On soil genesis in temperate humid climate. VI. The formation of a glossudalf in loess (silt loam)

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Summary

An in the South of the Netherlands frequently occurring type of a well-drained Grey Brown Podzolic Soil was investigated by chemical and macro- and micromorphological methods. The profile is considered to be a Holocene soil formation in originally calcareous wind deposits (loess). Under the infiltration conditions as found in flat positions, the continuing development of the textural B-horizon leads to a polygonal cracking in dry periods. In the wet season these cracks conduct water, saturating the surroundings of the cracks. Reduction processes come into play leading to a bleaching. Consequently, in vertical sections of the soil light coloured tongues are observed bordered with a yellowish red band and at some distance manganese mottles and concretions. In the tongues strong clay leaching occurs.

The largest amount of micromorphologically determined oriented clay bodies (notably channel and ped argillans) was found in the B_3 -horizon, whereas the B_{2r} -horizon had the highest clay content.

The classification of the profile as an Aquic Glossudalf was based on the discussion of chemical and morphological data.

1 Introduction

In the South of the province of Limburg, The Netherlands, Grey-Brown Podzolic soils are found, which show 'degradation' characteristics if present in nearly flat positions. The soils are formed in loess (silt loam), which is decalcified up to 3 metres and are of Holocene age (van der Broek, 1958/'59). In vertical section of the well-developed argillic horizon light coloured tongues are found, which form a polygonal pattern on cross section. Iron-manganese nodules can be observed scattered all over the profile, although some concentrations occur. Tongues as well as iron-manganese nodules seem to be inherent to the occurrence of reduction and oxidation processes. In this paper attention will be paid to the distribution of oriented clay bodies in the several horizons, the biological activity in the profile and the processes of reduction and oxidation.

2 Profile description and samples taken

Location: Elsloo, S. Limburg, The Netherlands. Topography: flat to nearly flat. Slope 0-3%; Drainage: well-drained. Relief: subnormal. Erosion: very little. Groundwater: very deep. Landuse: agricultural crops. Rainfall: 710 mm annually. Temperature: -0.8 °C (minimum) to 22.5 °C (maximum).

- HorizonDepth (cm)DescriptionAp0-26Light yellowish brown (10 YR 6/4 : d) yellowish brown (10 YR 5/4 : m)
silt loam. Firm. Very weak thick platy and moderate, fine subangular
blocky. Very few, very fine biopores. Common, fine fragments of gravel
and coal. Clear and smooth boundary.
- A₂ 26-45 Very pale brown (10 YR 6/3 : d) yellowish brown (10 YR 5/3 : m) silt. Friable. Very weak, very fine subangular blocky. Occasionally platy or spongy. Common, fine biopores. Very few, very fine, distinct iron-manganese mottles. On ped faces very thin coatings of silt. At the lower boundary some dark brown areas of B-material and some, coarse, distinct, light grey to very pale brown (10 YR 7/2½ : m) mottles occur. In the latter material common, fine, distinct, strong brown (7.5 YR 5/6 : m) mottles occur, occasionally in long bands at the upper and lower surface. Wormtracks are coated and sometimes filled with very dark grey (10 YR 3/2 : m) excrements or with moderate, granular and subangular blocky units. Roots follow mainly worm tracks. Clear and wavy boundary.
- A_{2g}/B_1 45--70 $60 \% A_{2g}$ -material + 40 % B_1 -material. A_{2g} -material: very pale brown (10 YR 7/4:d) -- yellowish brown (10 YR 5/4:m) silt, spongy. Common, very fine biopores. Friable. B_1 -material: brown (7.5 YR 5/2:d) -- dark brown (7.5 YR 4/2:m) silt loam. Firm. Very fine subangular blocky and moderate, thick platy. Few, very fine biopores. On the blocky peds white silt coatings and distinct, thin, dark yellowish brown clay coatings occur. The white coatings occur sometimes on the clay skins. Sometimes also white spots in the peds. Common, fine, distinct, black Fe/Mn-mottles and few, fine, faint, yellowish red (5 YR 5/8:m) Fe mottles in and common, medium, distinct, yellowish red (5 YR 4/6:m) Fe-mottles on the peds. Wormtracks as in A₂. Clear and irregular boundary.
- **B**_{1g}/**B**_{2t} 70–105 40 % **B**_{1g}-material and 60 % **B**_{2t}-material. **B**_{1g}-material: Light grey (10 YR 7^{1/2}/1:m) silt loam located as tongues in the **B**_{2t}-horizon. The tongues are vertical sections of a polygonal system of cracks or sometimes isolated rootholes. They reach a depth of 80 cm, starting in the **B**_{1g} with a width of 8 cm and discontinuously penetrating into the **B**₃; along the tongues a 1 cm wide yellowish red (5 YR 4/8) band occurs. In the tongues animal burrows are found filled with lighter coloured material. **B**_{2t}-material: light brown (7.5 YR 6/4:d) — dark brown (7.5 YR 4/3:m) silt loam. Compound weak prismatic structure breaking into moderate to strong, medium subangular blocks. Firm, Common to many, very fine biopores. Common, thin, prominent, dark brown clay coatings with occasionally light coloured silt. Few, fine, distinct, dark manganese mottles and few, fine, distinct, yellowish red (5 YR 4/6:m) iron mottles. The white coloured silt also occurs in the biopores. Wormtracks as in A₂.
- B₃ 105—145 Yellowish brown (10 YR 5/4:d) dark yellowish brown (10 YR 4/4:m) silt loam. Very weak, medium prismatic structure. Firm. Many, very fine biopores. Some distinct, thin, dark brown (7.5 YR 4/3:m) clay skins on peds. Also some coatings of light coloured silty material. Few, fine, yellowish red mottles. Few wormtracks, coated with brown (7.5 YR 5/2:m) material.
- C + 145 Very pale brown (10 YR 7/4:d) yellowish brown (10 YR 5/4:m) silt loam. Friable. Sponge structure with many fine biopores.

