in the tetrahedral layer – centers of the –Si-O^{-} type (Muller et al. 1992; Allard et al. 1994; Clozel et al. 1994). The third center (B) contains an O^{-} ion linked to two aluminum atoms of the octahedral layer (Clozel et al. 1995). EPR parameters for these centers differ in g-factor values and, in the case of centre B, in the presence of hyperfine structure (HFS) composed of 11 lines where the unpaired electron interacts with the nuclear spin of two neighbouring aluminum atoms. Centers of the A and B types differ also in their thermal stability; centers of the A′ and A types decompose at about 400–450°C and B centers only at 300°C. The relative content of A and B centers provides important information on the genesis of kaolinites. The quantity of A centers, stable below 450°C, enables estimation of the irradiation dose accumulated during the entire period of formation and diagenesis of the clay minerals. Some information about the migration of radioactive elements may also be deduced from the intensity ratio of component EPR signals (Muller, Calas 1989; Muller et al. 1992). The results of these investigations also apply to spin dosimetry (Allard, Muller 1998; Allard et al. 1994).

The ability to generate structural defects with irradiation and to determine their properties, in particular their thermal stability, attracted growing interest because of the common use of nuclear energy and the need to store radioactive waste materials. Clay minerals, exhibiting excellent sorption and isolating properties, are used in the construction of protection barriers in radioactive stores (Pusch 1992; Madsen 1998; Plötze et al. 2003).

The present work, focused on structural defects in clay minerals of mostly Polish occurrences, is a continuation of research on paramagnetic defects generated in kaolinites by thermally activated neutrons (Babińska et al. 2000). However, the work concerns a wider group of clay minerals (kaolinites, illites, smectites especially montmorillonites). It also considers other means of defect formation, e.g., irradiation of clay mineral deposits by neighboring radioactive elements and/or their contamination by other minerals and elements, especially transition metal ions. Structural defects in clay minerals other than kaolinites have been investigated less often. Friendlander et al. (1963) observed a sharp signal with $g \sim 2$ in natural illites and montmorillonites. Others reported selected results (Gournis et al. 2001; Pushkareva et al. 2002; Sorieul et al. 2002, 2005; Plötze et al. 2003; Shpak et al. 2003) on the generation of structural defects with ionizing radiation but these studies, with the exception of Sorieul et al. (2005), were not done systematically.

EXPERIMENTAL

Materials

The investigated kaolinite, illites and montmorillonite specimens were separated from genetically different deposits. The detailed characteristics of the particular minerals and of the rocks containing them are presented in Tables 1 and 2. Amounts of other clay minerals and quartz were negligible. Mineral and organic contaminations were removed using the method of Jackson (1958).

TABLE 1

Localization, age and genesis of the kaolinites studied

Deposit	Subordinate minerals*	Localization	Genesis	Age
Andrzej	Q, I	Żarów Lower Silesia	residual	Paleogene-Miocene
Biała Góra	Q	Biała Góra Tomaszów Depression	sedimentary	Aptian
Gawłówka	I	Gawłówka Lubartowska Lowland	sedimentary	Miocene
Grudzeń Las	I	Grudzeń Las Tomaszów Depression	sedimentary	Aptian
Jegłowa fraction <40 µm	Q	vicinity of Strzelin Lower Silesia	residual	Carboniferous
Kalno	I	vicinity of Żarów Lower Silesia	residual	Paleogene-Miocene
Maria-III fraction <40 µm	I, Q	Nowogrodziec near Bolesławiec Lower Silesia	sedimentary	Santonian
Stanisław	I, Q	the Izerskie Mountains Lower Silesia	residual	Paleogene
Stefanów, depth 663 m	I/S	Stefanów, borehole BP4 Lublin Upland	sedimentary	Liassic
Stefanów, depth 666 m	I/S	Stefanów, borehole BP4 Lublin Upland	sedimentary	Liassic
Stefanów, depth 671 m	I/S	Stefanów, borehole BP4 Lublin Upland	sedimentary	Liassic
Stefanów, depth 691 m	I/S	Stefanów, borehole BP4 Lublin Upland	sedimentary	Liassic
Turów	I, Q	the Izerskie Mountains Lower Silesia	residual	Paleogene
Wyszonowice fraction <0.3 µm	I, Q	Wyszonowice, vicinity of Strzelin Lower Silesia	residual	Paleogene-Miocene
Wyszonowice fraction 0.3–2 µm	I, Q			
Wyszonowice fraction 2–5 µm	I, Q			

* Admixtures present in separate samples: I – illite, Q – quartz, I/S – mixed layered illite/smectite.

