Iron oxides as weathering indicator and the origin of Luvisols from the Vistula glaciation region in Poland

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Abstract

Purpose The aim of the research was to determine the effect of lithogenic and pedogenic processes on the formation of Luvisols from the area of Vistula glaciation on the base of profile distribution of iron oxides and total iron in relation to texture and physicochemical properties. The indices of weathering of the soil material in genetic horizons were calculated, and changes in the content and forms of iron oxides were evaluated.

Materials and methods The predominant type of soil in the study area is Luvisols under agricultural use, formed from silt formations on loam. The analyses were made applying the following methods: grain size composition using the sieve method and hydrometer method, the interpretation of the results was performed according to the World Reference Base for Soil Resources classification, the pH of soils was measured with the potentiometric method, C-organic with the Walkley-Black dichromate method, the content of the following iron forms was determined (total iron (Fe_t) after the mineralization of soils in the mixture of HF and HClO_4 acids), free iron oxides were extracted using dithionite-citrate-bicarbonate method, and amorphous iron oxides after the ammonium oxalate extraction (using the Philips 9100PU apparatus). The clay mineralogy was estimated by X-ray diffraction analysis. **Results and discussion** It was observed that total iron enrichment occurs in *argic* horizons accompanied by iron depletion

in *luvic* horizons, while the profile distribution of iron is similar to the distribution of clay. The (Fe_d/Fe_t) ratio indicates a low degree of weathering; the highest values were observed in *argic* (Bt) horizons, which confirms the effect of the process of pedogenesis on the value of that index. In the soils investigated, crystalline iron oxides generally dominate over the amorphous forms. The mineralogical composition of clay fraction separated from the upper part of soils was different as compared to the underlying material.

Conclusions The results of the study showed that iron contents (together with the other indicators) and its forms can be used to distinguish soil layers of different origin. The depth distribution of Fe_d , Fe_o and Fe_t within soil profiles indicates that the soil material may be of different lithogenic origin in the studied pedons.

Keywords Iron oxides · Lithogenesis · Luvisols · Pedogenesis · Vistula glaciation

1 Introduction

The Pleistocene deposits formed as a result of Scandinavian continental glaciations cover much of northern and central Poland. The Vistula glaciation in Poland is consistent with the Weichsel glaciation in Germany, the Warta glaciation (Lindner 1984) in the eastern part of Europe, and the Wisconsin glaciation (Flint 1971) in North America and accounts for the formation of glacial deposits with various morphological and physicochemical properties. Date ranges for the Poznań phase and Kujawsko-Dobrzynska subphase are 18400kaBP (Wysota et al. 2008). The Luvisols is formed during the Kujawy-Dobrzyń subphase of the Vistula glaciation demonstrating a morphological profile variation, which could be due to the processes of lithogenesis and pedogenesis. The

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soil formation processes in the Luvisol profiles result in the differentiation of the chemical and mineralogical composition of soil material (Ranney and Beatty 1969).

One of the generally accepted methods in research on soil genesis is the analysis of iron forms, depending on the direction of the soil-forming processes, their type and intensity (Blume and Schwertmann 1969; Cornell and Schwertmann 2003). The iron compounds, especially their complex associations with humus colloids, determine the profile distribution of other elements (Tack et al. 1997) in soils. They affect the colour of soils and are indicators of their properties (Kabata-Pendias and Pendias 2010). Soils containing goethite are yellow or brown. Ferrihydrite is dark reddish-brown. Variations in crystal size and morphology may cause variations in these mineral-specific colours. With decreasing particle size, the colour of goethite changes from yellow for crystals in the micrometre size range to dark brown for crystals of ca. 0.01 μm in length. Mn for Fe substitution causes goethite to develop on olive (1–6 % Mn) to blackish colour (10 % Mn) (Schwertmann and Cornell 1991). Iron dynamics can be studied by different extractions. The ratio of oxalate to dithionite-extractable iron (Fe_o/Fe_d) indicates the degree of iron oxide crystallinity and can be used as a reliable indicator of soil age (McFadden and Hendricks 1985). Hence, the Fe_o/Fe_d ratio tends to decrease with soil age (Moody and Graham 1995). The absence of a clear time trend of Fe_o/Fe_d ratio can be explained by other factors (climatic conditions, parent material, redox processes and organic matter content) having greater impact on the Fe_o/Fe_d ratio than the time factor. The degree of weathering and formation of pedogenic iron oxides and hydroxides is expressed by the ratio of Fe_d/Fe_t . An increasing Fe_d/Fe_t ratio reflects the progressive weathering of Fe-bearing minerals with time (Arduino et al. 1986).