Remarks: Roots are strongly concentrated in the surface soil. In the subsoil they show preference for wormtracks.

Biopores: size: very fine: < 1 mm; few: $0-5/cm^2$, common $5-10/cm^2$, many $10-15/cm^2$.



Fig. 1 Schematical representation of the pedon.

A schematical and idealized picture of the profile is shown in Fig. 1. On this figure the places are shown where the samples for physical and chemical analyses and for micromorphological studies were taken. Moreover, coatings of the B_{2t} and B_3 horizon were sampled.

3 Methods

Large thin sections (8 \times 15 cm; see Jongerius and Heintzberger, 1963) have been prepared from undisturbed representative samples as indicated above. Descriptions have been according to the terminology, developed by Brewer (1964). Some characteristic features are made measured quantitatively by applying point-count techniques (see also Brewer, 1964). For each value, given in Figures 2, 3, 4, 1500 points have been counted, resulting in values to be read as ± 1 % (K = 1,96; confidence limits 95 %). The magnification used (125 X) resulted in a distance between successive points in the grid, that is larger than the size of the object to be counted (van der Plas and Toby, 1965).

The samples for the physical and chemical analyses passed the 2 mm sieve. The fine-earth material was analyzed with respect to: grain-size distribution, carbon, pH, c.e.c., exchangeable cations, 'free iron', total SiO₂, Fe₂O₃, Al₂O₃, TiO₂, MnO, CaO and MgO. The coatings were only analyzed with respect to total SiO₂, Fe₂O₃, Al₂O₃, TiO₂, CaO, MgO and carbon.

For the mechanical analysis the pipette method was used, whilst the suspension was 0.003 M with respect to Na₄P₂O₇. The sand fraction (> 50 μ) was sieved in a dry state and subdivided according to the american system.

pH was determined in 1:2.5 suspension in water and 0.01 M CaCl₂-solution (Schofield and Taylor, 1955).

Carbon was determined by oxidation with chromic acid (Allison, 1935) and the concentration of the green Cr^3 +-ions determined colorimetrically at a wavelength of 585 nm.

The cation exchange characteristics were determined according to Yaalon, van Schuylenborgh and Slager (1963). Na+ and K+ were estimated flame-photometrically according to the 'Kurvenschar'-method of Schuhknecht (1961). Ca²⁺ and Mg²⁺ were determined as outlined below. Exchangeable Al and H were determined by extraction with 1 N KCl (Jackson, 1958); in this extract Al was estimated colorimetrically with pyrocatechol violet (Wilson and Sergeant, 1963), whilst Al + H was titrated with standard NaOH-solution. The difference is then exchangeable H.

