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Recent and Paleo-Pedogenesis as Tools for Modelling past and future Global Change

Excursion C:
Deep weathering mantles of Upper Cretaceous and Tertiary periods in the Rhenish Massiv and the Vogelsberg area

(P. Felix-Henningsen)

September 21 - 27, 1997

Rauischholzhausen
Castle

Preface

Soils and soil characteristics give evidence of the development and chronological change of landscapes, according to their relationship to the soil forming factors. The relatively stable soil characteristics, such as the neoformed soil minerals, preserve important information over long periods. This is of special interest for the soil genetical and geo-scientifical interpretation of soils in old lands, in which soil formation over periods of several million of years led to thick polycyclic and polygenetic weathering mantles. The Rhenish Massif represents such an old land, which has existed for about 200 mio. years. Here a partly up to 150 m thick weathering mantle is still preserved. Kaolinite is a mineralogically key indicator in saprolites, paleosols as well as recent soils, which developed from old weathering products. Because kaolinite is not formed under the moderate humid climatic conditions in recent soils of this area, it indicates subtropical to tropical, warm humid climatic phases of the Upper Cretaceous and the Tertiary. Additional hydrothermally altered rocks with a diagenetic neo-formation of kaolinite locally occur in areas of the Tertiary and Quaternary volcanism. Today the autochthonous saprolite as well as the sedimentary kaolins display valuable deposits in the Rhenish Massif. Recent soils from old, kaolinitic weathering products display bad site properties, caused by lack of nutrients, low buffer capacity and water logging due to high bulk density. Therefore geologists, geomorphologists, agronomists and soil scientists are interested in kaolinic weathering products of the Rhenish Massif. The preparation of this excursion guide was undertaken by *V. Feußner-Stolz, M. Szibalski, A. Kollender-Szych, M. Schotte, T. Scholten* and *G. Werner* with great enthusiasm. All native English speakers will bear with us the occasional "German English" contained in the guide.

Gießen, September 1997 P. Felix-Henningsen

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Part I:

Red Paleosol out of Volcanites near Lich in the Anterior Vogelsberg

Red Paleosol out of volcanites near Lich in the Anterior Vogelsberg

(*E. Schönhals, 1986*)

Location:	2.5 km east of Lich, quarry „Eiserne Hose“ (iron pants)
Relief:	Weakly inclined plain toward the west, 185 m a. s. l.
Geology:	Volcanism of the Upper Miocene (basalt, basalt tuff)
Climatic data:	Precipitation: 620 mm about 9 °C mean annual temperature about -1 to 0 °C mean temperature in January 17 to 18 °C mean temperature in July 230 to 240 days period of vegetation (mean dayly temp. above 5°C)
Potential natural vegetation:	Melico-Fagetum (Luzulo-Fagetum) in colline stage
Soil formation:	Intensive weathering in tropical/subtropical climate during the Miocene and Pliocene, development of Plastosols and Latosols; during Pleistoceme destruction of Paleosols by erosion and solifluction
Soil asociation:	Wide patches of Red Plastosols, Red Latosols; Cambisols out of solifluction layers with varying content of loess loam over basalt; Rankers in knoll areas; Stagnic Gleysols in hollows
Land use:	Former bauxite mine, cultivated land in surrounding areas (mostly cereal crops and corn)

Description of soil profile:

Ah	0-8 cm	Dusky red (10 YR 3/4), humus, slightly clayey loam, pebbly-stony, pebbly-stony, crumb to subpolyhedric structure, packing density: low indistinct transition to
Ah Bj	8-30 cm	Dusky red (10 R 3/6), slightly humus loamy clay, strongly pebbly stony, subpolyhedric structure, packing density: low, well rooted, gradual transition to
Bj 1	30-70 cm	Dark red (2.5 YR 3/6), loamy clay, strongly pebbly-stony, prismatic structure degrading into subpoly-hedric stucture, packing density: medium, well rooted, gradual transition to
Bj 2	70-120 cm	Dusky red (10 YR 3/6), clayey loam, pebbly-stony, prismatic structure, packing density: high, gradual transition to
Bj 3	120-140 cm	Dark red (2.5 YR 3/6), clayley loam to loamy clay, strongly pebbly-stony, packing density: high to very high, gradual transition to
Bj 4	140- 180 cm+	Dark red (2.5 YR 3/6), clayley loam, strongly pebbly-stony, packing density: high to very high
II BjCr*		Red (2.5 YR 4/8), Basaltzersatz
II Cv*		Grey (10 YR 5/1), Basaltzersatz

Interpretation

The sequence of horizons given in the description is merely to a little extend the result of younger soil processes. Some agricultural influence is to be mentioned. According to the admixture of loess born material, the upper 70 cm of the profile appears as a younger cover sediment, which is in several place of the open cut also marked by a stone line. The grain size analysis contributes not much to this point because of the uncontrolled dispersion and „pseudo sand" formation of the iron rich material during the laboratory treatment. Thin sections give clear evidence of the loess components.

The following red material, down to a thickness of several meters consists of solifluction debris of Pliocene paleosols. The stones, mixed in nearly allover are nodules of gibbsite which normally preserve basaltic rock fabrics. The microsopic features of the red solum are manifold. They make evident the origin of the material as a weathering product of basaltic rock or tuff. More information, however, is to be found at the transition of red clay-loam into an unterlying basaltic saprolite of light gray colour. This part is discovered at the southern edge of the quarry.

Recognizeable units in the saprolite are chiefly iddingsite pseudomorphs after olivine, rim-formations according to pre existing pyroxene aggregates, and pseudomorphs of whitish clay after plagioclase feldspars. Solely the ore component, predominantly ilmenite and some magnetite, is present in unaltered condition. From this an alkaline-olivine-basaltic rock may be reconstructed as parent material.

According to ALTEMÜLLER & POETSCH (1984), a feature of general importance is the weathering of ilmenite into red iron oxides and uncoloured titanium oxides at the transition inot the red clay-loam. In thin sections under the microscope all stages of transformation are clearly observable, making evident that the red material in contact with the saprolite is a formation in place.

A continuous breakdown of the pseudomorphic clay fabric after plagioclase mineral patterns creates the higher density of the red clay-loam and also contributes to the noticeable translocation of reddish fine clay along cleavage planes in the saprolite. Clay material of the coatings consists mainly of kaolinite and halloysite and resemble so far the whitish clay matrix of the saprolite. The main difference is based on the content of fine dispersed iron oxides.

Profile 'Eiserne Hose', Lich

Horizon	Depth	Code	Stones	Particle size analysis [wt.-% of organic matter free dispersible fine earth]							
	[cm]		[wt.-%]	c Sand	m Sand	f Sand	c Silt	m Silt	f Silt	Clay	Texture
Ah	0-8	2.1.1		3.6	10.8	9.7	16.1	16.3	9.9	33.5	
AhBj	8-30	2.1.2		5.2	8.2	8.3	12.0	10.8	9.5	46.1	
Bj1	30-70	2.1.3		4.5	6.6	8.5	12.2	11.0	9.4	48.0	
Bj2	70-120	2.1A.1		7.7	8.4	9.1	12.1	11.2	.12.3	39.1	
Bj3	120-140	2.1B.1		5.7	6.4	8.5	12.1	11.1	11.7	44.6	
Bj4	140-180	2.1C.1		6.0	6.6	9.1	12.7	11.9	10.7	43.2	
IIBjCv	180-250	2.1D.1		3.4	14.0	32.7	22.1	10.5	5.7	11.6	
Cv	250+	2.1D.2		1.8	12.0	37.1	22.1	12.0	7.7	7.3	

Horizon	BD	Ks	K-fac	Water retention analysis [vol.-% water content]				PV			
	[g/cm3]	[cm/d]	[(t*h)/(mm*h	pF 0,0	pF 1,8	pF 2,5	pF 4,2	[Vol.-%]			
Ah											
AhBj	1.45				37.0	34.8	25.8	48.7			
Bj1	1.42				43.1	39.3	36.8	49.5			
Bj2	1.47				42.1	38.6	35.5	47.8			
Bj3											
Bj4											
IIBjCv	1.17				51.0	48.6	34.0	59.2			
Cv	1.19				49.7	47.4	35.8	58.7			

Horizon	pH		Corg	Nt	C/N	Fe(DCB)	Fe(AO)	Fe	Mn(DCB)		
	(H2O)	(CaCl)	[wt.-%]	[mg/g]		[mg/g]	[mg/g]	(AO/DCB)	[mg/g]		
Ah	5.7	5.0	1.43	1.23	11.6	85.2	2.7	0.03	1.1		
AhBj	6.1	5.6	0.84	1.01	8.3	104.0	2.4	0.02	0.5		
Bj1	6.2	5.7	0.68	0.80	8.5	116.9	2.5	0.02	0.4		
Bj2	5.2	4.9	0.30	0.51		139.0	2.7	0.02	0.3		
Bj3	5.2	4.9	0.30	0.21		142.7	2.6	0.02	0.3		
Bj4	5.1	4.9	0.32	0.45		146.8	2.5	0.02	0.3		
IIBjCv	5.5	4.8	0.10	0.28		74.9	1.5	0.02	0.8		
Cv	5.9	5.5	0.09	0.26		76.3	1.7	0.02	1.1		