Soils formed from glacial deposits often show genetic heterogeneity and lithological discontinuity (Birkeland 1999; Kühn 2001). Defining the relationship between lithogenesis and pedogenesis is one of the key problems on studying those soils. Evaluating the soil-formation pattern and the origin of soils based on the chemical composition of the soil mass requires reference to soil parent materials.

The aim of the present study was to determine the effect of lithogenesis and pedogenesis on the formation of Luvisols from Vistula glaciation sediments on the base of profile distribution of iron compounds, particularly iron oxides and hydroxides in relation to texture, the content of hardly weathered mineral-zircon, clay mineralogy and the physicochemical properties of soils.

2 Material and methods

The soil profiles selected for the study are located in the area of the South Pomerania Lake District on the flat bottom-moraine plains formed during the Vistula stadial, the Poznań

stage (Lindner 1992). Luvisols (IUSS Working Group WRB 2007) are predominant and under agricultural use, formed from silt formations on loam, with the following genetic horizon sequence: Ap-Et-Bt-C. Soil texture and the morphology of soil pedons suggest a lithological discontinuity within soil profiles in the region. Selected profiles were located on the flat area of ground moraine plane formed during the Poznań Phase of the Vistula Glaciation (Lindner 1984; Marks 2002). The samples for analyses were taken from the each genetic horizon of seven profiles. The location of the soil profiles (P1–Zarzewo; P2–Glewo; P3–Dyblin; P4–Strachoń; P5–Mokowo; P6–Grochowalsk; P7–Bachorzewo) was determined by using a GPS system (Fig. 1, Table 1).

The analyses were made applying the following methods: grain size composition using the hydrometer method, based on Stoke's law governing the rate of sedimentation of particles suspended in water, the interpretation of the results is based on the World Reference Base for Soil Resources classification (IUSS Working Group WRB 2007), the pH of soils was measured with the potentiometric method (pH in KCl (1 mol dm^{-3}) and pH in H_2O), C-organic with the Walkley-Black dichromate method, and the content of the following iron forms was determined:

- Total iron (Fe_t) after the mineralization of soils in the mixture of HF and HClO_4 acids (Crock and Severson 1980)
- Free iron oxides (Fe_d) were extracted using dithionite-citrate-bicarbonate method according to Mehra-Jackson (Mehra and Jackson 1960)
- Amorphous iron oxides (Fe_o) after ammonium oxalate extraction according to Tamm (Schlichting and Blume 1962) with the ASA method (using the Philips 9100PU apparatus)

The total content of zirconium in the soil samples was determined by the fusion of soil with potassium pyrosulphate, and its concentration in the solutions was determined with the spectrofluorimeter Hitachi F-2000 according to Wang et al. (2000).

For the characterization of lithogenic and pedogenic processes in the soils, the following indices were calculated:

- Weathering index (Fe_d/Fe_t)
- Iron activity index (Fe_o/Fe_d)
- Crystalline iron content ($\text{Fe}_c = \text{Fe}_d - \text{Fe}_o$)

Micromorphology study was done on undisturbed soil samples collected from the selected horizons of the studied profiles. The micromorphological features were described according to Fitzpatrick (1984). The thin sections were interpreted using the nomenclature of Stoops (2003).

The clay mineralogy was estimated by X-ray diffraction analysis of the clay fraction (<2 μm) separated by centrifugation on

Fig. 1 Research area

parallel (oriented specimens), Mg (saturated), Mg (saturated and ethylene glycol solvated), K (saturated) and K (saturated after heating at 550 °C). Analyses were performed on X-Pert Powder instrument, with CuK α radiation at 30 mA, 40 kV.

