

## THE STRUCTURAL STATE OF SOILS ON LOESSES

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**A b s t r a c t.** Amount and mineralogy of clay material separated from four geochemically linked loessial soil samples of various genesis due to a sequential dissolution of aggregating agents were studied by X-ray diffractometry, Mossbauer spectroscopy and magnetic measurements. Some regularities in the distribution of mineral (crystalline and amorphous) and organic soil compounds as related to pedoenvironmental conditions, were observed.

**K e y w o r d s:** loessial soil, aggregation structure, sequential disruption

### INTRODUCTION

A large number of soil physical properties result from the structural features of soil profile. These are directly related to the organization of soil aggregates i.e. to the specific distribution of mineral and organic components within aggregates [14]. This can be studied by various methods [17]:

- correlation of soil structural properties with the content of different aggregating compounds;
- microscopic observations;
- observing the aggregation effects produced by adding synthetic components;
- observing the dispersion of aggregated soils after removing particular aggregating compounds.

The latter method gives information about

the amount and nature of clay material aggregated by different agents (called clay categories), as well as about the nature of aggregating agents themselves. Clay categories of different soils are characterised by various properties depending on pedoenvironmental conditions [15].

In our previous works we studied the organization of soil aggregates in the steppe [1] and red-soils [2] by the consecutive removal of various aggregating compounds.

The aim of the present study is to determine the structural state of soils of various genesis developed from loess. Soils localized upon geochemically linked sites were selected to look for the possible similarities in structural forms.

### MATERIALS AND METHODS

Four soil samples localized upon geochemically linked sites and developed from loessial parent material were studied. The main properties of these soils are presented in Table 1.

The organisation of solid phase components into aggregates was estimated by a sequential selective dissolution procedure elaborated on the basis of literature [3-6,9,11]. The soils were treated step by step with progressing more powerful dissolving agents.

Table 1. Main properties of samples

Soil type and depth (cm)	Landscape position	C (%)	MgCO <sub>3</sub> + CaCO <sub>3</sub> (%)	Water soluble salts (%)	Exchangeable cations (meq/100g)				Iron forms		pH	Specific surface area (m <sup>2</sup> /g)	Total porosity (%)	Aver. pore radius (μm)	Bulk density (g/cm <sup>3</sup> )	Granulometric composition (%)	
					Ca	Mg	K	Na	Fe(d)	Fe(o)						<0.001 (mm)	0.01-0.001 (mm)
Chestnut soil (300-350)	divide sur-face	0.20	11.30	0.31	2.4	2.2	0.35	3.50	1.53	0.28	8.40	3.20	35.04	3.82	1.61	18.84	31.96
Typical Chernozem (20-53)	divide sur-face	1.70	5.35	0.17	12.4	5.6	0.36	0.21	1.70	0.19	7.80	5.50	28.00	3.80	1.83	25.88	44.88
Meadow flood-plain soil (0-24)	flood-plain	2.18	7.62	0.33	13.2	0.2	1.42	0.31	1.70	0.24	7.65	9.14	23.42	0.25	1.89	26.33	52.85
Paleosol (600-650)	divide sur-face	0.30	10.51	0.16	14.0	5.4	0.39	6.17	1.40	0.80	8.10	8.96	18.96	0.08	1.96	32.16	49.30

- I H<sub>2</sub>O - extraction of 'free' clay material,
- II 0.1 N NaCl - extraction of clay bound by polyvalent exchangeable cations,
- III 0.002 % Na<sub>2</sub>CO<sub>3</sub> (pH 9) - clay bound by amorphous aluminosilicates,
- IV 0.1 N NaOH+0.1 N Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (pH 11.5) - clay bound by easily soluble organic matter and less soluble aluminosilicates,
- V Tamm's reagent (pH 3.2) - clay bound by iron compounds,
- VI 0.1 N NaOH+0.1N Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (pH 11.5) - clay bound by organic matter - iron associates,
- VII sodium hypobromite (pH 13) - clay bound by hardly soluble organic matter.

After each step, <2 μm clay fractions (clay categories) were separated by centrifuging and the content of Si, Al, Fe, and organic matter was determined in supernatants.