'Free iron' was determined as outlined by Jackson (1958), iron being estimated colorimetrically with O-phenanthroline (Sandell, 1959).

Silica was determined by fusing the soil with anhydrous soda, dissolving the melt in dilute HCl and estimation of silicium as β -silicomolybdenic acid (Morrison and Wilson, 1963).

The other oxides were estimated in a solution obtained by destructing the material with hydro-

fluoric acid and sulfuric acid. Fe_2O_3 was estimated as the phenanthroline-complex (see 'free iron'), Al_2O_3 with pyrocatechol violet, TiO_2 with tiron according to a somewhat modified method reported by Sandell (1959), MnO as the formaldoxime complex (Schuffelen et al., 1961), CaO as the glyoxal bis (2-hydroxyanil) complex (Peaslee, 1964), and MgO as the red lake formed with titan yellow (Meyrowitz, 1964; van Schouwenburg, 1965).

4 Results

4.1 The occurrence of oriented clay bodies

The clear difference in clay content between the A_2 and B_{2t} is generally attributed to movement of clay minerals as a result of pedogenic processes (Brewer and Haldane, 1957; Buol and Hole, 1959, 1961; Kundler, 1961; Minishina, 1958; Schlichting and Blume, 1961; Soil Survey Staff, 1960, 1967). In the B_{2^3} , clay coatings (argillans) are found along the walls of pores in which birefringent clay minerals are oriented parallel to each other and to the walls. The determination of this orientation as well as the genesis is described elsewhere (Brewer, 1964; see further above). Apart from the occurrence along the walls of larger pores and on ped faces, oriented clay is also found as glaebules in the s-matrix and as cutans in the simple packing voids. Consequently the following types of oriented clay bodies could be distinguished (Fig. 2): 1) Very fine free grain argillans (oriented clay skins around silt sized mineral particles in capillary voids), strongly separated with a sharp boundary (1, Fig. 2).

2) Fine channel and ped illuviation argillans, strongly separated and with a sharp boundary (2, Fig. 2) (oriented clay skins on ped faces and in biopores).

3) Fine papules (aggregates of oriented clay inclosed within soil material and not observed to border on a pore or void), equant to prolate, with sharp irregularly rounded boundaries (3, Fig. 2).

When no distinctions have been made only the total amount is recorded (4, Fig. 2).

4.2 The occurrence of Fe-Mn nodules

The following distinctions have been made in the mottles and spots as mentioned in the profile description (see Fig. 3):



Fig. 2 The occurrence of oriented clay bodies.

Fig. 3 The occurrence of Fe-Mn nodules.



1) coarse Fe-Mn nodules with recognizable soil fabric, equant to prolate, with sharp boundary (1, Fig. 3);

2) like 1) but with rather diffuse boundary (2, Fig. 3).

4.3 The chemical characteristics of the profile

The chemical analyses have been laid down in Tables 1, 2, 3 and 4. Table 1 shows - clearly an illuviation of clay, a high base saturation although Al has already appeared in the exchange complex, an accumulation of dithionite-extractable iron and an inconstancy of the clay/free iron ratio, indicating that the iron translocation is not entirely bound to the clay translocation.

Tables 2 and 3 show the partial chemical compositions and molar ratios of the different soil horizons and their clay separates. From these tables can be concluded that we have to do here with a normal podzolic type of soil formation (see also: van Schuylenborgh, 1962, 1966; van Schuylenborgh and Bruggenwert, 1965). The composition of the clay fraction is rather constant, although a maximum Fe₂O₃-content can be noticed in the B_{2t} -horizon and the Al₂O₃ content decreases with depth. The trend in the SiO₂/Al₂O₃ ratio of the clay separates indicates an accumulation of alumina relative to silica. On the other hand, the Al₂O₃-content of the horizons increases with depth. These facts could be explained by assuming that weathering at some depths results in the formation of Al-poor clay minerals, whilst the free Al-hydroxides are subjective to the normal leaching, which is inherent to the podzolization process. The behaviour of iron as well is quite normal with respect to the podzolic type of soil formation.