Statistical evaluation of results was performed using Statistica 10 software by setting Pearson's linear correlation coefficients.

3 Results and discussion

The soils were classified as Haplic Luvisols (IUSS Working Group WRB 2007). The following genetic horizons were identified: Ap-Et-Bt-C. The feature differentiating the soils is the variation in thickness of diagnostic horizons: Et and Bt, across the profiles, which suggests a varied intensity of the illuvial process occurring in studied

Table 1 Location and geographic coordinates of the profiles

Profile no.	Location	District	Physiographic entity	Geographic coordinates	m a.s.l.	Climate	Parent material
P1	Zarzewo	South Pomerania Lake Northern Poland	ground moraine plane	52° 40' 0.84 N 19° 9' 22.14 E	90	Continental Sea	Silt/loam
P2	Glewo			52° 40' 56.06 N 19° 11' 39.12 E	84	Mean annual temperature ^a	
P3	Dyblin			52° 40' 0.15 N 19° 15' 16.44 E	89	Total annual precipitation 530 mm ^a	
P4	Strachoń			52° 39' 14.47 N 19° 18' 7.84 E	98		
P5	Mokowo			52° 38' 40.4 SN 19° 19' 7.504 E	98		
P6	Grochowalsk			52° 40' 51.49 N 19° 13' 6.06 E	95		
P7	Bachorzewo			52° 38' 51.07 N 19° 17' 7.29 E	90		

^a For each pedon

soils (Jaworska et al. 2014). The studied sites are located on the flat area of ground moraine plain (Lindner 1984), and there are no available data or evidence of erosion and/or redeposition processes causing such a difference in soil morphology.

Textural analysis allow for separating the following granulometric groups: silty loam, in the substratum of which loam is found (Table 2), except for horizon Ap in profile P1, where loam occurred deep down to 30 cm, and then sandy silt occurred with underlying loam (Table 2), similarly in horizons

Ap and Et in profile P5, deep down to 35-cm silty loam, underlying with loam, occurred.

Soil texture varies with depth within studied profiles. They are mainly silty loams with loamy material as their subsoil.

Generally, surface horizons contain 20–55 % of silt (0.05–0.002 mm), which corresponds to a silty loam texture. Illuvial horizons and parent material contain 16–52 % silt and 4–29 % clay, classifying them as loamy soils. The discontinuity in the grain size distribution within profiles may result from either leaching or periglacial processes. The clay content changes