TABLE 2

Localization and mineral composition of the studied samples of illites and smectites

Sample	Main mineral	Subordinate minerals*	Localization
Il-1	illite (sericite)	P	Silverton Caldera, USA
Il-2	illte/smectite	Q	Füzerradvány, the Tokay Mountains, Hungary
ŚWI	illite	K	Świerki, Intrasudetic Depression, Poland
ŚWII	illite	K, Q, Sk	Świerki, Intrasudetic Depression, Poland
Jelšovy Potok	Ca-Mg- montmorillonite	–	Jelšovy Potok, Slovakia
Wyoming	Na-montmorillonite	–	Wyoming, USA

* Admixtures present in separate samples: K – kaolinite, Q – quartz, Sk – feldspars, P – pyrite.

Methods

X-ray diffraction

XRD patterns of powdered samples were obtained using a Philips X'pert diffractometer with graphite monochromator (CuKα radiation, λ_{av} = 1.540562 A) and TUR-M62 (CoKα radiation, λ_{av} = 1.79021 A) in the 2θ range 4–70° with a step size of 0.02° 2Θ and a count time of 5 s per step. The X-ray patterns of sedimented and unoriented samples were measured and analysed using the XRAYAN program and the JCPDS data set.

EPR

EPR spectra were registered at 295 K and 77 K using a Bruker ELEXSYS 500 spectrometer operating in the X band (9.2 GHz) with the modulation frequency of 100 kHz. The simulation program EPRsim32 (Adamski et al. 2003) was used for the determination of the EPR signal parameters. The spectra intensities were calculated in arbitrary units as a double integral of the first derivative spectrum.

Chemical analysis

Actinide (U, Th) contents were determined using INAA, and potassium by Fusion ICP-OES methods (Hoffman 1992).

RESULTS AND DISCUSSION

Kaolinites

The kaolinite samples revealed complex EPR spectra containing signals of radiation induced defects (RID-s) and of iron in framework and/or extra-framework positions (Figs 1 and 2). In some samples, signals of V^{4+} ions were also observed (Fig. 3). The

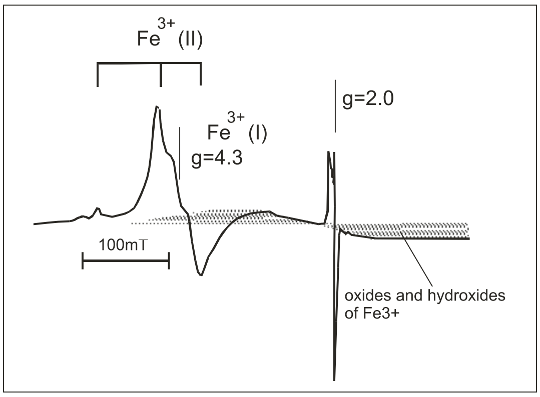

Fig. 1. EPR spectrum of typical kaolinite

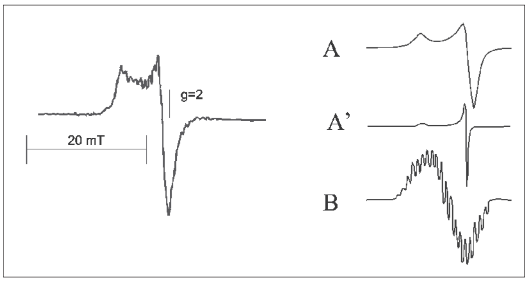

Fig. 2. Complex EPR spectrum of a radiation induced defect (RID) in kaolinite and the component signals