The constitution of the tongues (see description soil profile and Fig. 1), which are formed after the formation of the Grey Brown Podzolic Soil profile (see later), differs strongly from the horizons in which they are formed. Table 4 summarizes the chemical and physical characteristics of the tongue-material. When comparing the data with those of Tables 1, 2 and 3 it appears, that the grain-size distribution and organic matter content of the tongue-material situated in the B₁-horizon is very similar to that of the A₂-material. However, especially the Fe₂O₃- and MnO-content of the tongue-material in the B₁ is lower than those of the A₂-horizon. This indicates that a reduction-process is involved in the formation of the tongues; this is the more likely, as the yellowish-red band occurring along the tongues, show an accumulation

Hor.	Grain size distri- bution			pH		C %	Catio	ion exchange characteristics (m.e./100 g)				(100 g)	'free iron'	clay/ free iron
	>50 µ %	50–2 µ %	<2 µ %	H_2O	0.01M CaCl ₂		Ca	Mg	K	Na	Al + H	<i>c.e.c.</i>		
Ap	10.2	78.7	11.2	6.7	5.9	1.8	3.4	0.3	0.6	0.2	0.3	5.1	1.0	11.2
A2 B1	4.8	87.2 79.5	5.5 15.7	6.3	5.4 5.9	0.7	5.5 6.4	0.5	0.4	0.2	0.5	4.7 7.3	1.0	9.2
\mathbf{B}_{2t}	8.5	74.2	19.3	5.9	5.1	0.3	6.5	0.8	0.1	0.2	0.7	8.5	1.8	10.7
B ₃	6.4	76.2	17.4	6.1	5.6	0.2	6.9	0.6	0.1	0.2	0.3	7.9	1.7	10.2
C	13.2	77.5	9.3	6.0	5.6	0.1	3.1	0.5	0.1	0.1	0.3	4.9	1.3	7.1

Table 1 Grain size distribution, pH, org. C and 'cation exchange characteristics'

Table 2 Partial chemical composition of the horizons and the clay separates in percentages of dry matter

 Material	SiO2	Fe_2O_3	Al_2O_3	TiO ₂	MnO	CaO	MgO
Ap horizon	80.3	2.3	6.7	0.6	0.08	0.5	0.3
clay separate	46.3	10.8	20.3	1.2	0.10	n.d.	n.d.
A2 horizon	81.6	2.6	7.0	0.6	0.08	0.5	0.4
clay separate	46.0	12.0	20.6	1.2	0.10	n.d.	n.d.
B ₁ horizon	80.5	2.9	8.3	0.7	0.12	0.4	0.6
clay separate	45.4	12.1	19.5	1.0	0.08	n.d.	n.d.
B _{2t} horizon	77.6	3.9	9.0	0.7	0.08	0.5	0.6
clay separate	46.9	13.4	18.8	0.8	0.06	n.d.	n.d.
B₃ horizon	75.5	3.5	9.1	0.6	0.07	0.6	0.6
clay separate	45.6	12.8	18.2	0.8	0.05	п.d.	n.d.
C horizon	81.3	2.8	7.2	0.7	0.06	0.6	0.4
clay separate	46.1	11.5	17.4	0.9	0.04	n.d.	n.d.

Table 3 Molar-ratios in the horizons and their clay separates

Material	SiO_2/R_2O_3	SiO_2/Al_2O_3	SiO_2/Fe_2O_3	Al_2O_3/Fe_2O_3
Ap horizon	17	21	96	4.1
clay separate	2.9	3.9	12	3.0
A2 horizon	16	20	85	4.2
clay separate	2.8	3.8	10	2.7
B1 horizon	14	17	75	4.5
clay separate	2.8	4.0	10	2.5
B₂thorizon	12	15	54	3.7
clay separate	2.9	4.3	9.3	2.2
B ₃ horizon	11	14	57	4.1
clay separate	2.9	4.3	9.5	2.2
C horizon	16	19	80	4.1
clay separate	3.2	4.5	11	2.4

Number		Grain size distri- bution (%)			Į.	ρH	С %	Free iron
		< 2 µ	>50 µ	50–2 µ	H_2O	0.01M CaCl₂		10
1 2	tongue-material in \mathbf{B}_1 clay separate	9.0	83.4	7.6	5.6	5.1	0.7 n.d.	0.6 n.d.
3 4	tongue-material in B _{2t} clay separate	3.7	80.7	15.6	6.4	6.0	0.2 n.d.	0.7 n.d.
5 6	yellowish-red band along tongues clay separate	n.d.	n.d.	n.d.	5.3	4.9	0.2	2.6