Table 2 Selected properties and texture of soils grams per kilogram

No.	Horizon	Depth (cm)	pH (H ₂ O)	pH (1MKCl)	CEC (cmol ⁺ kg ⁻¹)	CaCO ₃ (%)	Corg. (g kg ⁻¹)	Content of fraction (%)			Silt/clay
								2–0.05	0.05–0.002	<0.002	
P1	Ap	0–30	6.40	6.24	14.3	–	8.2	60	38	2	19.0
	Et	30–56	7.07	6.99	10.4	–	2.1	41	57	2	28.5
	2Bt1	56–98	6.92	6.60	23.3	–	1.3	54	29	17	1.7
	2Bt2	98–110	7.52	7.45	30.1	–	0.0	48	32	19	1.7
	2C	110–150	8.14	8.00	25.6	Trace	0.0	63	26	11	2.4
P2	Ap	0–25	7.24	7.03	22.2	–	10.0	46	46	8	5.8
	Et	25–43	7.51	7.14	14.0	–	1.9	46	49	6	8.2
	2Bt	43–110	7.35	6.30	25.3	–	1.5	57	28	15	1.9
	2Ck1	110–130	7.95	7.46	24.5	3.8	0.0	65	21	14	1.5
	2Ck2	130–150	7.93	7.59	39.1	4.2	0.0	66	21	13	1.6
P3	Ap	0–25	6.21	5.80	12.6	–	13.0	48	48	4	12.0
	Et	25–40	6.84	6.44	10.8	–	1.7	40	55	5	11.0
	2Bt	40–95	8.07	7.21	27.5	–	1.2	62	21	17	1.2
	2Ckg1	95–125	8.48	7.87	29.4	3.5	0.0	56	29	15	1.9
	2Ck2	125–150	8.48	7.85	32.1	4.4	0.0	55	30	15	2.0
P4	Ap	0–30	5.98	5.50	12.4	–	11.6	42	49	9	5.4
	Et	30–50	6.45	5.94	12.1	–	3.2	46	50	4	12.5
	2Bt	50–80	7.81	6.92	21.5	–	1.2	63	25	12	2.1
	2C	80–120	7.84	7.04	19.3	Trace	0.0	67	23	10	2.3
	2Ck	120–150	7.59	6.77	25.4	2.6	0.0	68	25	7	3.6
P5	Ap	0–22	7.21	6.80	11.1	–	11.1	57	39	4	9.8
	Et	22–35	6.84	6.34	15.9	–	4.5	55	42	3	14.0
	2Bt	35–110	8.01	7.01	17.0	–	1.3	67	18	15	1.2
	2BC	110–130	6.93	6.85	16.1	–	0.0	66	21	13	1.6
	2C	130–150	7.31	7.06	6.6	Trace	0.0	66	24	10	2.4
P6	Ap	0–20	7.85	7.73	11.1	–	11.2	55	44	1	44.0
	Et	20–42	7.73	7.27	14.9	–	1.9	52	46	2	23.0
	2 EB	42–90	7.80	7.75	17.4	–	0.9	61	31	8	3.9
	2Bt	90–130	7.42	6.38	15.3	–	0.0	62	23	15	1.5
	2C	130–150	7.47	6.82	14.8	–	0.0	61	29	10	1.6
P7	Ap	0–23	7.23	6.65	12.5	–	9.9	49	43	8	5.4
	Et	23–43	8.02	7.59	12.7	Trace	3.2	36	54	10	5.4
	2 EBg	43–61	8.02	7.15	20.4	–	1.3	69	23	8	2.9
	2Btg	61–111	7.82	6.65	19.5	–	0.0	63	20	17	1.2
	2Cg	111–150	8.06	7.54	18.7	–	0.0	63	26	11	2.4

abruptly between Et and Bt horizons reflecting a change in parent material. The enrichment in clay particles in deeper horizons (Table 2) may result from clay illuviation, but according to Kühn (2003), it may be also due to a silty-cover bed above glacial material. The silt/clay ratio used as a measure of the uniformity of soil material within profile may prove the occurrence of two layers (Wagner et al 2007). Changes in the silt/clay ratio between layers reflect the major influence of the parent materials. Calculated silt/clay ratios in the upper part of analysed soil profiles (A and Et horizons) are

Table 3 Content of total iron (Fe_t), iron extracted with dithionite-citrate-bicarbonate (Fe_d), iron extracted with ammonium oxalate (Fe_o), total zirconium (Zrt) and crystallinity index (Fe_o/Fe_d), weathering index (Fe_d/Fe_t) and crystalline iron ($\text{Fe}_c = \text{Fe}_d - \text{Fe}_o$)