Horizon	Cation exchange analysis [cmolc/kg]								BS	
	Ca	Mg	K	Na	Al	H + Al	ECEC	CEC	[% CEC]	
Ah	5.7	0.9	0.40	0.02	0.4	10.3	8.9	17.5	40	
AhBj	6.7	1.7	0.16	0.04	nn	8.9	11.1	17.7	48	
Bj1	6.6	1.9	0.10	0.05	nn	8.0	10.2	17.1	51	
Bj2	2.6	0.9	0.04	0.07	nn	8.7	4.8	13.0	28	
Bj3	2.7	1.0	0.05	0.09	nn	8.8	5.2	13.0	30	
Bj4	2.7	1.0	0.05	0.09	nn	8.3	4.8	11.7	33	
IIBjCv	2.8	1.1	0.05	0.26	0.3	9.1	5.8	13.1	32	
Cv	3.0	1.2	0.12	0.22	nn	7.5	6.2	13.0	35	

Part II:

Lateritic bauxite in central Germany and implications for Miocene palaeoclimate

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Lateritic bauxite in central Germany and implications for Miocene palaeoclimate

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Abstract

Intense chemical weathering during middle Miocene times led to the formation of deep ferralitic weathering profiles on the Vogelsberg basaltic massif. Saprolite more than 50 m thick, was formed and, in its higher parts, bauxite concretions developed by absolute accumulation of aluminium. The tops of the profiles consist mostly of allochthonous, lateritic bauxite which has been mined intensively in the past.

Similar high latitude bauxites occur on the Paleogene basalts of Ireland. These formed during a phase of recognized greenhouse conditions with a climatic optimum near the Paleocene–Eocene boundary, while during the Miocene the climate was already changing toward Quaternary icehouse conditions.

However, the occurrence of deep weathering profiles with lateritic bauxite at the high palaeolatitude of 45°N may be interpreted as pointing to extreme climatic conditions also during the middle Miocene. The associated laterites and bauxites on middle Miocene basalts (17–15 Ma) provide evidence for a global climatic optimum around 17–14.5 Ma. Reduced uplift rates of the Himalayan–Tibetan Plateau and associated reduced CO_2 consumption, coupled with additional volcanogenic CO_2 production could have induced high atmospheric CO_2 and an intensification of the global greenhouse effect. This may be reflected in accelerated chemical weathering and bauxite formation. Basalt volcanism has thus provided both a source (eruption) and a sink (via weathering) of CO_2.

Keywords: bauxite; laterite; palaeoclimate; Miocene; weathering; volcanism

1. Introduction

Thick weathering crusts are reliable indicators of long periods of palaeoclimatic conditions similar to those which presently prevail in equatorial regions (Bardossy, 1994). As chemical weathering is a comparatively slow process its products do not record short term fluctuations of palaeoclimate but a long term average.

In Europe a belt with thick kaolinitic weathering crusts of Late Cretaceous to Early Tertiary age stretches from Britanny and the Massif Central over the Rhenish and Bohemian massif to Ukrainia and Khasakhstan (Störr et al., 1977). The age of most of these important kaolin deposits corresponds well to a phase of global greenhouse conditions with elevated contents of CO_2 in the atmosphere (Berner, 1994).

In Central Germany, however, Miocene rocks also have been affected by strong lateritic

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weathering processes which led to the formation of thick kaolinitic saprolite and also to laterite and bauxite (Schellmann, 1966). Although this area can be regarded as the cradle of laterite research (Liebrich, 1892; Harrassowitz, 1921, 1926) important details about the genesis of nodular bauxite remained unknown. This paper presents a detailed description of these laterites and their palaeoclimatic interpretation.

2. Miocene volcanism and lateritic weathering in Central Europe

In Central Germany, in the area between Kassel in the north and Frankfurt in the south, a long phase of continental conditions beginning in the Late Jurassic led to the development of a thick kaolinitic weathering crust (Schirrmeister et al., 1995). This pre-Eocene (Blanck et al., 1942; Pflug and Werding, 1964; Bühmann, 1974) or pre-middle-Oligocene (Kutscher, 1954; Birkenhauer, 1970) weathering phase altered the rocks to depths of up to 102 m (Diederich and Ehrenberg, 1977). During the Miocene volcanic activity in the northern extension of the Rhine Graben Rift System led to the eruption of flood basalts which now form the Vogelsberg volcanic massif. With an area of 2500 km^2 it is the largest basalt massif of Central Europe. The main phase of volcanic activity was during the middle Miocene between 17–15 Ma (Schricke, 1986; Ehrenberg, pers. comm., 1996). The composition was mainly tholeiitic and basanitic. Subordinately also trachytic lava and few volcaniclastics have been erupted. Weathering of these volcanic rocks led to the formation of a weathering crust with a thickness of up to 50 m (Schottler, 1921). Besides kaolinitic saprolite also bauxitic laterite was formed. The main area of distribution of this weathering mantle is in the southwestern Vogelsberg area (Fig. 1). Relics of laterite, however, occur up to Kassel in the north (Bargon and Rambow, 1966) and down to the Frankfurt area in the south (Heim, 1971). In the 1920's this bauxite was mined in about 20 mines (Moldenhauer, 1935). In 1918 Germany was the fourth largest producer of bauxite worldwide (Harrassowitz, 1924). Also supergene ironstones were intensively mined in the Vogelsberg area. They occur as goethite fillings along fractures in the saprolite (Friedrich-Lautz, 1963). The shape of the ironstone deposits follows the pattern of old valleys.

Complete lateritic weathering profiles are not exposed in the Vogelsberg area. At many places basaltic parent rocks are partly weathered to saprolite (locally called "Faulstein" = rotten rock). In the lower parts of weathering profiles smectite minerals are developed while in the higher parts the saprolite yields disordered kaolinite as clay mineral. The exposed profiles are truncated at different levels (Fig. 2). Bauxitic laterite in the Vogelsberg area mainly consists of soft red earthy material rich in fist-sized nodules of gibbsite and boehmite (Schwarz, 1987, 1988). Liebrich (1892) recognized that bauxite was formed by weathering of basalt. He and also Harrassowitz (1922) found favourable conditions for the study of bauxite while nowadays only one mine is left which is still accessible. This open pit mine called "Eiserne Hose" is located 2 km east of the town of Lich.

3. The bauxite-mine "Eiserne Hose"

In the mine "Eiserne Hose" both laterite and kaolinitic saprolite are exposed. Laterite had been mined as additive for the steel industry, while presently only saprolite is mined for specialized ceramic purposes. The drillholes with a depth of 30 m did not reach unweathered basalt. The exposed saprolite with a total thickness of 10 m is derived from tholeiitic basalt. It is underlain by saprolite derived from analcime basanite which reaches a depth of more than 30 m. Only some hundred metres north of the mine unweathered analcime basanite is exposed (Fig. 3).

The exposed weathering profile consists of 7 m of saprolite overlain by 6.5 m of laterite (Fig. 4). In parts of the mine laterite is covered by up to 1 m of loess with solifluction features and ice wedges. At the base of the saprolite the typical columnar jointing of the basaltic parent rock is clearly visible. Above, a zone with hard fist-sized concretions rich in gibbsite occurs (Schwarz, 1987). Towards the top of the saprolite the colour changes from gray to red. The overlying laterite