Table 4 Composition of the tongue-material at various depths in the profile

Number	Elemental analysis (%)							Molar ratios			
	SiO2	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	MnO	CaO	MgO	SiO2	SiO2	SiO2	Al_2O_3
								R_2O_3	Al ₂ O ₃	Fe ₂ O ₃	Fe_2O_3
1	80.7	1.4	6.1	0.7	0.06	0.4	0.2	20	23	149	6.5
2	47.9	8.5	20.5	1.4	0.06	n.d.	n.d.	3.1	4.0	15	3.8
3	80.4	2.6	8.4	0.7	0.04	0.7	0.5	14	16	84	5.1
4	45.0	8.5	18.8	0.8	tr.	n.d.	n.d.	3.2	4.1	14	3.5
5	77.3	4.7	8.6	0.7	0.10	0.6	0.5	11	15	44	2.9
6	44.8	14.8	18.5	0.7	0.09	n.d.	n.d.	2.7	4.1	8.0	1.9

of iron and manganese, whereas its pH-value is lower, which indicates an oxidationprocess to have been taken place in the surroundings of the tongues. The same can be stated with respect to iron and manganese about the tongue-material situated in the B_{2t} -horizon. Therefore we have indicated the tongue-material in the B_1 as A_{2g} and that in the B_{2t} -horizon as B_{1g} , as the latter has a granulometric composition entirely similar to that of the B_1 -horizon (compare Table 4 with Table 1). The yellowish-red bands seem to have also accumulated clay, as the cation-exchange capacity is much larger than that of tongue-material, viz. 7.7 and 3.7 m.e./100 g, respectively.

The clay-fractions of the tongue-material and of the bands are similar with respect to the molar SiO_2/Al_2O_3 ratio, indicating that no decomposition of clay is involved in the process.

More about the formation of the tongues will be reported later (5.2).

5 Discussion

5.1 The process of clay illuviation

If the increase of clay content in the B-horizon is fully attributed to illuviation, the highest content of oriented clays would have been found in the horizon with the highest clay content (B_{2t}). Fig. 2, however, shows the highest content of oriented clays to be present in the B₃-horizon, whereas the B_{2t} has the highest clay content (Table 1). Fig. 2 shows furthermore that a) the share of channel and ped argillans in the total

content of oriented clays increases in the sequence $B_2 \rightarrow B_3$; b) the share of papules decreases in the same sequence.

We believe that these phenomena can partly be attributed to faunal activity in the upper part of the profile. As a result some argillans are mixed through the s-matrix with the subsequent appearance of papules; some argillans can have been destroyed even. To illustrate this faunal activity the larger voids have also been counted (Fig. 4).



Fig. 4 Voids larger than 40 μ .

We distinguish:

1) channels (biopores, cross sectional size > 150μ);

2) pedotubules (animal burrows with various cross sectional sizes up to 2 mm, filled with excrements);

3) vughs (irregular voids with welded walls).

It appears that in the upper part of the profile a larger part of the pore space is occupied by these voids than in the lower part. Only here aggrotubules are found decreasing in volume with depth. Compound packing voids are present between the excrements in these burrows. They are not found in the B_3 -horizon. However, the clay content of the B_{2t} -horizon is larger than can be accounted for by calculating the amount of clay disappeared from the A-horizon, assuming a parent material of uniform composition and absence of erosion.

It has to be concluded that in the B_{2t} -horizon clay has been formed by weathering processes (see: Scheffer, Meyer and Gebhart, 1966), which confirms the results of the chemical analyses (4.3). The clay particles formed in this way are not necessarily well-oriented to each other. This is indicated by the fact that in the C-horizon no free grain argillans are found; only very thin (5 μ) accumulations of weakly oriented clay occur around the skeletan grains. The considerable content of free grain argillans in the B-horizons indicate a domination of transport over short distances and sedimentation processes in voids of capillary size.

The clay composition indicates that the silicate part is not strongly weathered in the upper horizons, so that the greater content in the B-horizon cannot be attributed to the destruction of the clay in the A-horizons. The analysis of the clay coatings of the B_{2t} and B_{3} -horizon revealed that the C-content was respectively 0.3 and 1.1%.