No.	Horizon	Fe_t (g kg ⁻¹)	Fe_d	Fe_o	Fe_c	Zrt	Fe_o/Fe_d	Fe_d/Fe_t
P1	Ap	7.89	2.52	0.99	1.53	0.11	0.39	0.32
	Et	7.17	1.85	0.97	0.88	0.12	0.52	0.26
	Bt1	16.06	7.35	2.08	5.27	0.14	0.28	0.46
	2Bt2	14.63	5.82	1.03	4.79	0.10	0.18	0.40
	2C	13.47	4.31	0.37	3.94	0.09	0.09	0.32
P2	Ap	5.67	2.36	1.20	1.16	0.15	0.51	0.42
	Et	16.65	1.90	1.23	0.67	0.16	0.65	0.11
	2Bt	14.64	3.24	1.38	1.86	0.10	0.43	0.22
	2Ck1	9.21	3.41	0.36	3.05	0.11	0.11	0.37
	2Ck2	13.23	3.36	0.43	2.93	0.12	0.13	0.25
P3	Ap	8.03	1.60	0.74	0.86	0.14	0.46	0.20
	Et	8.03	1.02	0.79	0.24	0.17	0.77	0.13
	2Bt	16.02	3.93	1.20	2.73	0.12	0.31	0.25
	2Ckg1	14.34	2.52	0.70	1.82	0.10	0.28	0.18
	2Ck2	15.37	3.68	0.42	3.26	0.09	0.11	0.24
P4	Ap	7.79	2.35	0.87	1.98	0.19	0.16	0.30
	Et	10.43	3.34	1.04	2.30	0.17	0.31	0.32
	2Bt	15.95	5.71	1.34	4.37	0.11	0.23	0.36
	2C	14.23	4.26	1.29	2.97	0.13	0.30	0.30
	2Ck	11.10	2.83	0.79	2.04	0.11	0.28	0.25
P5	Ap	8.34	2.40	1.08	1.32	0.17	0.45	0.29
	Et	8.09	2.00	1.23	0.77	0.18	0.62	0.25
	2Bt	16.36	4.81	1.36	3.45	0.10	0.28	0.29
	2BC	14.81	4.10	0.36	3.74	0.10	0.09	0.28
	2C	15.84	2.95	0.43	2.52	0.10	0.15	0.19
P6	Ap	9.09	2.07	1.07	1.00	0.16	0.52	0.23
	Et	7.99	2.39	0.92	1.47	0.16	0.38	0.30
	2 EB	13.27	6.41	1.34	5.07	0.15	0.21	0.48
	2Bt	8.32	6.09	0.97	5.12	0.09	0.16	0.73
	2C	9.07	7.36	1.03	6.33	0.11	0.14	0.81
P7	Ap	12.25	2.36	0.90	1.46	0.17	0.38	0.19
	Et	13.88	2.00	0.94	1.06	0.20	0.47	0.14
	2EBg	21.54	5.55	1.55	4.00	0.17	0.28	0.26
	2Btg	19.05	5.80	1.16	4.64	0.12	0.20	0.30
	2Cg	18.51	3.70	0.47	3.23	0.12	0.13	0.20

noticeably higher compared to underlying Bt and C horizons (Table 2). This might be connected with the different origin of upper layer. A similar texture differentiation was reported by Kühn (2003). The genesis of so-called silty cover-bed (Kopp and Kowalkowski 1990) is mostly of Holocene pedogenic origin. It is however accepted that during the Late Weichselian processes like repeated freeze-thaw cycles, cryoturbation and also eolian input, etc. led to the formation of the so-called silty cover bed (Kopp and Kowalkowski 1990). The variety of factors that lead to the formation of these soils might interfere causing a complex mixture of processes responsible for the formation of solum. This applies particularly to soils characterized by vertical differentiation of mineral material, frequently encountered among the glacial deposits. The values of typological indicators (Table 3) indicate that the soil material may be of different origin in the studied pedons.

The presence of two sola in the studied profiles is also expressed by cation exchange capacity (CEC) (Table 2). The cation exchange capacity values are distinctly lower in the top soil than in the underlying material, indicating some discontinuity.

Soil pH is in the range of 5.5–8.0 (Table 2). Lower pH values were observed in surface horizons with silty loam texture (Table 2). The soils are generally deficient in CaCO_3 . The parent material, in profiles P1, P2, P3, P4 and P5, is the only location where CaCO_3 occurs in the range 2.6 to 4.4 %. Carbonate-leaching is typical for this type of soils (Dąbkowska-Naskręt and Jaworska 1997). The soils analysed contain 8.29–12.98 g kg⁻¹ of organic carbon. A low content of organic matter is characteristic for arable Luvisols due to the dominance of mineralization over humification process of organic remains (Haynes 2005). The intensity of those processes mainly depends on the air-and-water conditions and the type of land use.