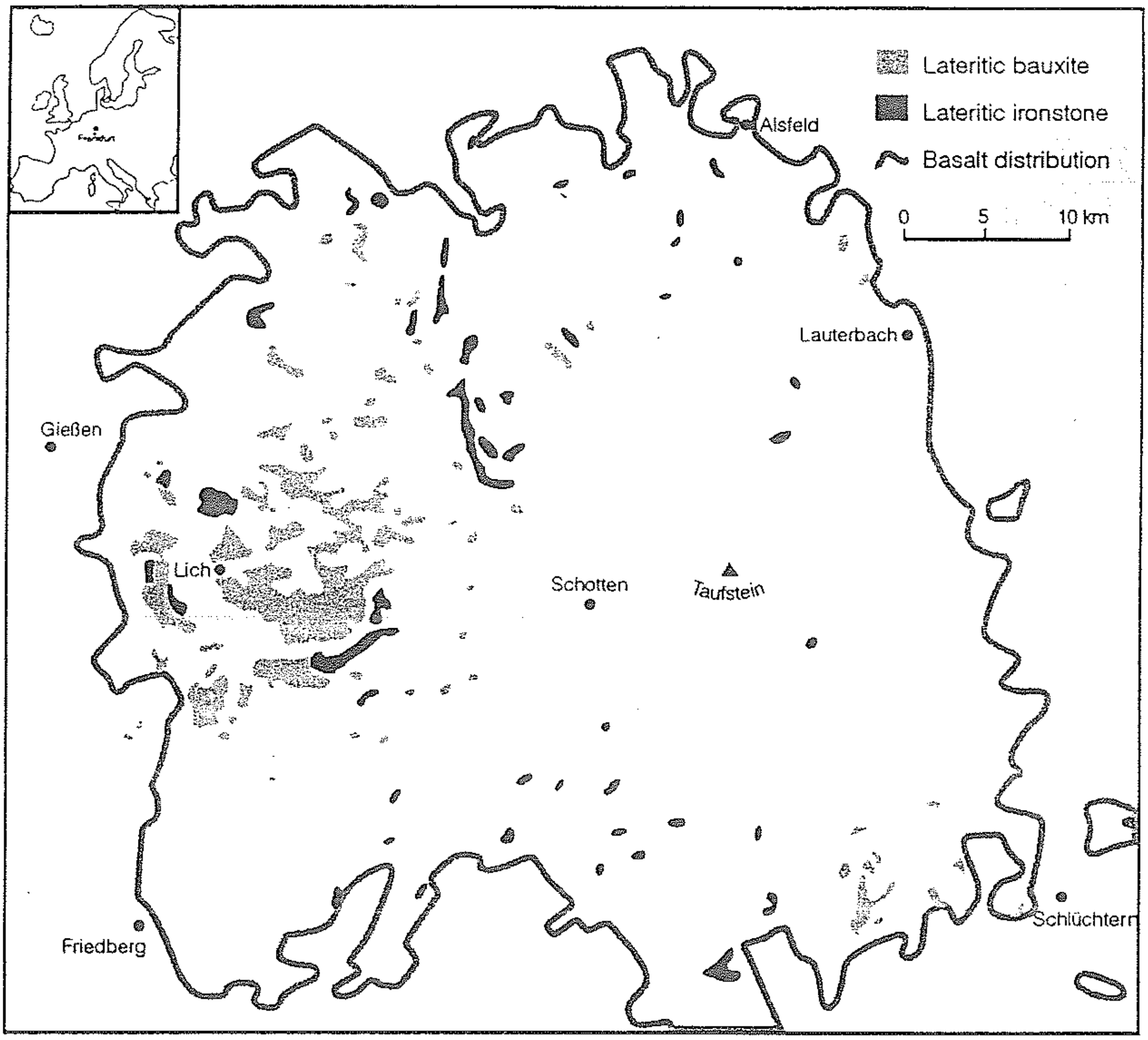

Fig. 1. Distribution of lateritic weathering products in central Germany.

consists of a layered section of alternating horizons with different contents of red or yellow clay, bauxite nodules, ironstones, and of reworked gray saprolite.

4. Basalt weathering and formation of nodular bauxite

Except magnetite and ilmenite, all primary minerals of the basalt are altered. Olivine is transformed to iddingsite, which consists mainly of goethite. Plagioclase-laths of the tholeiitic basalt form white kaolinite, while pyroxene is transformed into a mixture of kaolinite and goethite (Fig. 5). The neoformed kaolinite is of poor crystallinity with a strong *b*-axis-disordering. According to the classification of Brindley et al. (1963) it can be regarded as meta-halloysite. Crandallite-group minerals are also abundant as a minor component in the saprolite. During the formation of saprolite no or only minor iron is

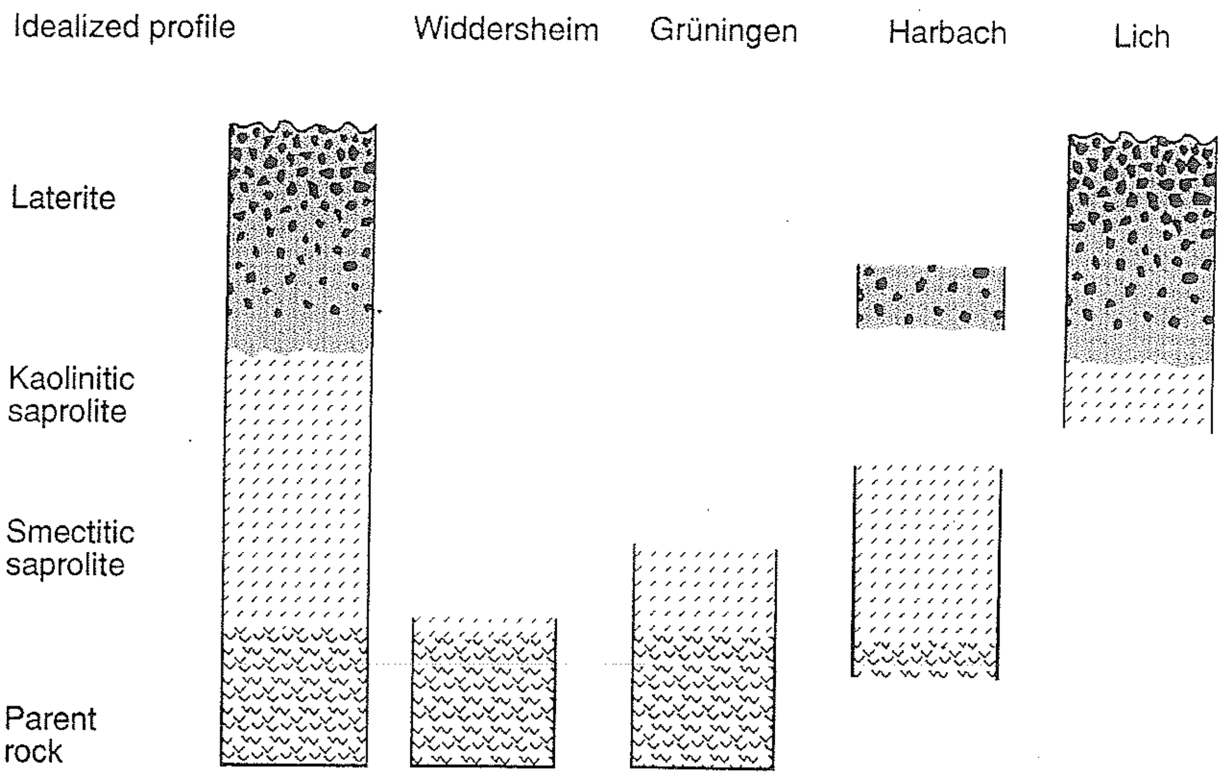

Fig. 2. Schematic sections of weathering profiles exposed in the Vogelsberg area.

leached from the weathering profile. This is indicated by the constant iron-content per volume unit of both basalt and saprolite. Thus, along with Ti, Zr, Nb, and Al, Fe belongs to the stable elements. This is indicated by the strong correlation of Fe with the less mobile Ti (Fig. 6). Saprolite is formed by a relative enrichment of stable elements due to the leaching of alkaline and earth alkaline elements and silica. The formation of bauxite nodules within the saprolite is a result of an absolute enrichment of Al resulting in a dilution of stable elements as shown in Fig. 6 and in the isovolumetric mass balance calculation (Fig. 7, calculation of vol.% following Brimhall and Dietrich (1987): concentration in weathered product [vol.%] = concentration [M.%] * (bulk density of weathered product/bulk density of protolith)). The relic textures of basalt are preserved in both saprolite and bauxite nodules (Fig. 5). Absolute enrichment of Al is further indicated by the filling of voids with idiomorphic crystals of gibbsite (Fig. 5). Similar nodules with bauxite minerals occur also on basaltic rocks in Hawaii (Sherman and Ikawa, 1959) and Cambodia (Mitsuchi, 1976), and at Sierra Leone (Prasad, 1987). Bauxitic and ferruginous nodules with relic textures of parent rocks are also abundant in stone-line profiles (Lecomte, 1988; Schwarz, 1996).

5. Lateritization and reworking of laterite

Towards its top the saprolite attains a red colour. According to thin section investigations of Altemüller and Poetsch (1984) this is a result of the neoformation of hematite at the expense of corroded ilmenite. This is supported by X-ray diffractograms which clearly show decreasing ilmenite and increasing hematite and anatase contents at the top of the saprolite. Also the width at half height of the basal reflection of kaolinite decreases, indicating an increasing crystallinity