This indicates that there is primarily a translocation of clay as a clay-humus-complex (see also: de Coninck, 1967).

5.2 The process of tongue-formation

To our opinion the tongue-formation is a normal continuation of the process of clay illuviation in Grey Brown Podzolic Soils under humid climates and normal water infiltration. The continuous clay illuviation and the formation of clay in situ lead to a moment on which the clay content of the B-horizon has become so high that polygonal cracks can be formed during dry periods. (It is imaginable that such cracks can also be formed by e.g. a climatic change introducing a different type of vegetation with a higher transpirational capacity). With considerable rainfall the cracks will function as water leads. Upon this wetting, the material swells and a reductional environment is created in the zone along the cracks. The reduction state is strongly enhanced by the fact that the cracks are preferably used as rooting channels; part of the roots die upon water saturation and oxygen is used for the destruction of the organic material. Then iron and manganese can be reduced. The reduction depends on the form in which Fe and Mn are present; some of the possible redox-couples are listed below:

$$\begin{aligned} & \text{Fe}(\text{OH})_{3} \ (a,s) + 3\text{H}^{+} + e \rightleftharpoons Fe^{2+} + 3\text{H}_{2}\text{O} & (1) \\ & (a = \text{amorphous}; s = \text{solid}) \\ & \text{E}_{b1} = \text{E}_{1}^{0} - 0.059 \ \text{lg} \ [\text{Fe}^{2+}] - 0.177 \ \text{pH}; \\ & \text{E}_{1}^{0} = 1.057 \ \text{V} \\ & (\text{see appendix: a)} & (1a) \\ & (\text{E}_{h} = \text{redox-potential}; \\ & \text{E}_{1}^{0} = \text{standard reduction potential}; \\ & [] \text{ means activity}) \\ & & \omega \text{-FeOOH} \ (s) + 3\text{H}^{+} + e \overleftrightarrow \text{Fe}^{2+} + 2\text{H}_{2}\text{O} & (2) \\ & \text{goethite} & (2) \\ & \text{goethite} & (2) \\ & \text{goethite} & (2) \\ & \text{E}_{h2} = \text{E}_{2}^{0} - 0.059 \ \text{lg} \ [\text{Fe}^{2+}] - 0.177 \ \text{pH}; \\ & \text{E}_{2}^{0} = 1.005 \ \text{V} \\ & (\text{see appendix: b)} & (2a) \\ & \text{Fe}_{3}\text{O}_{4} \ (s) + 8\text{H}^{+} + 2e \overleftrightarrow \text{3Fe}^{2+} + 4\text{H}_{2}\text{O} & (3) \\ & \text{magnetite} & (2a) \\ & \text{E}_{h3} = \text{E}_{3}^{0} - 0.089 \ \text{lg} \ [\text{Fe}^{2+}] - 0.236 \ \text{pH}; \\ & \text{E}_{3}^{0} = 0.982 \ \text{V} \\ & (\text{see appendix: c)} & (3a) \\ & \text{MnO}_{2} \ (s) + 4\text{H}^{+} + 2e \overleftrightarrow \text{Mn}^{2+} + 2\text{H}_{2}\text{O} & (4) \\ & \text{pyrolusite} \\ & \text{E}_{h4} = \text{E}_{4}^{0} - 0.030 \ \text{lg} \ [\text{Mn}^{2+}] - 0.118 \ \text{pH}; \\ & \text{E}_{9}^{4} = 1.208 \ \text{V} \ (\text{Weast, 1966)} & (4a) \\ & \gamma \text{-MnOOH} + 3\text{H}^{+} + e \overleftrightarrow \text{Mn}^{2+} + 2\text{H}_{2}\text{O} & (5) \\ & \text{manganite} \\ & \text{E}_{h5} = \text{E}_{5}^{0} - 0.059 \ \text{lg} \ [\text{Mn}^{2+}] - 0.177 \ \text{pH}; \\ & \text{E}_{5}^{0} = 1.495 \ \text{V} \\ & (\text{see appendix: d)} & (5a) \\ & \text{Finally, always the } \text{H}_{2}\text{O}/\text{O}_{2}\text{-couple is present in the soil:} \\ & \text{O}_{2} + 4\text{H}^{+} + 4e \swarrow 2\text{H}_{2}\text{O} & (6) \\ & \text{E}_{h6} = \text{E}_{6}^{0} + 0.015 \ \text{lg}_{Q}\text{O}^{2} - 0.059 \ \text{pH}; \\ & \text{E}_{6}^{0} = 1.229 \ \text{V} \ (\text{Weast, 1966)} & (6a) \\ & \text{(5a)} \\ \end{array}$$