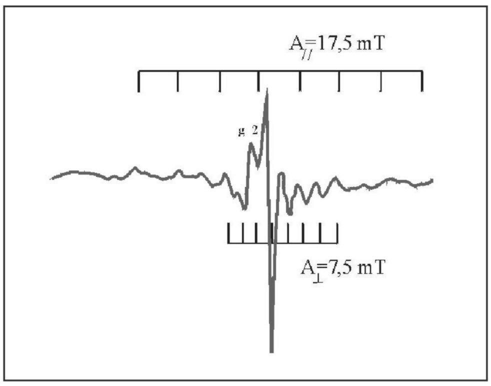

Fig. 3. EPR signal of V^{4+} ions in kaolinite from Biała Góra

kaolinites from the Tomaszów Depression (Grudzeń Las and Biała Góra) show intensive V^{4+} signals, whereas those from the Lublin Upland (BR4, Stefanów) show weak signals.

The EPR signals of RID-s differ in total intensity and in relative proportions of centers of the O^- type (A, A′ and B) which were calculated by simulation of the spectra and are presented in Table 6. Two groups of kaolinite samples may be distinguished: Group I with small (3×10^3–15×10^3au) and Group II with high (19×10^3–32×10^3 au) total RID-s contents (Table 3).

The influence of radioactive elements on the amount of generated structural defects depends on their activity and on the type of emitted particles. Thus, the influence of the U, Th and K contents on the total number of defects D is given by formula (2) given below (Ikeya 1993):

$$D = \underbrace{k(267U + 74Th)}_{\alpha} + \underbrace{(12U + 2Th + 86K)}_{\beta} + \underbrace{(12U + 4Th + 27K)}_{\gamma} \quad (2)$$

where:

k – coefficient of effectiveness of α radiation,
Th, U – content of particular element (in ppm),
K – potassium content (in %).

TABLE 3

Intensity of EPR signals of radiation induced defects (RID-s) in kaolinites

	Kaolinite	Signal intensity [au]/g
Group I	Turów	3×10^3
	Gawłówka	3.2×10^3
	Biała Góra	4.4×10^3
	Kalno	6.8×10^3
	Grudzeń Las	8×10^3
	Stanisław	8.4×10^3
	Wyszonowice 2–5	15×10^3
Group II	Wyszonowice 0.3–2	19×10^3
	Stefanów 671	19×10^3
	Wyszonowice <0.3	20×10^3
	Jegłowa	20×10^3
	Maria III	22×10^3
	Andrzej	24×10^3
	Stefanów 663	24×10^3
	Stefanów 666	32×10^3

As the effectiveness of β radiation and that of γ radiation are similar, the corresponding k coefficients were assumed = 1. In the case of α-radiation, the effectiveness is much lower and the coefficient k is usually estimated by irradiation of a standard with an appropriate dose. In the present work, we assumed the value of k = 0.1 obtained for quartz.

The results of calculations relating the number of RID-s and the radioactivity of elements present in the samples are given in Figure 4 and Table 4. The experimental points reveal two correlations represented by lines A and B. Correlation A (correlation coefficient = 0.99) involves samples of the same age, similar genesis and closely comparable mineral compositions (Stefanów 663, 666, 671 and 661). In this case, the linear relationship between contents of radioactive elements and the total number of radiation induced defects is clear. It is not so for line B (correlation coefficient = 0.69) which involves samples from different deposits mentioned in Table 4. The samples from Wyszonowice (Table 3) present another type of correlation relating the total number of defects to grain size (Fig. 4, line C). The smallest (< 0.3 μm) grain fraction contains the highest number of RID-s whereas that with the largest (2–5 μm) grains shows the lowest RID-s contents. In this case, there is no correlation between numbers of defects and content of radioactive elements.