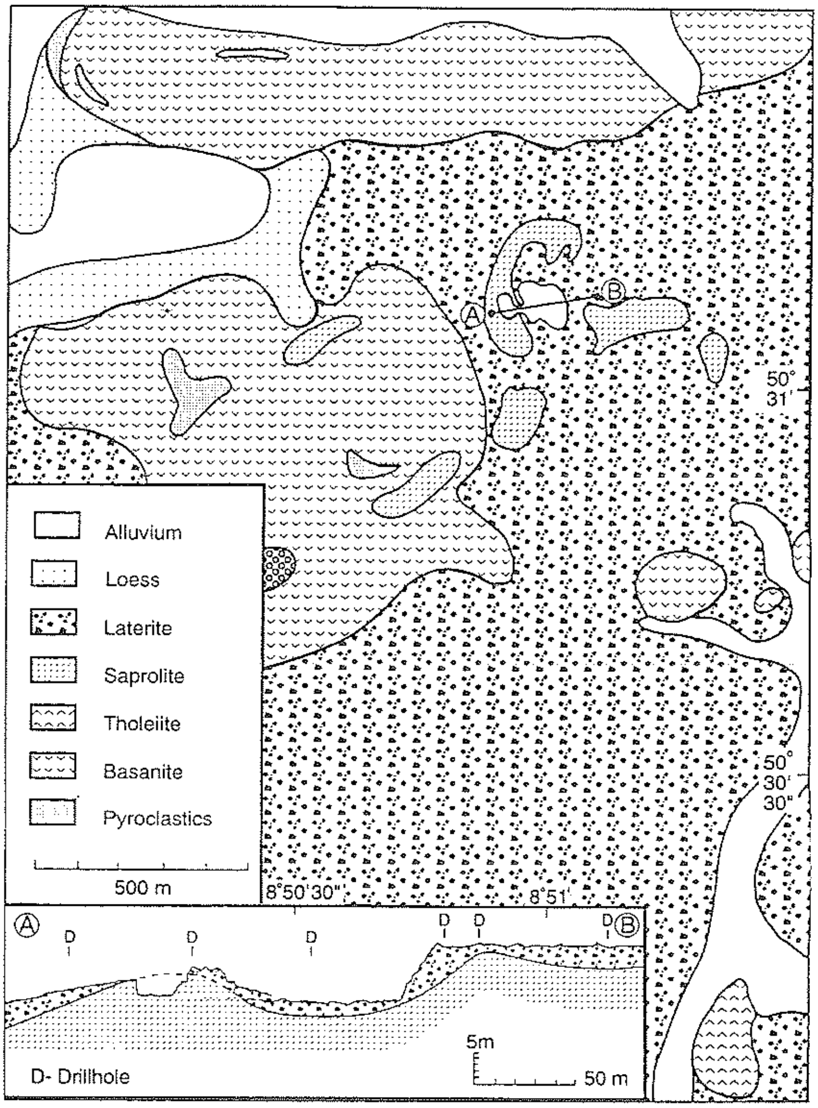

Fig. 3. Geologic sketch map of the vicinity of the bauxite mine "Eiserne Hose".

towards the top of the profile. The overlying laterite consists mainly of hematite and goethite along with kaolinite, gibbsite, anatase, magnetite, and ilmenite. The predominance of magnetite over ilmenite could point to a different parent rock composition. While tholeiitic basalts are rich in ilmenite, basanites have higher contents of magnetite. A scatterplot of the less mobile elements Nb and Ti reveals the different parent rocks (Fig. 8). While weathering products derived from trachytic parent rocks have a high Nb/Ti-ratio, those from tholeiitic basalts, like the saprolite at "Eiserne Hose", have a low ratio. The laterite at "Eiserne Hose" has an intermediate ratio identical with weathering products which are known to be derived from basanitic basalts. The alternation of layers with a different degree of weathering along with the changes in Nb/Ti-ratio indicates that the laterite is of sedimentary origin. Differences in Fe and Al-contents are the result of the predominance of either bauxite nodules or ironstones as coarse particles (Fig. 9). However, the high contents of

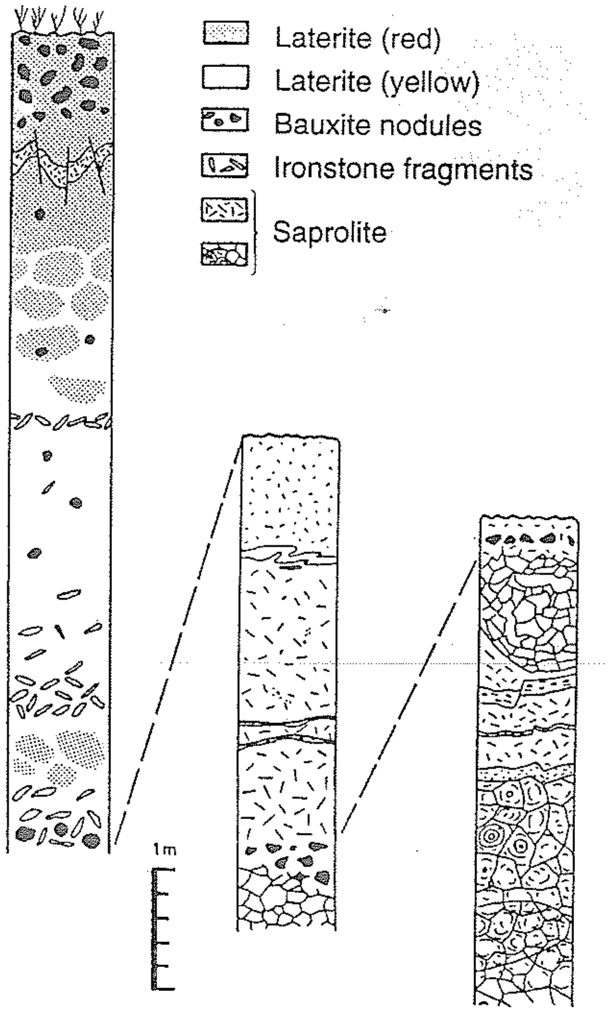

Fig. 4. Weathering profile of saprolite overlain by laterite as exposed at the "Eiserne Hose"-mine.

relatively stable elements Zr, Ti, and Nb indicate a strong residual enrichment and thus a lateritic origin of this material. The iron-rich laterite also yields high contents of V which is an indicator of lateritic weathering processes (Schwarz, 1992, 1995).

6. Palaeoclimatic conditions

The late Palaeocene to early Eocene was one of the warmest intervals in Earth's history (Sinha and Stott, 1994; Frakes et al., 1994; Robert and Kennett, 1994). This is indicated, for example, by floral remains of broad-leaved evergreen forests at high latitudes such as Spitsbergen and West Greenland (Wolfe, 1980). In Northern Ireland bauxite occurs between Palaeocene basalts (Eyles, 1952; Smith and McAlister, 1987). This phase of global warmth could be related to a greenhouse effect triggered by enhanced CO_2-release due to extensive regional metamorphism associated with the India–Asia collision and the closing of Tethys (Kerrick and Caldeira, 1993). Warm conditions in the late Eocene were followed by distinctly cooler climates throughout the Oligocene starting with the buildup of the Antarctic ice sheet during early Oligocene times (Kennett and Borch, 1986; Ehrmann and Mackensen, 1992). The drop in temperature throughout the Eocene is also indicated by plant fossils (Wolfe, 1995) and oxygen isotopic data (Miller et al., 1987) as shown in Fig. 10.

A possible reason for this global cooling is the rapid uplift of the Himalayas and the associated increase in chemical weathering rates which consumes high amounts of CO_2 and thus leads to a reduced greenhouse effect (Vincent and Berger, 1985; Raymo et al., 1988). Increased relief acts to accelerate chemical weathering by increasing mineral surface areas via mechanical weathering (Berner, 1995). Thus at times of accelerated tectonic exhumation of orogens an increase of chemical weathering rates will produce a drawdown of atmospheric CO_2. Uplift of the Himalayan orogen during the past 40 Ma may have lead to accelerated CO_2 consumption and thus cooling (Raymo and Ruddiman, 1992). An increase in silicate weathering rates during that period is further supported by the rising $^{87}Sr/^{86}Sr$ ratio of seawater (Fig. 10). This rise, however, can be explained not only by uplift of the Himalayas but also by increasing delivery of finely ground rock material resulting from glacial activity (Blum and Erel, 1995).

The beginning of Miocene was again characterized by warmer conditions. The early Miocene experienced a rapid shift in atmospheric CO_2-levels from 5 times preindustrial levels at 20 Ma to 1.5 times preindustrial values by 15 Ma (Arthur et al., 1991). This is accompanied by an

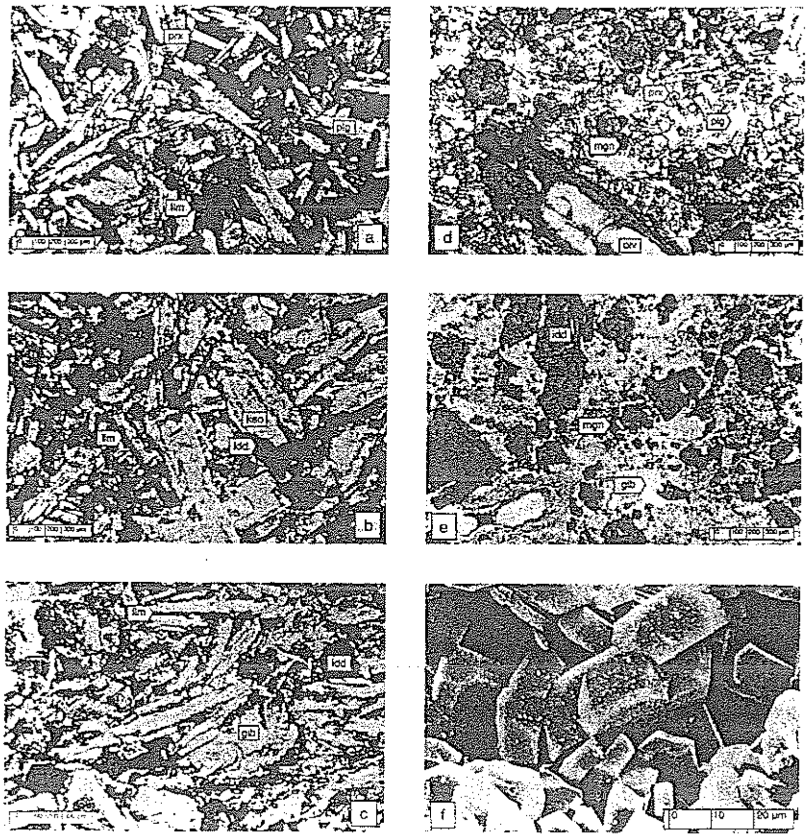

Fig. 5. Thin sections of tholeiitic basalt (a), saprolite (b) and bauxite nodule (c) derived from tholeiitic basalt, basanitic basalt (d), bauxite nodule derived from basanitic basalt (e), and SEM-image of gibbsite crystals growing into voids of a bauxite nodule (f).