The mineralogy of clay categories was examined by X-ray diffractometry on DRON-3.0 apparatus (Cu<sub>Kα</sub> - radiation, Ni-filter). Specimens were prepared by sedimentation from water suspension on 25x25 mm glass slide. Organic matter was removed with 10 % H<sub>2</sub>O<sub>2</sub>, sesquioxides of Fe and Al by Mehra and Jackson extraction. Specimens in Mg-, K- and Li-forms, saturated with ethylene glycol and heated to 350 °C and 550 °C were examined. The relative abundance of major clay mineral groups was quantitatively determined by the Biscay method [8].

Room-temperature Mossbauer spectra were recorded with a MS1101E spectrometer with a constant-acceleration drive system (<sup>57</sup>Co/Cr source with an activity of about 32mCi). The velocity scale was calibrated relative to Fe and sodium nitroprusside. The relative content of total and divalent iron in clays was established

from the numerical analyse of the Mossbauer spectra using UNIV programs [12].

The measurements of magnetic susceptibility was performed with KAPPABRIDGE KLY 2 (Geofyzika Brno).

Additionally, for the A and C horizons of the dark chestnut soil, the distribution of water-stable aggregates and their main properties were studied. Water-stable aggregates were obtained by wet sieving and their mineralogical and granulometric composition, organic carbon (oxidation with dichromate) and carbonates content were determined. The sequential disruptions of aggregating agents was performed for aggregates of 2-1 mm and 0.05-0.002 mm.

## RESULTS AND DISCUSSION

As the dark chestnut soil was investigated in more detail, we discuss the results obtained for this first (Table 2 and 3).

The A horizon of the dark chestnut soil contains more macroaggregates and less microaggregates than the parent material, however, the content of carbonates is higher in aggregates from the C horizon. Carbonates content decreases with decreasing aggregate size. The amount of organic matter in aggregates increases with increasing content of clay fraction. Aggregates, as a rule, are richer in organic carbon than soil material.

Aggregates of 0.25-0.05 mm exhibit some specific properties. These contain much more fraction >50 μm than the coarser aggregates. Organic matter content is markedly lower than in other aggregates. Clay fraction from 0.25-0.05 mm aggregates contains no minerals with swelling lattice and is enriched with mica whereas the clay fraction, separated from other

Table 2. Content of water-stable aggregates (dark chestnut soil)

Horizon	Water-stable aggregates (%)					
	3-2	2-1	1-0.5	0.5-0.25	0.25-0.05	<0.05
	(mm)					
A	0.8	1.5	6.9	7.8	29.2	53.8
C	0.3	0.9	2.4	1.6	33.4	61.4

Table 3. Main properties of aggregates

Horizon	Aggregates (mm)	C (%)	CO <sub>2</sub> carb. (%)	Kaolinite (%)	Chlorite (%)	Hydromica (%)	Smectite (%)	Granulometric composition (%)			
								>0.05	0.05-0.01	0.01-0.002	<0.002
A	>1	1.60	2.54	11	11	66	12	8.59	46.36	13.18	31.86
	1-0.5	1.47	3.96	17	16	53	14	10.37	47.06	14.96	27.66
	0.5-0.25	1.69	3.39	14	13	61	12	7.40	50.38	13.64	28.58
	0.25-0.05	0.93	2.64	10	7	80	3	33.01	41.12	9.44	16.43
	0.05-0.002	1.60	0.98	15	14	59	12	-	52.27	16.86	30.87
	<0.002 soil	3.30	n.d.*	11	11	60	18	-	-	-	-
C	>1	0.30	5.86	14	14	55	17	15.08	49.94	12.50	22.48
	1-0.5	0.30	6.71	10	11	67	12	14.85	51.75	11.62	21.78
	0.5-0.25	0.30	5.58	14	13	55	18	15.45	47.87	12.95	23.73
	0.25-0.05	0.06	5.29	10	8	79	3	40.44	42.45	7.98	9.13
	0.05-0.002	0.18	5.31	11	10	61	18	-	57.84	17.25	24.91
	<0.002 soil	0.54	n.d.	14	12	60	14	-	-	-	-
				12	11	56	21	n.d.	n.d.	n.d.	n.d.