The distribution of different forms of Fe within profiles is shown in Table 3. The content of total iron (Fe_t) ranged from 7.17 to 21.54 g kg⁻¹ (Table 3).

The lowest Fe_t contents occurred in A_p horizons of all the investigated profiles (Table 3). The profile distribution of Fe_t was similar to the clay distribution, indicating a secondary illuviation of iron with clay (Deng et al. 1998). Since hydrous Fe oxides are often associated with clay minerals (Kabata-

Table 4 Significant correlation coefficients ($p < 0.05$)

Variable	Fe_t	Fe_d	Fe_o	Fe_c
Clay fraction	0.584*	0.602*		0.641*
Fe_d	0.457*		0.381*	0.973*
Fe_c	0.440*			
Corg	-0.549*	-0.505*	0.102	-0.547*

*Significant

Fig. 2 Weathering index values

* Numbers related to genetic horizons described in Table 1

Pendias and Pendias 2010), the Fe_d content correlates significantly with the content of clay fraction in the studied soils ($r=0.602$, $p<0.05$) (Table 4). The relationship between Fe_t content and soil texture mostly on the content of fraction <0.002 mm was also reported by Muhs et al. (2001). Due to chemical weathering of silicates and aluminosilicates and because of the mineralization of organic residue, releasing iron oxides can be accompanied by a slight increase in the clay fraction (Duchaufour and Sochiers 1978).

The contents of free pedogenic iron (Fe_d) varied across the profiles, similarly as the contents of total iron (Table 3). The highest contents were found in Bt horizons, accompanied by the depletion in Et horizons, which points to eluviation of free iron with clay by lessivage (Schlichting and Blume 1962). Secondary iron oxides are much smaller particles than $2\ \mu\text{m}$ (usually less than $500\ \text{nm}$); they are therefore mostly components of the colloidal fraction (Waychunas et al. 2005).

The ratio of free iron to total iron (Fe_d/Fe_t) was the highest in argic horizons, while in luvis horizons of profiles P4 and P5, those values were generally lower (Table 3, Fig. 2), which can confirm the effect of lessivage process. Free iron content and the colloidal clay show a significantly positive correlation (Table 4).

The weathering index also reflects the degree of the transformations of the soil substrate, i.e. the release of iron oxides during silicate weathering. In the soils investigated, low Fe_d/Fe_t ratios indicate a low degree of weathering. The profile distribution and the content of non-silicate iron (Fe_d) depend mainly on weathering intensity and parent material (Okuda et al. 1995). Generally, the largest accumulation occurs in enrichment horizons (Bt) (Table 3), which is also reported

by Blume (1988). The lowest Fe_o contents are found in the parent material except for profile P6 (the least in horizon Et) and P4 (the least in horizon Ap). The dominance of amorphous over crystalline iron oxides suggests a relatively young soil age (McCahon and Munn 1991). In studied soils, due to climatic conditions, the crystalline iron oxides generally dominate over amorphous forms (Cornell and Schwertmann 2003). Temperate climate favours the formation of goethite which forms almost exclusively from ferrihydrite. However, the “ageing” of amorphous iron oxides is governed by many soil and climatic parameters (Stucki et al. 1988). Iron oxide transforming process is related to pH, temperature, the presence of ferrous ions, and the type of anions, such as chloride sulphate and oxyanions. Iron(hydro)oxide system is also redox sensitive (Lin et al. 2008; Das et al. 2011).

The amorphous iron oxides, released during weathering, get crystallized with time. The rate of that process depends considerably on the pedoenviromental conditions. In the Bt and C horizons, amounts of crystalline iron oxides (Fe_c) are higher than Fe_o (Table 3). The highest Fe_c contents were detected in the illuvial horizons and the parent rock (Table 3). This could be due to the inhibiting effect of organic matter on the processes of crystallization (Schwertmann 1988). It has been recognized that the ratio of Fe_d to Fe_t is basically controlled by pedogenic weathering.

We determined the iron crystallinity index (Schwertmann 1966) by applying the ratio of amorphous iron to free iron Fe_o/Fe_d (Fig. 3), with activity index values to define the interaction between active iron forms and their crystalline forms (Dąbkowska-Naskręt 1996).