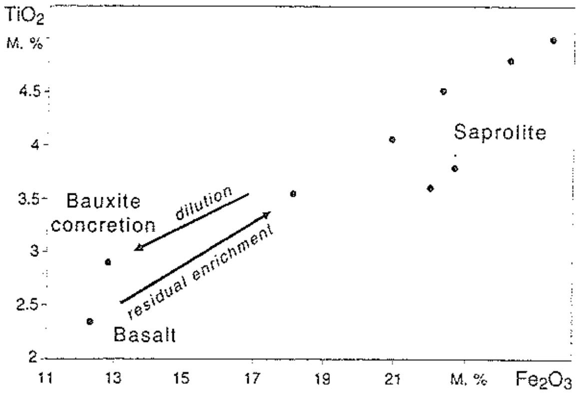

Fig. 6. Scatterplot of immobile Fe_2O_3 vs. TiO_2 indicating concentration and dilution processes.

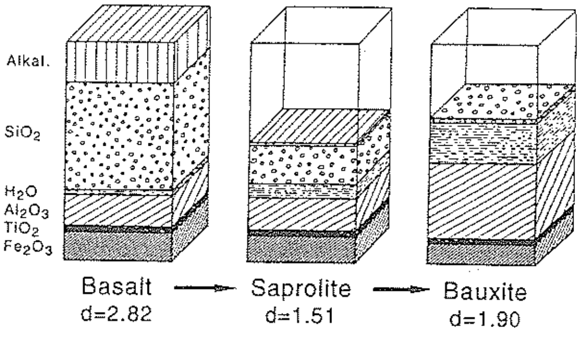

Fig. 7. Composition of basalt and its weathering products shown under isovolumetric conditions in volume-percent.

increase in slope of the $^{87}Sr/^{86}Sr$-curve resulting from a rapid exhumation of Himalayan metasedimentary rocks (Harris, 1995). At least six kilometers of unroofing occurred on the Himalayan–Tibetan Plateau between 21 and 17 Ma (Hodges et al., 1992). During that interval also cooling and a major phase of ice growth in

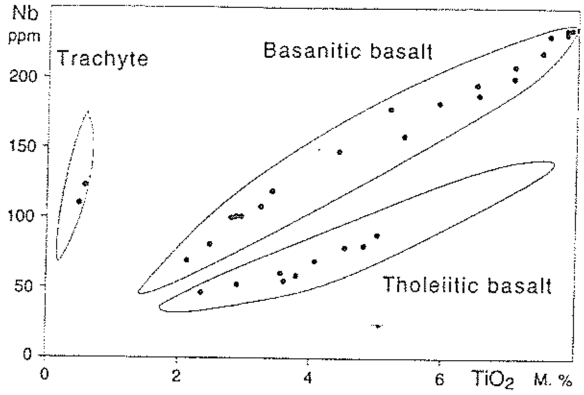

Fig. 8. Scatterplot of Ti and Nb indicating different basaltic parent rocks.

Antarctica took place (Leckie and Webb, 1983; Oslick et al., 1994). According to Raymo (1994) the decrease of atmospheric CO_2 levels was further accelerated by high burial rates of organic carbon due to an expansion of the oxygen minimum zone as a result of increased supply of nutrients leading to a higher productivity in oceanic upwelling zones.

In the middle Miocene, however, the cooling scenario seems to have come to a halt. The steep rise of the $^{87}Sr/^{86}Sr$ ratio is followed by relatively constant values before they rise again in the late middle Miocene (Hodell and Woodruff, 1994). The two periods of steepened slope of the $^{87}Sr/^{86}Sr$ ratio coincide with major phases of uplift and denudation of the Himalayan–Tibetan Plateau region at 21–17 Ma and at 11–7 Ma (Sorkhabi and Stump, 1993). Between these phases a period with less uplift, less chemical weathering and thus lower CO_2-consumption could evolve (Raymo and Ruddiman, 1992). The palaeoclimatic record indicates a climatic optimum between 17 and 14.5 Ma which, according to Hodell and Woodruff (1994) is attributed to a sudden production of high amounts of CO_2 released by the extrusion of the Columbia River flood basalts between 17 and 15 Ma.

The assumption of a middle Miocene climatic optimum is mainly based on the oxygen isotopic record. Deep ocean isotopic paleotemperatures derived from benthic foraminiferal oxygen isotopes indicate an 8°C maximum around 16 Ma (Flower and Kennett, 1994). On the continent the isotopic record of supergene alunite draws an even more expressed peak during the Middle Miocene (Arehart and O'Neil, 1993). Palynological data from the Northern Atlantic point to a short warming phase during the middle Miocene (Engel, 1992). Plant associations in middle Miocene peats of the Lower Rhine Embayment in Germany indicate a mean annual temperature of 16–21°C followed by a rapid cooling (Mosbrugger, 1994). Reconstruction of precipitation rates indicate values between 1200 and 1400 mm per year. From 14.5–14.1 Ma a phase of increased organic carbon-rich deposition (and thus CO_2-consumption) coincides with deep-water cooling and major East Antarctic ice sheet growth (Flower and Kennett, 1993a,b, 1994). Associated with the late middle Miocene cooling trend was a sudden divergence of high- and low-latitude temperatures with a dramatical drop in high-latitude temperatures (Savin et al., 1975). A climatic change is also indicated by the development of a stratified ocean during late middle Miocene within the Monterey Formation in southern California (Raymo, 1994; Schoell et al., 1994).

7. Discussion

The intense weathering of middle Miocene basalt in the Vogelsberg area provides another point of evidence indicating extraordinary climatic conditions. Bauxitization is restricted to volcanics of middle Miocene age in that region while on other rocks no comparable weathering products formed. The K/Ar model ages of basalt in the Vogelsberg area range between 19 and 13 Ma with some younger ages at 10 Ma. The maximum of model ages culminates at 17–15 Ma. The eruption of the sheet basalts probably occurred in a time-span of less than 1 Ma which is less than the analytical error of the age determinations (Harre et al., 1975). Also the eruption of Columbia River Basalt Group is attributed to a very short period of time between 17 and 15 Ma (Hooper, 1990). In the Vogelsberg the model ages of the tholeiitic basalts which are the parent rocks of the saprolite at "Eiserne Hose" vary between 15.5 and 16.2 Ma (Harre et al., 1975). Age determinations

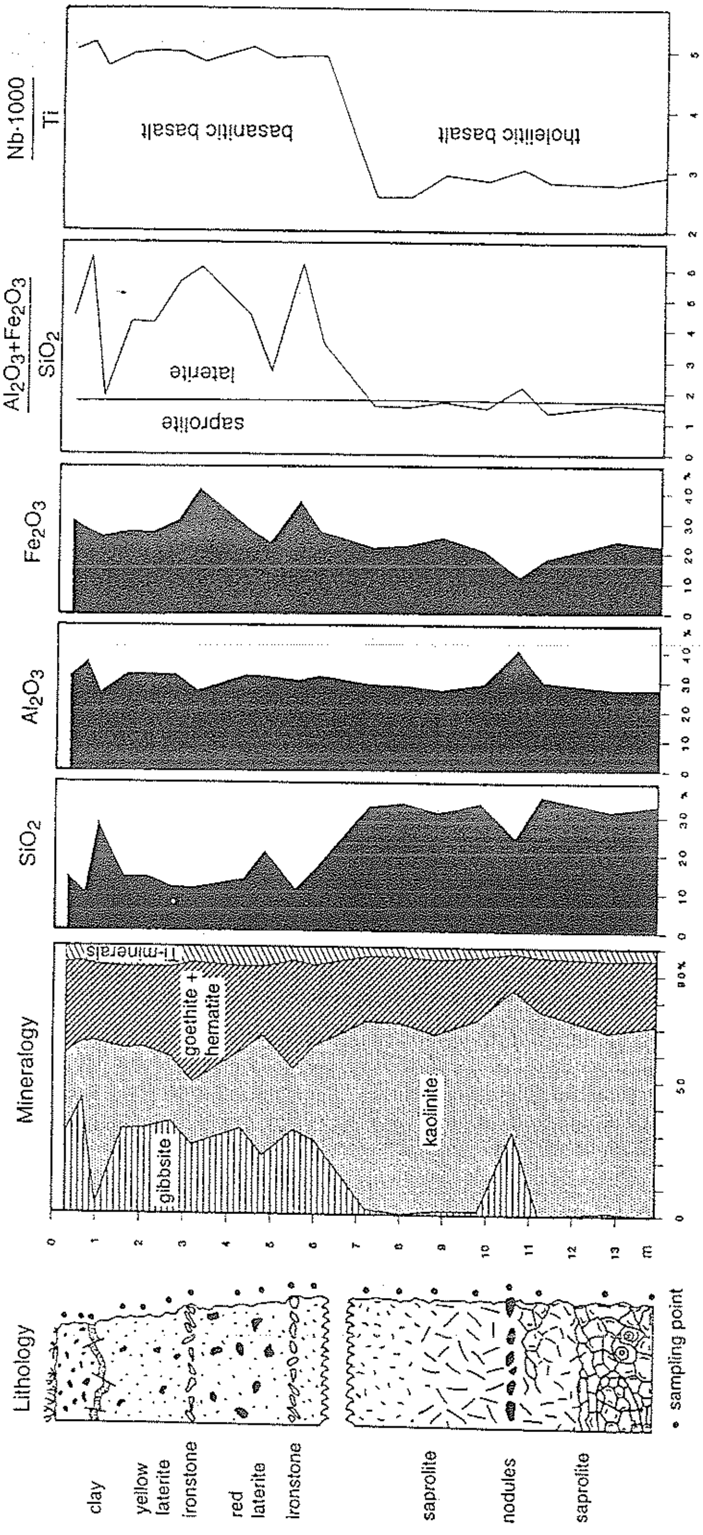

Fig. 9. Lithology, mineralogical composition and geochemical parameters of tholeiite-derived saprolite overlain by basanite-derived laterite at Eiserne Hose near Lich.

