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CLAY MINERALOGY AND IRON STATE AS INDICATORS OF SOIL FORMING PROCESSES IN TYPICAL SOILS OF LUBLIN UPLAND REGION

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A b s t r a c t. Mineralogy and iron distribution were evaluated for genetic horizons of some soils typical for Lublin Upland Region and were attributed to soil pedogenic processes. Differences in the degree of mineral weathering and the profile distribution of iron were observed for various groups of soil types.

K e y w o r d s: clay minerals, iron, soils of Lublin Upland

INTRODUCTION

Soil mineralogy is one of the principal soil characteristics responsible for most of soil physicochemical properties. The degree of soil minerals weathering is a very useful feature for evaluation of soil genetical processes and their rate [11].

Iron status markedly influences the chemical and physical properties of soils and sediments. The significance of Fe compounds as suitable indicators of certain pedogenic environments has been recognized by many researchers [6,8]. One of such indicators is magnetic susceptibility (MS), related to the presence of ferromagnetic minerals. Its vertical distribution in soil profile is very sensitive to the kind of pedogenic and landscape geochemical processes [1]. The presence of divalent iron in the crystal lattice of minerals reflects the degree of mineral weathering [1].

The purpose of the present paper is to observe the indicators of soil processes such as: magnetic susceptibility, divalent iron distribution, profile distribution of clay minerals in soils typical for Lublin Upland Region.

MATERIALS AND METHODS

The material under experiments consisted of 9 soil profiles characteristic for Lublin Upland Region taken according to their genetic horizons. Some physicochemical properties of the samples are presented in Table 1. More details about exchange characteristics of the soils studied can be found in [2].

Clay mineralogy of soil profiles under investigation was determined by X-ray diffraction on a DRON-3 apparatus (CuKα-radiation, Ni- filter). Specimens were prepared by sedimentation from water suspension on 25x25 mm slide. Organic matter was removed from clay fraction by 10 % H_2O_2 combustion and non-silicate sesquioxides by Mehra and Jackson extraction. The quantitative evaluation of the relative abundance of major clay mineral groups was performed by the Biscay method [3].

The identification of minerals was based on the spectra for Mg forms, ethylene glycol saturated, and 350 °C and 550 °C heated clays.

The iron state in soils was established by means of Mossbauer spectroscopy and magnetic susceptibility measurements.

Room - temperature Mossbauer spectra were obtained with MS1101E spectrometer with a constant-acceleration drive system ($^{57}Co/Cr$ source with an activity of about 32 mCi). The velocity scale was calibrated relative to iron and sodium nitropruside. The numerical analyses of Mossbauer spectra were performed using UNIV programs [4].

Magnetic susceptibilities of soils (MS) and clays (MSC) were performed with KAPPABRIDGE KLY 2 (Geofyzika Brno).

RESULTS AND DISCUSSION

The mineralogical composition of clay fraction of soil profiles studied is presented in Table 2.

The Mossbauer spectra for all soils studied and their different horizons are more or less similar to each other, however some peculiarities exist, especially in divalent iron distribution. From the spectra one can conclude that in all the investigated samples the main part of iron (>70 %) occurs in the structure of silicates. The crystalline forms

Table 1. pH, granulometric composition and surface area of genetic horizons of investigated soil

Soil	Horizon	pH		Percentage of fractions						S** (m^2g^{-1})
		H_2O	KCl	a*	b	c	d	e	f	
JAB	A	7.3	6.8	32	8	32	18	6	4	23.6
	B	7.1	5.9	34	4	35	16	5	6	7.2
	C	7.0	6.5	97	0.5	0.5	0.5	0.5	0.5	1.5
ROG	A	6.1	4.9	13	3	41	29	7	7	15.0
	B	5.2	3.9	17	7	29	19	7	21	34.4
	C	6.0	4.5	37	6	34	13	1	3	21.0
MACH	A	7.4	6.9	2	9	45	13	14	16	35.6
	B	8.2	7.5	0	7	46	23	7	17	35.6
	C	8.4	7.7	0	11	49	22	4	14	24.6
TAR	A	7.5	7.0	10	10	40	22	8	10	20.5
	B	8.0	6.6	15	12	34	14	3	22	51.5
	C	nd	nd	44	6	12	12	9	17	21.0
RUD I	A	7.0	6.1	4	11	40	26	7	12	22.5
	B	6.4	4.9	1	7	35	25	4	28	60.9
	C	nd	nd	5	3	23	30	9	30	68.8
RUD III	A	6.1	5.0	17	6	20	15	6	36	68.0
	B	6.2	4.8	13	8	13	11	5	50	121.4
	C	8.1	7.2	6	4	16	26	15	33	74.0
WER	A	6.1	5.2	2	12	52	20	4	10	42.8
	B	7.7	6.9	1	5	51	21	5	17	34.1
	C	8.2	7.7	0	12	46	21	5	16	25.2
SOB P	A	5.3	4.1	69	11	11	5	2	2	7.8
	B	5.4	4.6	75	9	10	3	1	2	4.1
	C	6.4	5.1	89	4	2	1	1	3	5.8
SOB G	A	7.4	6.7	36	12	21	11	3	17	29.0
	B	7.7	6.7	45	15	20	9	4	7	13.1
	C	7.5	6.2	59	24	9	3	1	4	7.5