\*n.d. - not determined.

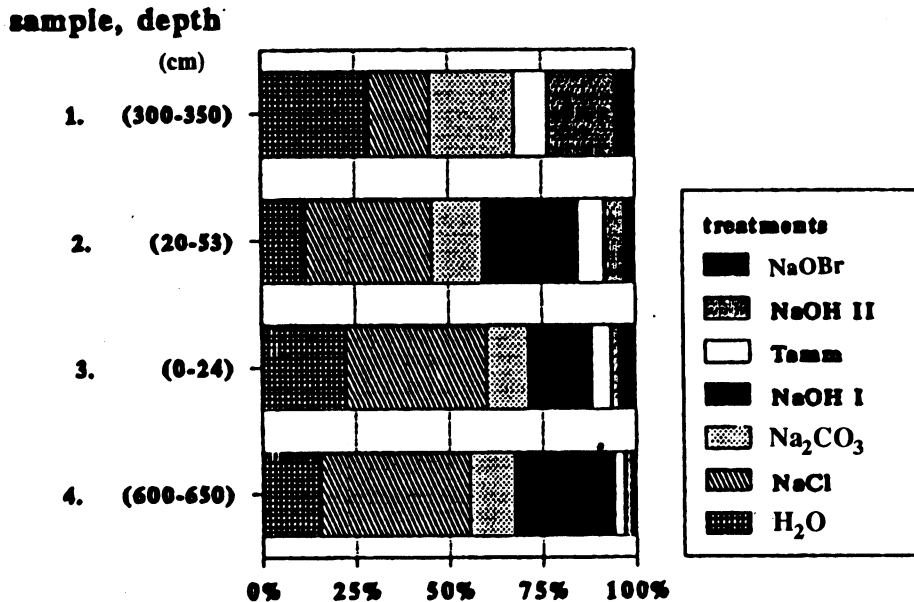


Fig. 1. Differential disruption (% of total clay content) for different treatments of studied soils.

Table 4. Organic matter composition in NaOH extracts

Sample	Initial soil		IV treatment		VI treatment	
	C (%)	HA/FA	C (%)	HA/FA	C (%)	HA/FA
2	1.7	2.5	1.0	2.7	n.d.	0.2
3	2.2	n.d.	0.4	3.3	0.2	1.7
4	0.3	n.d.	0.3	+∞	0.4	1.1

aggregates and the original soil, has a different mineralogical composition. Aggregates of 0.25-0.05 mm appear to be elementary soil particles.

The marked differences between mineralogy of aggregates from A and C horizons were not observed.

The amount of clay categories separated from the studied soil samples, during the sequential disruption procedure, is presented in Fig. 1. It is necessary to mention that after completion of the procedure the soil clay fraction was separated totally. In all samples the amount of WDC is high (up to 28 % of clay extracted after 1st treatment), which is a characteristic feature of loesses. In soils of a subor-

dinate position in the landscape the aggregating influence of Si- and Fe-increases. The distribution of clay categories in A horizons does not differ markedly from C horizons, which may be due to the genesis of the loessial deposits.

Data presented in Table 4 indicate that the humic to fulvic acid ratio HA/FA in extracts decreases with decreasing aggregate size: in supernatants from VIth treatments HA/FA is less than from IVth treatments. Bartoli *et al.* [7] and Bremner and Genrich [10] also showed that organic matter of higher MW and more aromatic is concentrated in coarser aggregates. The processes of soil aggregates formation stabilise the part of organic matter occurring within aggregates [13].