The electrons needed for the reduction are delivered by the oxidation of another component in the soil. Generally this is an organic acid. As a modell substance we shall use protocatechnic acid, because this is actually shown to be present in the soil organic matter fraction as decomposition product of lignin and because the oxidized form is reasonably stable:



+ $2H^+$ + 2e, or, as it behaves also as an acid:

where Red3- represents the radical

 $\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{array} \quad \text{and } 0x - \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{array} \right)$

(7)

For (7) we have:

 $E_{h7} = E_{7^0} + 0.030 \text{ lg } \frac{[\text{ox}]}{[\text{red}]} + 0.030 \text{ lg } \alpha_{\text{H}}; E_{7^0} = 0.084 \text{ V}$ (Ball and Chen, 1933) (7a)

where [ox] = [HOx] + [Ox⁻], $[red] = [H_3Red] + [H_2Red⁻] + [HRed²-] + [Red³-] and <math>\alpha_H$ is equal to the expression mentioned in the appendix (e).

To decide whether or not reactions (1) to (6) proceed to the right side under the influence of a sufficient amount of protocatechnic acid, we have to prepare a Voltacell of half-cell (7) with the half-cells (1) to (6). For the combination (7) and (1) this gives:

$$2Fe(OH)_{3} (a,s) + Red^{3-} + 6H^{+} \xrightarrow{} 2Fe^{2+} + Ox^{-} + 6H_{2}O$$
(1,7)
$$K_{1,7} = \frac{[ox] \ [Fe^{2+}]^{2}}{[red] \ [H^{+}]^{6}}$$

At a given pH value $K_{1,7}$ can be calculated from the combination of (1a) and (7a) (see appendix: f). The logarithm of $K_{1,7}$ appeared to be: 17.8 at pH 6. In the same way $K_{2,7}$, $K_{3,7}$, $K_{4,7}$, $K_{5,7}$ and $K_{6,7}$ can be calculated. At pH 6 the logarithms are, respectively: 16.1, 15.3, 22.8, 32.4 and 47.1 (all values for a temperature of 25 °C and 1 atmosphere total pressure). This means that all reactions will proceed to the right side and that oxygen is reduced by protocatechuic acid firstly, followed by the two forms of manganese and finally by the different forms of iron. Inversely, we can state that upon entry of air the ferrous-iron will be oxidized at lower partial oxygen pressures than manganous ions. This is the reason why the layer immediately bordering the tongues does not contain manganese concretions, whereas at some distance these concretions and mottles can be found. The consequence of the oxygenpotential difference from the cracks into the aggregates is also the fact that the Fe-Mn mottles have diffuse boundaries, if they are formed in situ in a recognizable soil fabric. Also nodules with sharp boundaries (Fig. 3) are found in horizons A_2 and B_1 ; we think that these result from the transportation over short distances as a result of faunal activity (see: 4.2).

5.3 The classification

In 4.3 we found that the tongue-part occurring in the B_1 -horizon has the composition of the A_2 -material, whilst the part occurring in the B_{2t} -horizon has the composition of the B_1 -horizon. This was confirmed by micromorphological analysis. The sample from the tongue deep in the B_{2t} -horizon contains a considerable amount of oriented clay bodies; the sample from the tongue material from the B_1 -horizon contains only a negligible amount. Therefore, it seems as if soil formation has proceeded to a more advanced stage along the cracks, which is understandable as those cracks function as water leads. This is possibly also the reason why the yellowish-red bands along the tongues have a high content of oriented clays (see Fig. 2): the soil solution containing some dispersed clay and moving downwards through the relatively permeable tongues, is sucked into the relatively dry B_{2t} -horizon. Upon drying oriented clay is deposited along the borders of the tongues.

It can be concluded that the tongues are not completely filled with A_2 -material and that we cannot speak of a tonguing of the albic horizon (i.c. A_2 -material) into the B_2 -horizon.