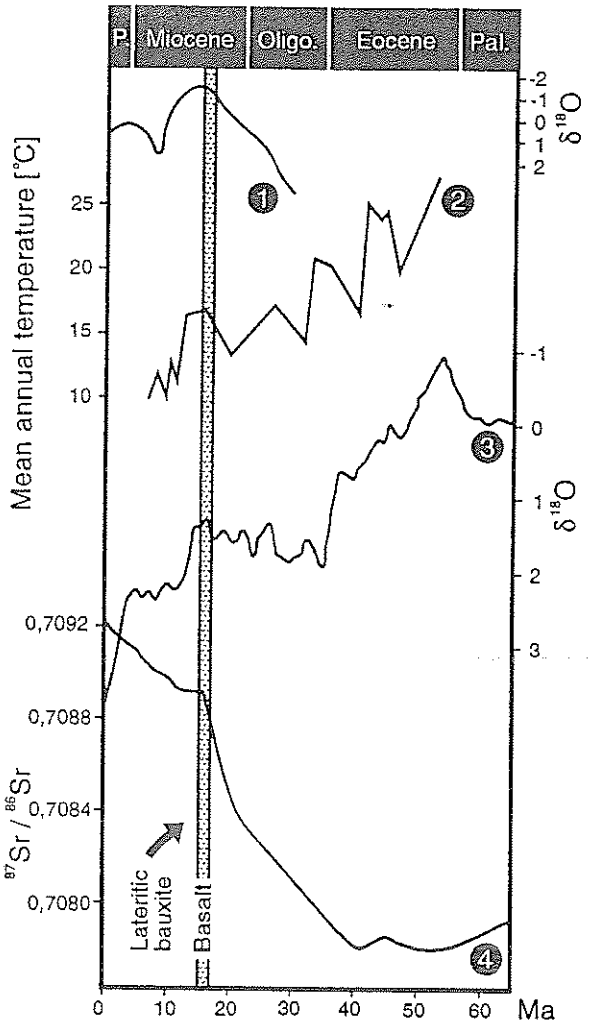

Fig. 10. Bauxitization of the Vogelsberg basalt and Tertiary palaeoclimate proxies. *1* = oxygen-equivalent isotopic data of supergene alunite (Arehart and O'Neil, 1993). *2* = mean annual temperature estimates for leaf assemblages from near-coastal sites at 45°N (Wolfe, 1995). *3* = benthic foraminiferal oxygen isotopic record from the Atlantic Ocean (Miller et al., 1987). *4* = seawater Sr isotopic data (Richter et al., 1992).

($^{40}Ar/^{39}Ar$) of similar tholeiitic basalts in Frankfurt vary between 15 and 16 Ma (Fuhrmann and Lippolt, 1987). Palynological data from the youngest intrabasaltic layers also points to a middle Miocene (Badenien) age (Hottenrott, 1988).

Thick kaolinitic weathering crusts point to high rates of chemical weathering, exceeding the rate of physical erosion. Such conditions of deep chemical weathering were given during periods in Earth's history when greenhouse conditions prevailed (Valeton, 1994; D'Argenio and Mindszenty, 1995). During such periods "tropical" lateritic weathering was possible in a palaeolatitude of 45°N as in the example of the Vogelsberg (Schwarz, 1993; Schwarz et al., 1993). Similar conditions of high latitude lateritic weathering processes during greenhouse periods are also known from the Ordovician of northeast Africa (Germann et al., 1993, 1994; Schwarz, 1994, 1995). In the Monaro Region of New South Wales (Australia) bauxitization of early Tertiary basalts at a paleolatitude of 57.5°S formed under cool humid climate and tectonic stability (Pratt et al., 1992; Taylor et al., 1992). Climatic phases with elevated atmospheric atmospheric CO_2 and an enhanced greenhouse effect could explain such weathering products at high latitudes (Bird et al., 1990). It remains yet unexplained by general circulation modeling how the extremely low latitudinal surface temperature gradient during times of increased CO_2 such as the Eocene could develop (Sloan and Rea, 1995).

During the Miocene a variety of lateritic weathering products formed on basaltic parent rocks also at other places. In northern Bavaria thick saprolite formed (Sobanski and Valeton, 1994), in the Massif Central in France interbasaltic fersiallitic palaeosols occur (Dejou and Chesworth, 1979; Pierre and Dejou, 1990), ferruginous bauxite developed on the Columbia River Basalts in the United States (Cummings and Fassio, 1990; Bestland et al., 1994). Gibbsitic laterite of Miocene age is also found in the Czech Republic (Tecin) and Poland (Rybnik), allochtonous bauxite of the same age is known from Nagyvázsony and Öcs in Hungary and near Vroderon in NW-Greece (Bardossy and Dercourt, 1990). As for the Vogelsberg it is interesting to note that bauxite and laterite formation was not followed by the development of a ferricrete, which often caps ferralitic profiles in tropical areas (Schwarz, 1994). Ferricretes typically form under tropical climates with an expressed dry season and deep weathering profiles overlain by ferricretes thus give evidence of humid climates with a subsequent shift towards savannah-type climate (Tardy et al., 1991; Schwarz, in press).

Hodell and Woodruff (1994) assume a significant increase of atmospheric CO_2 due to the extrusion of 1000 km^3 of basalt at the Columbia River the volcanism during the middle Miocene. Compared to that the Vogelsberg area (2500 km^2 covered by basalt) with a thickness of more than 490 m in the central part (Ehrenberg et al., 1979) is only a minor CO_2 source. This basaltic sources, however, also acted as another effective sink of CO_2 as a result of the subsequent weathering event. The termination of lateritization in the Vogelsberg area probably took place in the late middle Miocene. A drop in palaeotemperatures in the late middle Miocene is indicated by the oxygen isotopic record (Wright and Miller, 1992), the delta-D-values for supergene alunite (Arehart and O'Neil, 1993), palaeoenvironmental changes in South America (Alpers and Brimhall, 1988), by plant remains (Mosbrugger, 1994; Wolfe, 1994) and by significant faunal changes (Quade and Cerling, 1995). At 10–9 Ma also the buildup of the Arctic ice sheet started (Schaeffer and Spiegler, 1986) and a temperature decrease of about 10°C occurred in Iceland between 10 and 9.5 Ma (Mudie and Helgason, 1983).

8. Conclusion

The age of the basaltic parent rock of the Vogelsberg lateritic bauxite corresponds to a global climatic optimum between 17 and 14.5 Ma. Several factors initiated this climatic optimum. At least six kilometers of unroofing occurred on the Himalayan–Tibetan Plateau between 21 and 17 Ma. This phase of accelerated CO_2-consumption by weathering was followed by a period with reduced uplift rates as indicated by a change in slope of the $^{87}Sr/^{86}Sr$ isotope curve at 16 Ma. Consequently less CO_2 was consumed thus raising the atmospheric CO_2-concentration. Additionally, eruption of basalt on the Columbia Plateau between 17 and 15 Ma could have contributed to a rising CO_2-concentration.

High atmospheric CO_2 during the Middle Miocene lead to an enhanced greenhouse effect with an increase of precipitation and weathering. As a consequence lateritic weathering processes could be active not only in equatorial regions but also in a paleolatitude of 45°N. The Vogelsberg laterite with bauxitic nodules is similar to stone-line profiles in present day tropical areas. The occurrence of such laterites at high latitudes might thus represent a valuable paleoclimatic indicator for extreme climatic conditions.

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Part III:

Deep weathering mantles of Upper Cretaceous and Tertiary periods in the Rhenish massiv

1 Summary

Morphological, mineralogical and geochemical investigations were carried out on overlapping exposures and drill cores of the autochthonous Mesozoic-Tertiary weathering mantle (MTV). The exposures give a complete picture of the weathering mantle from the fresh slate up to the recent land surface as well as the spatial distribution related to neo-tectonics and relief. The aim of the investigations was to reconstruct the genesis and the quaternary superimposition of the weathering mantle. Younger investigations of kaolinized rocks focussed on the type and intensity of hydrothermal alteration, due to ascending thermal CO_2 waters. In both study areas - the transition area from the Northeastern Eifel to the Lower Rhine Embayment and the Eastern Hunsrück - large-dimensional relics of the younger peneplain (R1-plain) and its thick weathering mantle exist as a result of the relatively weak tectonic elevation.