Fig. 3 Activity index values

In the soils investigated, the Fe_o/Fe_d ratio was the highest in eluvial horizons and the lowest—in parent material, which points to a greater activity of pedogenic iron and a lower degree of iron oxide crystallization in the luvic horizons. Profile P4 in C horizon was the only one in which the index value was the highest and in horizon Ap—the lowest (Table 3). The highest value of that index in humus horizons reported by Schwertmann (1966) is not confirmed by the present research (Table 4). Values of activity index in investigated Luvisols may therefore also indicate a similar mineralogical composition of parent materials and similar climatic conditions during their genesis.

The above data on the distribution of different forms of iron within soil profiles suggest genetic non-uniformity of the soil material. To confirm it, another indicator was used, i.e. the distribution of hardly weathered mineral—zircon (ZrSiO_4). It was observed (Stiles et al. 2003) that the content of Zr,

which occurs in soils principally in the form of ZrSiO_4 , is similar in each horizon of soil formed from the uniform material. In other case, it is different in soil strata due to their different origin and, in consequence, different composition in relation to hardly weathered components like zircon.

The boundary between Zr contents within each soil profile occurs at the same depth as the abrupt change in sand grains contents, i.e. 40–56 cm (Table 3).

Moreover, mineralogical composition of clay fraction reflects the occurrence of two different strata in studied profiles. On the diffractograms of clay fraction from the topsoil, peaks attributed to illite, kaolinite and chlorite were detected (Fig. 4). In the underlying material illite, smectite and vermiculite together with hydroxy interlayered minerals are present. Moreover, chlorite is absent in the deeper sola due to the disappearance of 1.42-nm peak in the clay fraction saturated with potassium and heated to 550 °C. Vermiculite is also

Fig. 4 X-ray diffraction patterns of clay fraction <2.0 μm

Ap horizon in P6 profile

Bt horizon in P6 profile

Fig. 5 Photomicrographs of the lithogenic and pedogenic features of the soils. Cross-polarized light (XPL)

present as 1.44-nm peak in Mg-saturated sample contracted to 1.00 nm after saturation with potassium (Fig. 4). The occurrence of kaolinite is confirmed by lack of the 0.712-nm peak and the 0.357-nm peak (second-order kaolinite peak) after heating to 550 °C. Thin section analyses of the material from the upper layer confirm the presence of silt particles and loamy material in the deeper part of profile (Fig. 5).

The statistical analysis of the results (Table 4) indicates a significant positive correlation between Fe_t and clay contents and also between Fe_d contents and clay fraction, Fe_o , Fe_d and Fe_c with colloidal clay.

4 Conclusions

In the soils investigated, Bt horizons are distinctly enriched with Fe_t and is accompanied by the depletion in *luvic* horizons, while the pattern of Fe_t mimics clay distribution, indicating coilluviation of iron and clay.

The weathering index (Fe_d/Fe_e) in the soils assumes the values corresponding to the formations with a low degree of weathering, with the highest values in *argic* horizons and distinctly lower ratios in the *luvic* horizons and parent rock, confirming the effect of the process of pedogenesis on the value of that index.

Crystalline iron oxides prevailed over the amorphous forms, which could have been due to the slightly inhibiting effect of organic matter on the processes of crystallization of those compounds in soil.

The iron activity index (Fe_o/Fe_d) was higher in the eluvial horizons and the lowest—in the parent material, which points to a greater activity of pedogenic iron in the *luvic* horizons of the studied soils. Moreover, it indicates a lower degree of iron oxide crystallization in eluvial (*luvic*) horizons.

The results of the study showed that iron contents (and their indicators) and iron forms can be used to distinguish soil layers of different origin. Other indicators like zircon distribution and mineralogical composition of clay fraction within soil profile reflecting the occurrence of two layers enhance the above results. The depth distribution of Fe_d , Fe_o and Fe_t within soil profiles indicates that the soil material may be of different lithogenic origin in the studied pedons.

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