*Granulometric fractions: a) 1-0.1, b) 0.1-0.5, c) 0.05-0.02, d) 0.02-0.005, e) 0.005-0.002, f) <0.002 mm;
**S - surface area, BET, water vapour adsorption.

of iron oxides are mainly super dispersive (less then 15 nm) which can be seen from the absence of the sextet of lines on the spectra obtained at room temperature.

The data related to the distribution of iron forms in soil profiles, including relative bulk Fe content in the clay fraction (FeR), percentage of divalent iron in FeR (FeII), and relative values of magnetic susceptibility of the soil (MS), the clay (MSC), as well as MS values recalculated according to the contents of clay fraction (MSc) and the sand+silt fraction (MSs), are presented in Table 2.

In chernozem soil WER (Werbkowice) smectite is the dominant clay mineral in C horizon. Mg-form of this mineral is characterized by a high value of d_{001} (>1.8 nm). Such peculiarity of the diffractogram can be connected with different reasons: super dispersive state [7], hydration of the lattice [9], the presence of organic substances or inorganic polymers in the interlayers [10]. The content of hydromica and kaolinite is rather low. Mineral phases are well crystalline.

Clay fraction from B horizon contains the same minerals but their reflexes are lower and wider. Smectite is characterized by the normal d_{001} value (about 1.4 nm) of Mg-form of specimen.

Clay fraction from A horizon is very degraded, diffractograms have a high amorphous character. The irregular interstratified mica-smectite, hydromica, kaolinite, and high dispersed quartz are present.

The distribution of the relative bulk Fe content within the profile indicates some accumulation of iron in the B horizon. Clay

Table 2. Mineralogical composition and iron distribution in genetic horizons of investigated soils

Soil	Horizon	KC*	I	S	FeR	FeII	MS	MSC	MSc	MSs
JAB	A	37	44	19	6.5	8.3	574	22.3	343	583
	B	56	39	5	5.5	11.1	142	28.3	435	122
	C	39	50	11	6.2	7.4	3	32.9	506	5
ROG	A	38	62	0	5.4	6.7	540	38.1	586	536
	B	37	32	31	10.8	3.8	885	29.6	455	998
	C	39	50	11	8.7	2.9	75	16.9	200	69
MACH	A	14	64	22	9.6	3.6	3016	143.7	2213	3169
	B	17	39	44	10.3	4.1	1841	60.3	928	2028
	C	18	33	49	8.0	7.7	950	17.5	269	1056
TAR	A	28	63	9	7.7	4.7	1312	56.6	872	1361
	B	12	33	55	9.7	1.8	2549	45.3	698	3071
	C	0	25	75	6.1	1.9	261	16.1	247	263
RUD I	A	21	53	26	10.4	4.4	635	35.9	552	646
	B	9	25	66	14.4	2.7	1385	25.0	385	1783
	C	0	25	75	8.0	5.7	138	9.1	140	137
RUD III	A	12	40	48	10.7	4.9	1055	13.6	209	1531
	B	6	12	82	10.9	1.2	611	10.0	154	1068
	C						189			
WER	A	10	67	23	8.6	4.7	2748	116.4	1793	2854
	B	15	37	48	11.7	4.3	2157	59.2	912	2412
	C	15	26	59	9.5	5.5	1239	22.6	348	1409
SOB P	A	nd	nd	nd	6.3	9.5	1176	48.9	753	1185
	B	nd	nd	nd	8.7	8.5	578	38.1	586	578
	C	33	56	11	11.1	3.9	1070	21.1	324	1093
SOB G	A	18	49	33	8.6	8.1	1432	25.0	385	1645
	B	27	47	26	9.6	4.7	1034	30.4	486	1148
	C	18	41	41	10.5	4.0	547	23.4	360	557

*KC - kaolinite + chlirite; I - illite; S - smectite; FeR - relative content of iron in clay fraction (area under Mossbauer peak); FeII - percentage of divalent iron in FeR; MS - magnetic susceptibility of soil (relative value); MSC - magnetic susceptibility of clay (relative value); MSc - magnetic susceptibility of clay fraction in soil; MSs - magnetic susceptibility of sand + silt fraction.