A weaker dependence is evident when the age of the kaolinites is compared with the intensity of the EPR signals of the RID-s (Tables 1 and 3). Although the older specimens

TABLE 4

Content of radioactive elements in kaolinites

Kaolinite	Th [ppm]	U [ppm]	K [%]	D (from equation 2)	Intensity of RID-s signals [au]
Andrzej	50	11	0.18	1 248	24
Biała Góra	14	1.1	0.11	255	4.4
Gawłówka	6	2.3	0.92	300	3.2
Jegłowa	33	4.3	0.03	663	20
Kalno	13.8	5.8	0.25	507	6.8
Maria III	14.3	3.3	0.26	388	22
Stanisław	10.3	1.5	0.03	216	8.4
Stefanów 663	10.8	2.9	0.21	177	24
Stefanów 666	15.1	2.6	0.26	315	32
Stefanów 671	6.6	2.8	0.14	362	19
Stefanów 691	10.2	0.5	0.13	246	12
Turów	35.8	4.2	0.09	703	3
Wyszonowice <0.3	13	2.1	0.59	347	20
Wyszonowice 0.3–2	25.3	1.9	0.72	508	19
Wyszonowice 2–5	49	2	0.65	839	15

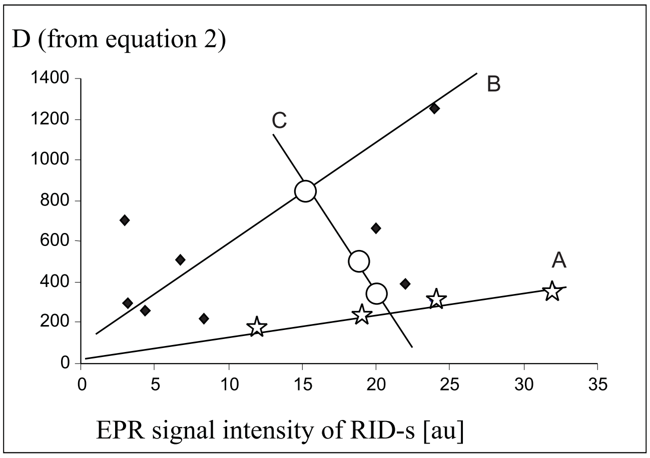

Fig. 4. Intensity of EPR signals of radiation induced defects (RID-s) in kaolinites as a function of the content of radioactive elements [presented as D from equation (2)].
The kaolinites from Wyszonowice are marked as circles, kaolinites from Stefanów as stars, whereas other kaolinites as solid diamonds.

generally gave more intensive EPR signals indicating higher RID-s contents, a few exceptions from this pattern were noted. For example, Cretaceous kaolinites from Grudzeń Las and Biała Góra exhibit EPR signals of rather weak intensity in spite of the relatively old age of these minerals. In contrast, relatively young Tertiary kaolinites from the Andrzej open pit containing significant numbers of defects reveal relatively intensive EPR spectra – reflecting, most probably, high contents of radioactive elements (50 ppm Th and 11 ppm U).

The contributions of particular components to the EPR signals of the RID-s in the kaolinites were calculated by numerical analysis of simulated EPR spectra. The EPR parameters are given in Table 5 and the quantitative data in Table 6. In most cases, the fits

TABLE 5

Parameters of EPR signals of RID centers in kaolinites

Center	g factor	Parameter a [mT]
A′	2.0410+/–0.001	
	2.0071+/–0.0001	
A	2.0150+/–0.001	
	2.0538+/–0.001	
	2.0047+/–0.0005	
B	2.0221+/–0.0001	0.76+/–0.5
	2.0434+/–0.0005	0.78+/–0.5
	2.0049+/–0.0005	0.77+/–0.5

TABLE 6

Contribution of component signals of RID-s in kaolinites

Kaolinite	Component signals of RID-s [%]		
	A′	A	B
Gawłówka	28	43	29
Kalno	26	52	22
Stanisław	11	60	29
Wyszonowice <0.3	12	60	28
Wyszonowice 0.3–2	11	60	29
Wyszonowice 2–5	13	61	26
Andrzej	5	63	32
Maria III	19	63	18
Stefanów 666	31	63	6
Stefanów 671	31	63	6
Jegłowa	12	65	23
Stefanów 663	30	65	5
Turów	28	66	6
Grudzeń Las	15	67	18
Biała Góra	10	72	18

of the experimental and simulated spectra are satisfactory. The only exceptions are the samples from Biała Góra and Turów. In the former case, the reason probably lies in high contents of vanadium and, in the latter, in significant contents of other mineral phases.