Furthermore ped faces can be found covered with a white dust especially in the tongues, but also in the B-horizons themselves; this white dust is composed of clear skeleton grains (discontinuous skeletans; Brewer, 1964). All these observations imply an ever deeper leaching of the clay, a process that is most pronounced along voids conducting water (Am. Soil Survey Staff, 1967).

Taking all these facts into consideration we classify this soil as an Aquic Glossudalf.

Appendix

a) The standard redox potential of reaction (1) can only be calculated if the standard free-energy of formation of amorphous iron hydroxide is known. Garrels and Christ (1965) report a value of -166.0 kcal/mol at 25 °C and 1 atmosphere pressure. For reaction (1) we have then:

b) Biedermann and Schindler (1957) gave for the equilibrium reaction:

 $Fe^{3}+ + 2H_2O \longrightarrow FeOOH (s) + 3H+$

an equilibrium constant of $10^{-3.96}$. From this we can calculate the standard free-energy of reaction: $\bigwedge F^{0}{}_{r}$ = -1.364~lg~K

 $= 1.364 \times 3.96 = 5.4$ kcal.

It is then possible to calculate the standard free-energy of formation of a-FeOOH:

Reaction (2) gives then:

$$E^{0}_{2} = -\frac{\triangle F^{0}_{r}}{nF} = \frac{23.2}{23.1} = 1.005 V$$

c) Reaction (3) gives:

$$\begin{split} & \bigtriangleup F^0{}_r \,=\, 3 \,\bigtriangleup F^0{}_{fFe}{}^{2+} \,+\, 4 \,\bigtriangleup F^0{}_{fH_2O} \,-\, \bigtriangleup F^0{}_{fFe_3O_4} \\ & = -3 \,\times\, 20.3 \,-\, 4 \,\times\, 56.7 \,+\, 242.4 \,=\, -45.3 \,\, \text{kcal at } 25 \,\, ^\circ\text{C} \,\, \text{and} \,\, 1 \,\, \text{atm.} \\ & E^0{}_3 = - \,\, \frac{\bigtriangleup F^0{}_r}{nF} \,\, \frac{45.3}{2 \,\times\, 23.1} = \, 0.982 \,\, \text{V} \end{split}$$

d) Reaction (5) gives:

All values for standard free-energies of formation were taken from Garrels and Christ (1965).

e) If it is supposed that the dissociation constant of the oxidized acid is equal to he first dissociation constant of the reduced acid, the expression for α_H is:

$$\alpha_{\rm H} = \frac{[{\rm H}^+]^3 + [{\rm H}^+]^2 {\rm K}_{a1} + [{\rm H}^+] {\rm K}_{a1} {\rm K}_{a2} + {\rm K}_{a1} {\rm K}_{a2} {\rm K}_{a3}}{{\rm K}_{a1} + [{\rm H}^+]}$$

where K_{a1} , K_{a2} and K_{a3} are the first, second and third dissociation constant of protocatechuic acid, respectively. Own determinations gave the following values for the negative logarithms:

 $pK_{a1} = 4.49 \pm 0.00$; $pK_{a2} = 9.13 \pm 0.01$; $pK_{a3} = 11.32 \pm 0.05$ at 25 °C. This means that $\alpha_{H} = 10^{-12}$ at pH 6, 10^{-10} at pH 5 and 10^{-8} at pH 4. f) For reaction (1,7) we can state, that at equilibrium:

 $1.057 - 0.177 \text{ pH} - 0.059 \text{ lg} [Fe^2+] = 0.884 + 0.030 \text{ lg} \frac{[\text{ox}]}{[\text{red}]} + 0.030 \text{ lg} \alpha_{\text{H}}$

Rearranging we obtain:

 $lg \frac{[\text{ox}] [\text{Fe}^2+]^2}{[\text{red}] [\text{H}+)^6} = \frac{0.173}{0.030} - lg \ \alpha_{\text{H}} = 5.8 - lg \ \alpha_{\text{H}} \text{ or, according to p. 67: } lg \ K_{1,7} = 5.8 - lg \ \alpha_{\text{H}}$ At pH 6, we have: $lg \ K_{1,7} = 5.8 + 12 = 17.8$.

In a similar way it is possible to compute $K_{2,7}$, $K_{3,7}$, $K_{4,7}$, $K_{5,7}$ and $K_{6,7}$.

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