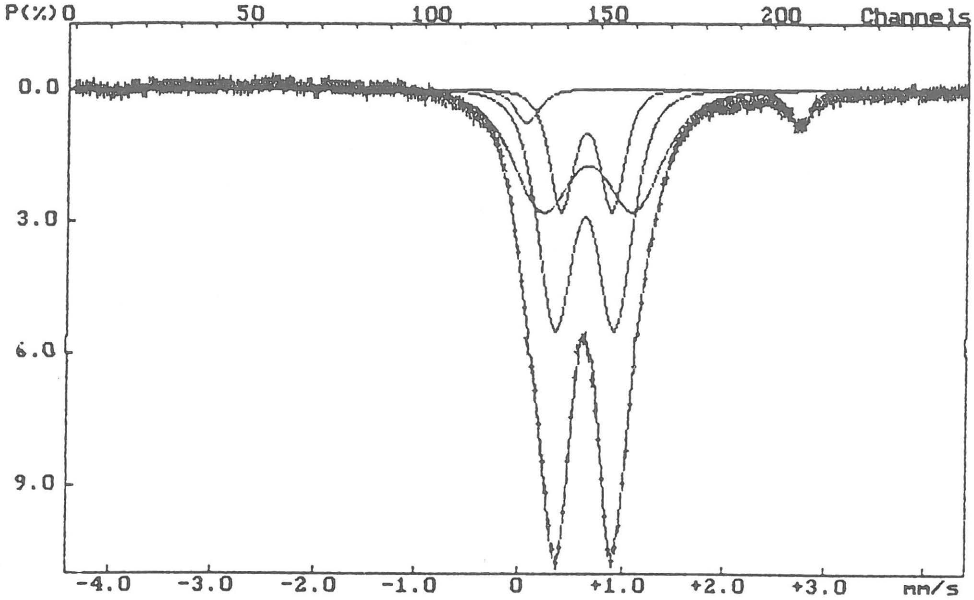

Fig. 1. Typical Mossbauer spectrum ROG (Rogóżno B horizon) for investigated soils.

materials are apparently not highly weathered as it is seen from the similarity of the FeII values across the profile. The numerical analysis of the Mossbauer spectra (Fig. 1) indicates that the divalent iron can be present mainly in chlorite minerals. However, it is also possible that all the investigated horizons are weathered more or less uniformly except the less weathered material from the C horizon. The profile distribution of the MS values indicates its accumulative character. Crystalline iron occurs mostly in fractions coarser then clay. The ratio of MS values for A and C horizons is higher for clay then for coarser material, which indicates that the degree of iron transformation is higher in the clay.

The increase of the surface area down the profile is in agreement with the smectite and clay fraction content. The dominant soil forming process appears to be the destruction of clay minerals, especially smectites. However, it has to be considered as a recent soil forming process, because the opposite - formation of montmorillonite is a proven pedogenic process in chernozems. The decrease of the structural order of minerals, increase of dispersion, amorphisation of the material, and the appearance of newly formed microcrystalline forms of iron (MSc) can be distinguished.

Mineralogical composition of MACH (Machnów) chernozem is similar to WER (Werbkowice) and similar processes can be attributed for both soils. An increase of hydromica content occurs in both cases.

Bulk iron content does not markedly differ between all horizons of MACH (Machnów) profile, however the divalent iron percentage increases downwards, which indicates the higher intensity of minerals weathering in upper horizons. The values of MSc indicate the intensive accumulation of crystalline iron forms in the upper horizon, and the ratio of MSc for A horizon to MSc in C horizon is higher then for Werbkowice soil, indicating the higher degree of soil material transformations.

For the black earth soil JAB (Jabłoń) the clay fraction of C horizon contains predominantly minerals with nonswelling lattice: hydromica, kaolinite, chlorite, highly dispersed quartz and feldspars. In the swelling phase, irregular interstratified mica-smectite is present with very low intensities of the diffractogram reflexes indicating low crystallinity of the mineral.