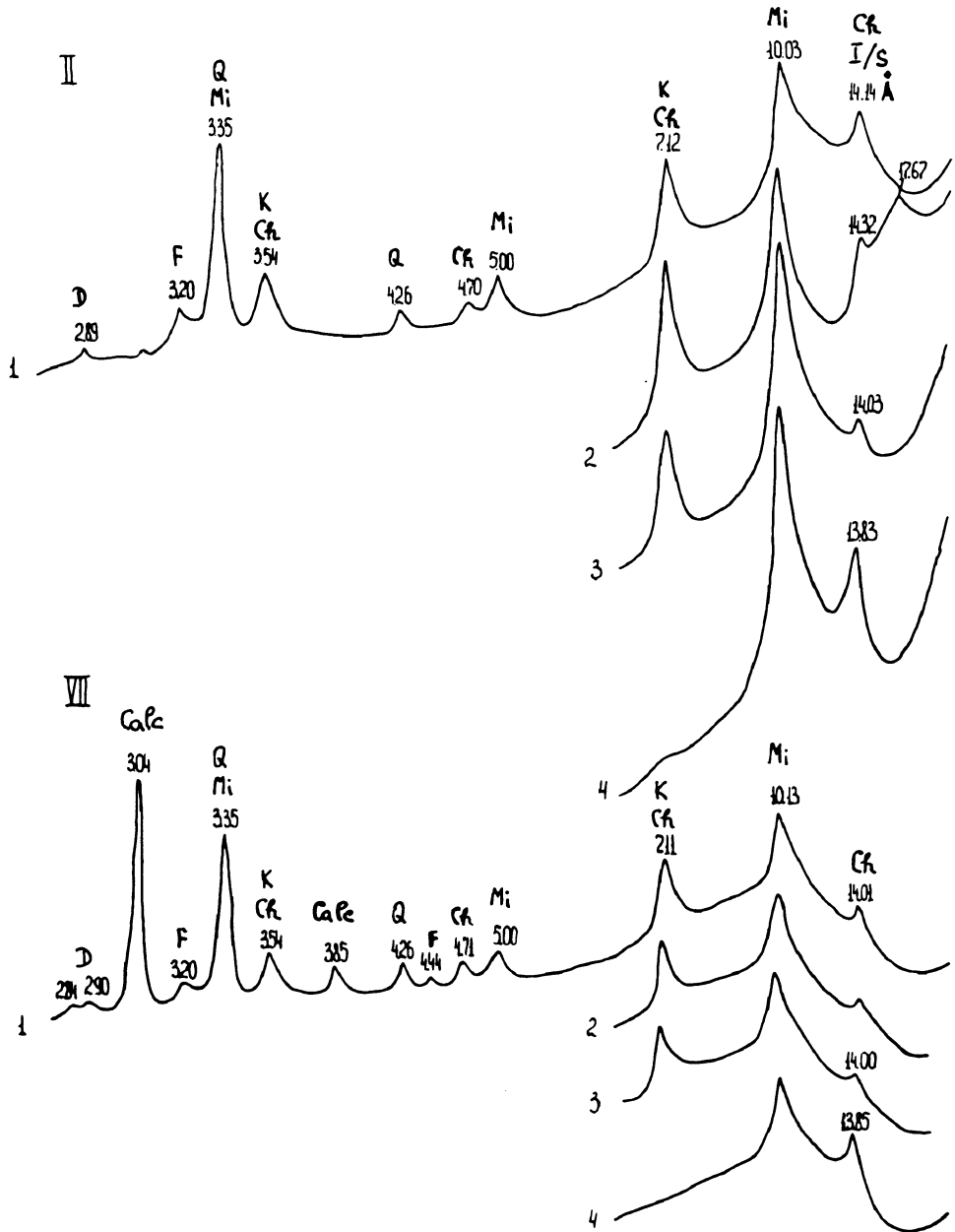


Fig. 2. Examples of X-ray diffractograms of II and VII categories of clay fraction (sample 1). 1 - Mg; 2 - Mg, ethylene glycol; 3 - Mg, 350 °C; 4 - Mg, 550 °C.