In both study areas the parent rocks are predominantly Lower Devonian clay and silt slates. Depending on the region, layers of sand stone (graywacke), quartzite and quartz veines are inserted. Samples of the slates were geochemically and mineralogically analysed in order to evaluate the intensity of weathering and to compare the balances of elements. An increase of the sand fraction in stones is simultaneous with an increase of the content of quartz and a decrease of the Ti/Zr-ratio. From coaly-bituminous organic substance results the black-greyish colour of the slates. The mineral composition of the slates is uniform in both areas. The main constituents are illite, muscovite (~ 30 %) and quartz (~ 40 %) and 25-30% of Fe-Mg-chlorite (Fe-rhipidolite). Chlorite shows the lowest weathering stability and is relatively easily soluble in acids.

Under warm and humid climates of the Upper Mesozoic and the Tertiary a weathering mantle up to 150 m thick was formed. It can be subdivided into the genetic units "solum" and "saprolite". The solum developed by pedogenetical processes and shows soil horizons with neo-formation of structure. With respect to the morphogenesis of the peneplain due to climatic changes, the solum represents the youngest formation of the weathering mantle.

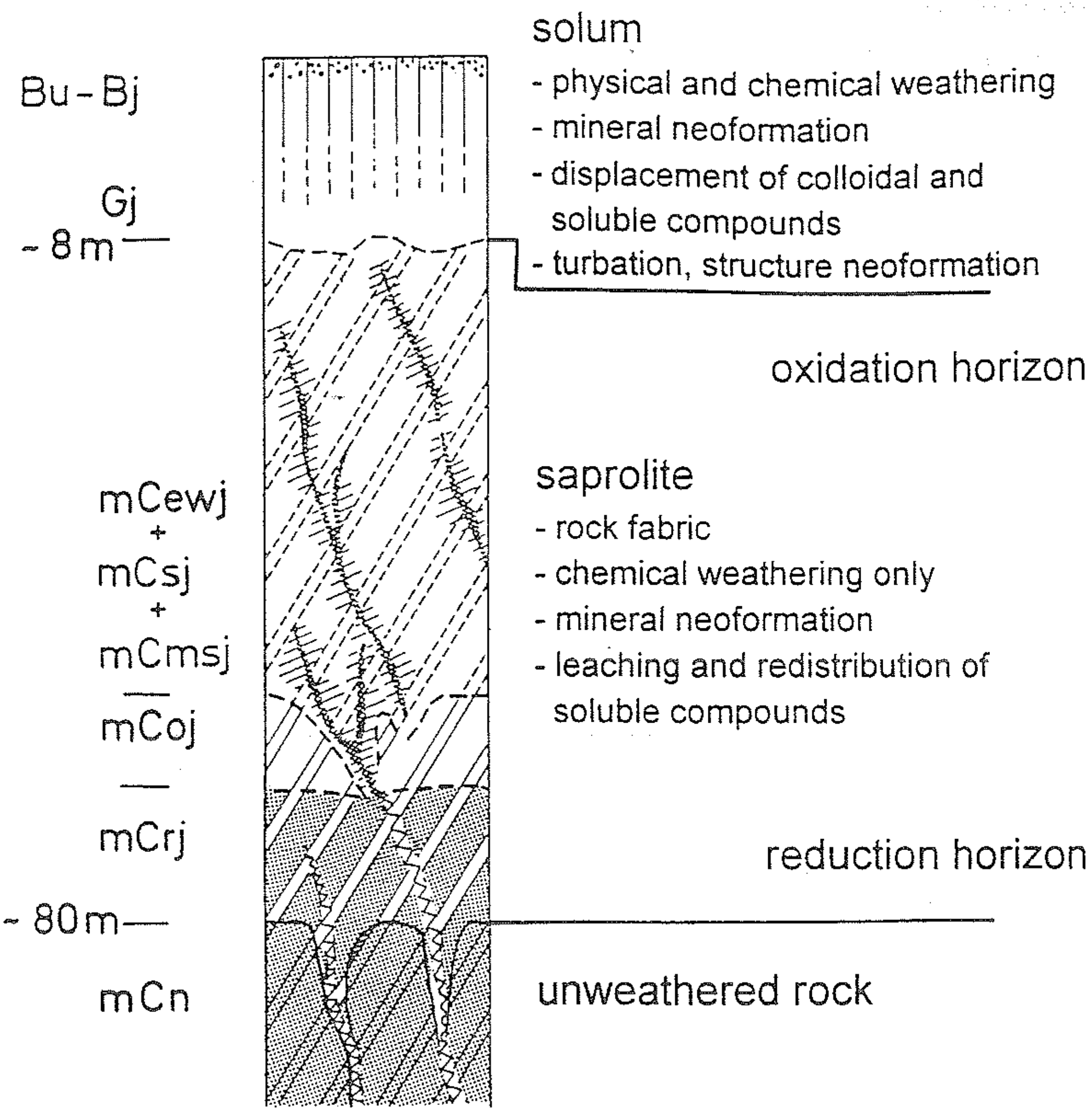


Figure 1: The Mesozoic-Tertiary weathering mantle of the Rhenish Massif - genetic units, morphological classification, and horizon symbols

mCrj:	*reduction zone, black-greyish colour of the fresh slate*
mCoj:	*oxidation zone, brown-, to greyish olive colour, weak eluation, no accumulation of oxides*
mCewj:	*bleached zone, white to light greyish colour*
mCsj:	*accumulation zone of sesquioxides, yellow, brown, red and purple colours, relatively weak accumulation of oxides (<10% Fe_d)*
mCmsj:	*massive, brown, red and purple-reddish iron stones ("Hunsrück iron stones") (>10% Fe_d in the bleached saprolite)*

The saprolite underlying the solum was developed by deep weathering. It shows an undisturbed rock structure.The conditions for the saprolite formation were long aged tectonic repose periods and a warm and humid climate accelerating the weathering processes. During these phases the advance of the weathering base exceeded the amount of denudation at the land surface. The saprolite is morpho-genetically divided into an oxidation horizon and a reduction horizon. Each of them can have a thickness of more than 40 metres. In both of the main horizons zones of characteristics were formed, which are designated by the horizon symbol "mCj" in combination with additional feature symbols (see fig. 1). The zones do not only run horizontally but also vertically, because their formation was related to the permeability of the rock.

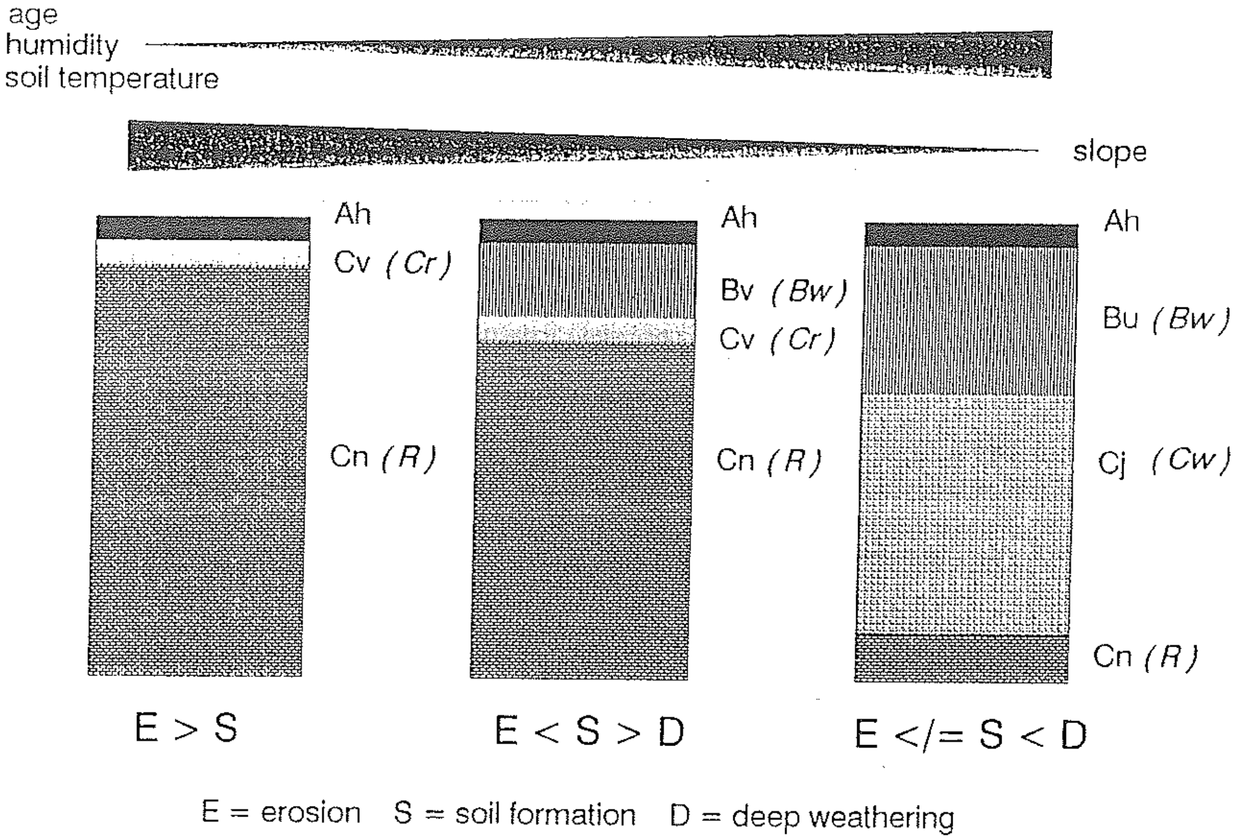


Figure 2: Factors and processes determining the formation of a weathering mantle (regolith), which consists of a solum and saprolite; horizonation according to German soil systematics (AK BODENSYSTEMATIK 1985) and FAO/UNESCO legend (1989) respectively