Mineral composition of clay fraction of B and A horizons is the same, however, the peaks for A horizon are lower and wider. The content of chlorite in A horizon is lower, and the presence of irregular interstratified mica-smectite is more evident.

Granulometric composition varies markedly in the profile, indicating its heterogeneity. The variations of the surface areas can be related with the variations of the granulometric composition, increase of dispersion and the formation of swelling phases. The latter is probably reflected in the increase of exchange capacity in A horizon. Interstratified mica-smectite formation in the course of degradation and chlorites destruction can be considered.

Bulk iron content is quite similar for all the horizons. The distribution of FeII is apparently connected with the content of chlorites. The content of oxidized forms of iron (MSc, MSs) is low within the profile and the ratio of MSc in A horizon to MSc in C horizon is lower than 1, indicating the low degree of soil transformation. The minerals are weathered in a small extent, probably due to soil redox conditions as a result of periodic flooding.

Clay fraction from C horizon of TAR (Tarnawatka) brown soil contains smectite as a dominant mineral phase. The reflexes on diffractograms are wide and slightly asymmetric, indicating the transformation of the material.

Smectites from B horizon are characterized by some interstratification. Hydromica and kaolinite are present.

In the A horizon hydromica and kaolinite predominate. The low amount of swelling phase is a part of interstratified mineral of uncertain structure.

Soil profile has heterogenic granulometric composition. Clay fraction composition of C horizon differs from A and B horizons confirming the lytological nonhomogeneity. The absence of kaolinite and low content of hydromica in parent material cannot be explained by the mineral transformations. In the upper part of soil profile destruction of smectites can take place. These data are related with the results of specific surface area.

Bulk iron content in the clay is the highest in B horizon, due apparently to the accumulation of iron compounds. The percentage of divalent iron is the lowest in this horizon and almost equal to the C horizon, which may be due to the differences in lytology.

Magnetic susceptibility is the highest in the B horizon, which is connected with the high content of iron in the coarse fractions. The ratio of MSc (A) to MSc (C) is about 3.5, which shows the high degree of soil minerals transformation but lower then in chernozems.

Clay fraction from C horizon of RUD (Rudnik I) brown soil contains smectite as a dominant mineral phase. The reflexes are intensive and sharp. The reflexes of hydromica are not intensive and rather wide. In B horizon strongly crystalline kaolinite is present additionally.

A horizon composition differs from the two lower ones. It contains interstratified mica-smectite, hydromica and kaolinite with symmetrical reflexes of high intensity. Highly dispersed quartz also occurs.

The distribution of the clay fraction in the profile has an elluvial character. The increase of kaolinite and mica contents occurs in the upper part of the profile. The above tendencies are in agreement with the surface area distribution and granulometry.

The tendencies of iron distribution for Rudnik I soil are similar to Tarnawatka brown soil, however the value of FeII in the C horizon is here somewhat higher, which can be due also to lytological peculiarities. The ratio of MSc (A) to MSc (C) is about 3.7.

For leached brown soil RUD (Rudnik III) the C horizon is formed from a calcareous rock.

The main component of clay fraction of B horizon is smectite of good crystallinity, exhibiting well defined and sharp reflexes. Hydromica and kaolinite content is low. The reflexes are broad and not well formed.

The smectite in A horizon is somewhat interstratified. The hydromica and kaolinite content increase up the profile. The influence of soil forming processes on the clay minerals seems to be rather weak.

Granulometric composition and surface areas agree well with the mineralogy. The clay minerals transformations are probably directed to the formation of interstratified mica-smectite via the potassium ions adsorption by smectite lattice. Hydromica and kaolinite are stable under these conditions.

Bulk Fe distribution in Rudnik III is homogeneous within the two upper horizons. For C, calcareous horizon data were not obtained. The value of FeII is lower in B horizon. The magnetic susceptibility values indicate, however, the accumulative character of the soil profile.

As far as the Rudnik I and Rudnik III profiles are localized upon the same field on a hill relief and the first one is situated on the top and the second on the bottom of the hill, it can be concluded that the upper part of the relief is more weathered and the lower part contains less transformed material. It is expressed in the higher content of smectites in A horizon of Rudnik III soil.

Clay fraction from C horizon of podzolic soil ROG (Rogóżno) is predominated with smectite. The minor minerals are hydromica and kaolinite.

In B horizon irregular interstratified mica-smectite, hydromica, kaolinite and highly dispersed quartz occur.

In A horizon hydromica, kaolinite, vermiculite, highly dispersed quartz and feldspars occur. The swelling minerals are absent.