The mineralogical composition of clay categories is similar to the original soil mineralogy estimated without chemical dispersion, however the relative content of minerals in

clay categories varies. These variations are in close similarity with data obtained for clay categories of water stable aggregates. As a rule, loosely bound clay is characterised by a

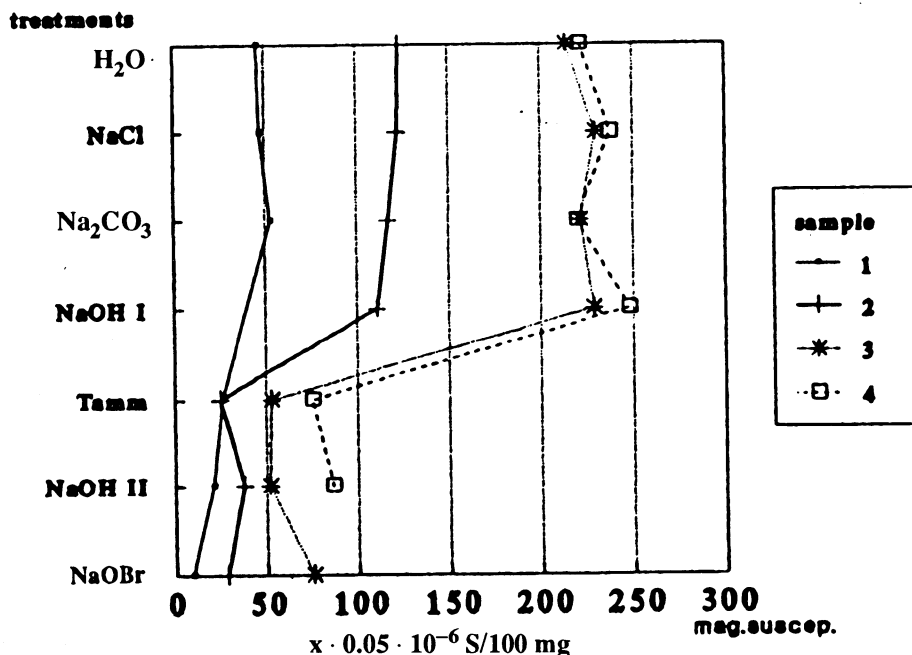


Fig. 3. Magnetic susceptibility of clay categories of studied soils.

Table 5.  $\text{Fe}^{2+}$  content (%) in silicates in clay categories

Treatments	Sample			
	1	2	3	4
$\text{H}_2\text{O}$	21.9	16.9	11.7	15.7
$\text{NaCl}$	15.8	14.6	8.4	1.9
$\text{Na}_2\text{CO}_3$	18.2	23.1	10.0	21.8
$\text{NaOH I}$	n.d.	22.4	14.4	18.7
Tamm	27.1	20.6	15.9	35.3
$\text{NaOH II}$	30.3	19.2	18.2	23.5
$\text{NaOBr}$	47.8	19.1	14.8	n.d.

greater content of swelling phase, i.e., by randomly interstratified mica-smectite; whereas closely bound clay consist mainly of non-swelling minerals containing a large amount of carbonates and 'primary' minerals (feldspars, quartz). This is shown in Fig. 2. The carbonates can possibly appear as 'coatings' on primary minerals grains [16].

The divalent iron occurs in the clays studied due to Fe substitution in the crystal lattice

of silicates. Table 5 demonstrates the differences of FeII for clay categories. In general, closely bound clay is characterised by higher content of FeII. This may be due to a lower degree of weathering of the better aggregated material and/or of the presence of other mineral phases.

Magnetic susceptibilities of clay categories reflecting the presence of crystalline iron forms are presented in Fig. 3. One can see that the magnetic susceptibility for a given soil is roughly constant before the Fe dissolution procedure is applied (Tamm reagent). After the procedure the magnetic susceptibility decreases, reaching an approximate constant value. This may be interpreted as due to the occurrence of crystalline iron, as separate particles, not bound to particular minerals. The differences of magnetic properties between the studied soils are significant, which may be due not only to the landscape but also to micro-environment conditions [1].

## CONCLUSIONS

Closely bound clay of all samples studied has similar properties. The material of clay categories is more chemically transformed than the parent material.

Soil aggregates are characterised by a heterogeneous distribution of mineral (crystalline and amorphous) and organic components.

No marked differences for the structural state of the soils studied were indicated by the sequential dissolution method.

Water-stable aggregates of 0.25-0.05 mm markedly differ from the other size aggregates in granulometry, mineralogical composition, and organic matter and carbonates content.

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