The Tertiary kaolinites exhibit smaller contents of A centers and higher contents of B centers than do the Cretaceous and older kaolinites. The kaolinite from Turów is an exception. The observed relations accord with the relatively lower thermal stability of B centers compared to A centers. The kaolinites from deposits enriched in silica (Maria III, Gawłówka, Grudzeń Las, Biała Góra, Jegłowa, Stanisław) exhibit a B signal with a well-resolved hyperfine structure.

Illites

Two samples from Świerki containing illite-kaolinite (raw sample SW-1, and SW-2 – the < 2 μm fraction from SW-1) and two samples of illite (Il-1 from Silverton Caldera, USA and Il-2 from Füzerradvány, Hungary) were investigated. The EPR spectra of these samples consist of the following component signals:

- signal with g = 4.3 and g ~ 9, characteristic of Fe^{3+} ions in octahedral positions with rhombic distortion,
- a broad signal at g ~ 2, ascribed to oxides and hydroxides of Fe^{3+},
- a sharp RID-related signal of at g = 2.

In the background of these complex spectra, signals of small intensity, composed of six lines, representing Mn^{2+} ions were always present. Though manganese could be removed by chemical treatment from the Świerki illite, the characteristic HFS of manganese was still present in other samples despite repeated treatments. It may be speculated that this difference in response to attempts at removing impurities may reflect the presence of different mineral forms of manganese. In the Świerki samples containing characteristic dendritic crystals manganese may be incorporated in soluble carbonates, whereas in illites SW-1 and SW-2, isomorphic substitution of trace amounts of Fe^{3+} and Mn^{2+} may occur in structure of the other minerals.

In spite of the similarity of kaolinite and illite structures, the EPR signals of RID-s centers in the illites (Fig. 5) do not exhibit the characteristic HFS related to the interaction of the nuclear magnetic moment of aluminum with that of the unpaired electron. In the case of the illites, a small anisotropic signal with g = 2.011 was usually observed unless it was not obscured by the HFS of Mn^{2+}. In some cases, a set of a dozen lines separated by 0.4 mT was also present (Fig. 6). This signal with EPR parameters

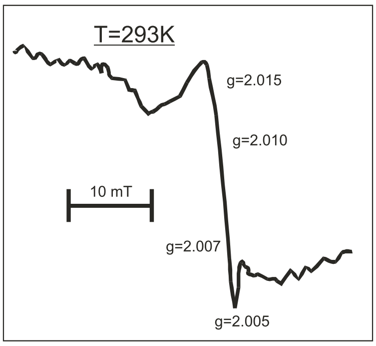

Fig. 5. EPR signal of RID-s in illite SW-1

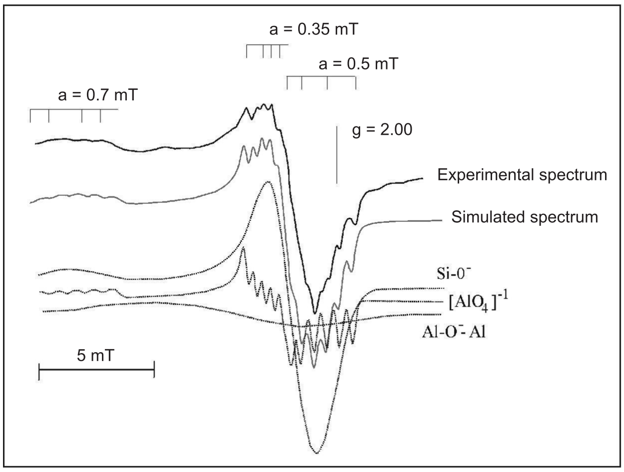

Fig. 6. EPR signals of the center $[AlO_4]^0$ in illite SW-1

$g_1 = 2.012$; $g_2 = 2.005$; $g_3 = 2.06$, $a_1 = 0.35$ mT, $a_2 = 0.5$ mT and $a_3 = 0.3$ mT is probably due to quartz admixture. It was ascribed, in agates, to a hole center $[AlO_4]^0$ by Götze et al. (1999).