Bulk Fe accumulates in the B horizon of Rogóżno soil and the FeII content decreases down the profile, which is a characteristic feature of podzols. The ratio of the MSc (A) to MSc (C) is equal to 2.9. In the A horizon a greater part of crystalline iron occurs in clay fraction.

The elluvial-illuvial character of the profile can be seen from the smectites content, the granulometric composition and iron distribution. The soil forming processes may be related with the destruction of smectitic minerals, which are the main phase of clay fraction in the C horizon. The increase in quartz and feldspars contents in the A horizon may be due to the physical destruction of the materials of coarser fractions. The lessivage of the smectites may also occur.

Mineral composition of the C horizon of pseudopodzolic sandy soil SOB (Sobieszyn P) is as follows: hydromica, kaolinite, vermiculite, irregular interstratified phase and highly dispersed quartz.

Clay fraction from B horizon contains vermiculite as the dominant phase, kaolinite, highly dispersed quartz, a minor amount of hydromica and trace amounts of chlorite.

A horizon clay contains mainly vermiculite, a rather high quantity of highly dispersed quartz, and kaolinite. The accumulation of the amorphous material occurs.

Overall Fe content increases down the profile. FeII content decreases in this direction but the degree of mineral destruction is lower then in Rogóżno podzolic soil. Magnetic susceptibility is two times lower in B horizon then in A and C horizons, indicating some irregularities of the crystalline iron distribution. In this horizon the quantity of crystalline iron is equal in clay and coarser fractions. In the A and C horizons crystalline Fe connected with coarse fractions prevails. The ratio of MSc (A) to MSc (C) is about 2.3.

The dominant soil-forming process seems to be the destruction of the mica-group minerals. The amorphisation of soil material is well pronounced on the diffractograms of the heated samples. The increase in surface area up the profile is apparently connected with the increasie in amorphous material content while the clay fraction content remains approximately constant.

The loamy soil SOB (Sobieszyn G) is localized upon the same agricultural plot, a few hundred meters from the Sobieszyn P soil. The clay fraction from C horizon of this soil contains irregular interstratified mica-smectite, hydromica, kaolinite and highly dispersed quartz. All phases are characterized by intensive and sharp reflexes.

Clay fraction from B horizon contains so-called hydroxy-interlayered or chloritized smectite. The specific feature of this mineral is a partial collapse of 1.4 nm peak upon heating of specimen to 350 °C.

A horizon composition is similar to that of the C horizon, however the reflexes are slightly wider. The clay fraction content and surface area are markedly higher in the A horizon.

Overall Fe content increases down the profile and FeII content decreases. The degree of mineral destruction is similar to that in SOB P soil. The crystalline iron content decreases down the profile and the ratio of MSc (A) to MSc (C) is about 1.1. In the clay fraction of the B horizon the quantity of crystalline iron is higher then in A and C horizons. The degree of silicates destruction is higher in B horizon.

The level of mineral destruction is principally different between Sobieszyn P and Sobieszyn G due to the podzolic processes occurring in the first and the carbonate accumulation in the second soil.

CONCLUSIONS

For the investigated soils the crystalline iron forms occur mainly in granulometric fractions coarser then clay. The iron oxides in clay fractions occur predominantly in superdispersive forms.

FeII distribution within the profiles is different and can be regarded as an indicator of soil forming processes. The ratio of the magnetic susceptibility for A and C horizons is connected with soil typology. For chernozems this value varies from 9 to 5, for brown soils and pseudopodzols it is lower: 3.5 to 2.5, and for black earth less then 1.

Processes of mineral transformations in chernozems consist in the formation of interstratified mica-smectites as a result of illitization, destruction of the material which is expressed in the lowering of structural and textural regulations, the increasing of the dispersion. The relative increase in mica content as a stable in this conditions phase takes place.

Direction and intensity of mineral transformations in brown soils are similar to those taking place in chernozems.

Transformation of fine grained matter in podzolic and pseudopodzolic soils consists in the destruction of the separate mineral phases: predominantly smectites in the first and mica in the second case, however the lessivage process can occur also. The appearance of quartz and feldspars in marked amount in clay fraction of A horizon of Rogóżno soil seems to be a result of primary mineral grains crumbling.

Transformation of clay minerals in black earth consists in destruction of chlorites and interstratification of mica-smectites in the course of mica degradation.

The soil forming processes are expressed in the character of mineralogical and physicochemical profile characteristics.

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