Montmorillonites

The EPR spectra of the montmorillonites from Wyoming and Jelšovy Potok (Fig. 7) show, as the other clay minerals, EPR spectra composed of three signals – Fe^{3+} ions in octahedral positions with rhombic distortion (g = 4.3), Fe^{3+} in oxides/hydroxides (g ~ 2) and RID-s (g = 2). The last signal is complex due to the presence of defects of different thermal stability. On heating of the Wyoming montmorillonite for 1 hour at 200°C, 300°C and 400°C, the complex EPR signal decreased making visible the component lines of at least two different paramagnetic centers at g ≈ 2.006 and g ≈ 2.011 (Fig. 8).

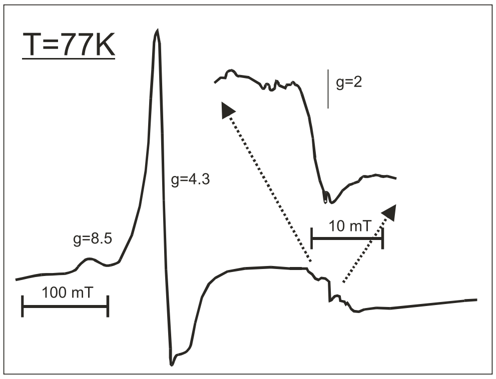

Fig. 7. EPR signal of montmorillonite from Jelšový Potok

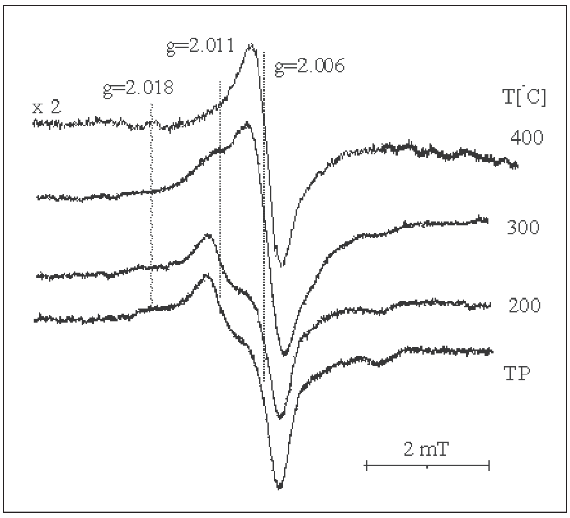

Fig. 8. EPR signal of montmorillonite from Wyoming after heating at 200, 300 and 400°C.
TP – room temperature

Similar centers were found by Sorieul et al. (2005). Simulation of the EPR spectra registered at the X-band and Q-band revealed parameters of two component signals: orthorhombic with $g_x = 2.004$, $g_y = 2.010$, $g_z = 2.065$ and isotropic at $g = 2.019$.

CONCLUSIONS

RID-type structural defects are present in considerable amounts only in kaolinites. The total amount and relative content of particular RID-s centers in kaolinite depend on several factors, e.g., total content and activity of radioactive elements, kaolinite age and grain size. The dependence on age is especially significant for centers of the type B which exhibit low thermal stability.

Other clay minerals, e.g., illites and montmorillonites, in some cases show weak signals of the RID type. In these cases, the intensity of the signals is often negligible compared to the overlapping signals of impurities, e.g., Mn^{2+}, present in the bulk of the crystals or adsorbed on their surfaces.

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Badania paramagnetycznych defektów w minerałach ilastych metodą EPR

Streszczenie

Punktowe defekty strukturalne typu RID-s były badane metodą elektronowego rezonansu paramagnetycznego (EPR) w próbkach kaolinitu pochodzących z różnych złóż Polski. Stwierdzono w nich zależność między ilością defektów strukturalnych a zawartością pierwiastków promieniotwórczych. W przypadku kaolinitu pochodzącego z jednego ze złóż (Wyszonowice) sygnał EPR zależy też od uziarnienia minerału. Pozostałe badane minerały ilaste (illit, montmorillonit) ujawniają jedynie słabe sygnały typu RID.