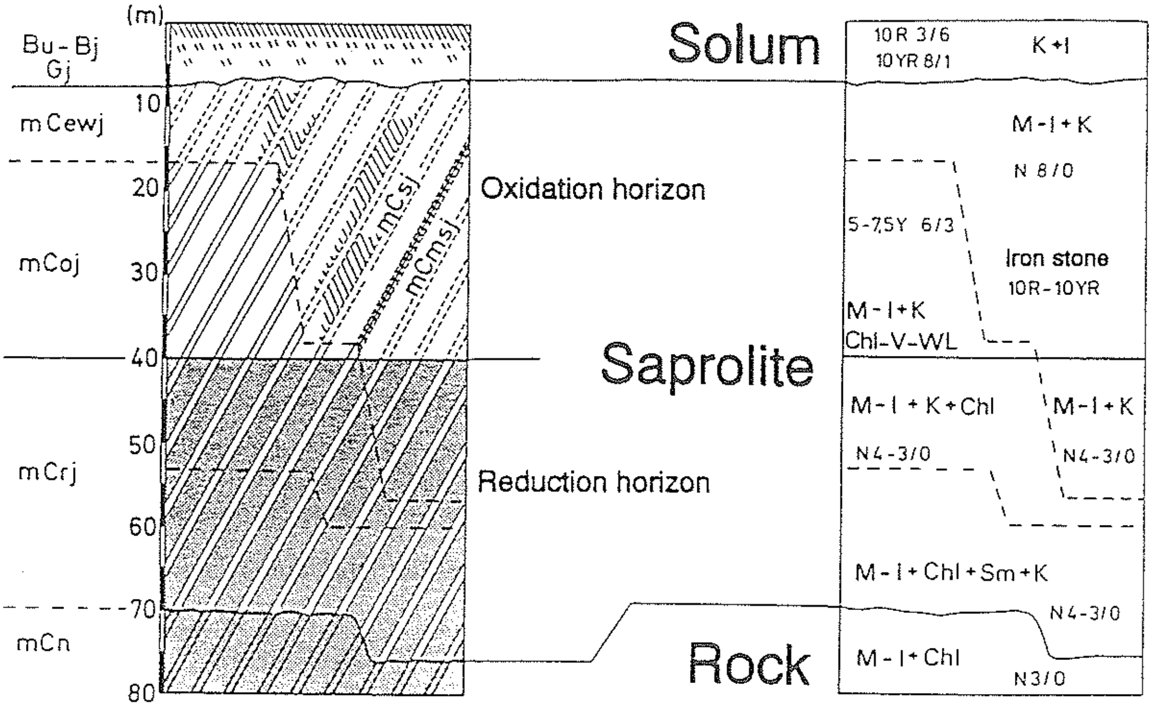


Figure 3: Morphological and mineralogical subdivision of the Mesozoic-Tertiary weathering mantle (Chl = primary Fe-Mg chlorite; Sm = smectite; M-I = muscovite-illite; Chl-V-WL = chlorite-vermiculite mixed layer minerals; K = kaolinite, explanation of horizon symbols see fig. 1)

In the reduction horizon of the weathering mantle the slates were kaolinized under water saturation and leaching of solutants. The deepest zones of the reduction horizon include kaolinite and smectite side by side as a neo-formation after chlorite. With increasing permeability in upper zones and leaching due to a higher weathering intensity of the saprolite, smectite disappeared from the mineral association. The residual chlorite was completely kaolinized or transformed to 1:1 chlorite-vermiculite mixed layer minerals under oxidizing conditions due to a decreasing ground water level. In the bleached saprolite ("Weißverwitterung") that forms the uppermost, up to 40 metres thick zone of the oxidation horizon, kaolinite is the only neo-formation beside residual muscovite-illite and quartz.

Additional to the hydro- and protolysis and the neo-formation of minerals, leaching of soluble elements was the third process of deep weathering. Leaching processes prevented chemical equilibria in the pore solution and enabled the advance of the weathering basis with depth. The leaching of mobile elements occured under reducing conditions. Its intensity was controlled by the movement of ground water within the permeable rock zones. Mass losses of the weathered slates by leaching amounts to about

25-30 vol.- %, related to the unit weight of fresh slates. The results of isovolumetric balances show, that in all zones of the saprolite silica has the highest proportion of the total mass losses. It originates from the solution of quartz and illites rich in Si. The increasing pore volume of the weathering rock enhanced the permeability of the saprolite and the efficiency of deep weathering.

During phases of lower ground water level, oxidizing conditions within the bleached zone of the saprolite resulted in the decay of primary coaly-bituminous organic substances, as well as in the formation of oxide accumulation zones and Hunsrück iron stones. The accumulation of oxides was orientated to the permeable zones of the rock, which already were aerated, while the adjacent fine pores of the rock were still saturated by water leading to reducing conditions. Therefore, over a distance of several metres the diffusion of mobile elements followed a redox and concentration gradient. In the deepest parts of the oxidation horizon the Hunsrück iron stones completely consist of goethite, frequently accompanied by Mn oxide concretions. The content of hematite increases in the upper zones. Ore microscoping and mineralogical investigations prove that the oxide enrichment was bound to an epigenetic displacement of kaolinite.

A fossil pre-Oligocene soil, superimposing the bleached saprolite was investigated as an example for the solum of the weathering mantle. Similar to other autochthonous Tertiary paleosols, the investigated profile can be subdivided from top to bottom into a concretionary layer, a plinthite layer and a bleached layer. According to the German soil systematics, it can be classified as a ferralitic Red Plastosol, which nearly corresponds to a Ferrali-Gleyic Acrisol according to the legend of the FAO soil map. The horizonation of the soil, as well as the oxide accumulation within the pores, mark a primary soil genesis under the influence of a high ground water level. Compared to the saprolite, the clay contents of the soil horizons distinctly increased, especially in the fine clay fraction. The mineral association reflects a progressive kaolinization of illite-muscovite from the saprolite to the top soil. In contrast with the saprolite, the neo-formed kaolin minerals of the soil clay fraction predominantly consist of DMSO-intercalation disordered kaolinite ("fireclay minerals"). A neo-formation of gibbsite could not be proved.

In respect to the relationship between the autochthonous weathering mantle and Tertiary tectonics as well as Tertiary sediments, two main genetic periods can be stratigraphically defined. The older period with high ground water levels reaching up to the soil horizons lasted from the Lower Tertiary to the Upper Oligocene. During the Lower Miocene, decreasing ground water levels due to tectonical uplift and semi-arid climatic conditions led to the formation of up to the 40 metres thick bleached saprolite ("Weiß-erwitterung") and the Hunsrück iron stones. It is likely that a second period of deep reaching oxidation took place during the Pliocene.

The soils of the Miocene landscape were extensively removed by Upper Tertiary erosion processes. With the beginning of the Quaternary, about 2 million years ago, the more or less eroded saprolite probably outcropped at the land surface. During the cold periods of the Pleistocene, processes of cryoturbation, solifluction and regressive erosion led to a further removal of the weathering mantle and a dissection of the peneplain. At the slopes of the deeply incising river valleys and at the edges of the stronger uplifted fault blocks, the reduction horizon of the saprolite or the fresh slates were exposed. Superficial periglacial layers were deposited on top of the autoch-thonous relics of the weathering mantle. They can be subdivided by heavy minerals, texture and morphology into a stratigraphic sequence of three layers. Due to cryoturbation and congelifraction, the saprolitic rock changed into a structureless loam, which was redistributed by fluvial or solifluidal processes.

Relics of this substratum remains as "Gray Loam" on top of the eroded saprolite and forms the basal sequence. They are overlain by solifluction layers of the middle sequence, which contain loessial loam. Soil horizons from these layers micromorphologically display periglacially reworked or redeposited argillans of an interglacial Luvisol. There fore, a Riss age for the deposition of the loess can be assumed. The uppermost sediment layer is formed by eolian loessial pumice dust, which was deposited in the late glacial during the Younger Tundra Age.

The Holocene soil development in the Quaternary superficial layers was marked by progressive weathering of silicates and the influence of logged surface water. On the other hand, clay migration was hardly important. The Gray Loam does not represent the Tertiary solum on any account. As a sediment, which derived from the underlying saprolite, a designation as "Gray Plastosol" on the systematical level of soil type or subtype according to the German Soil Systematic does not seem to be justified.

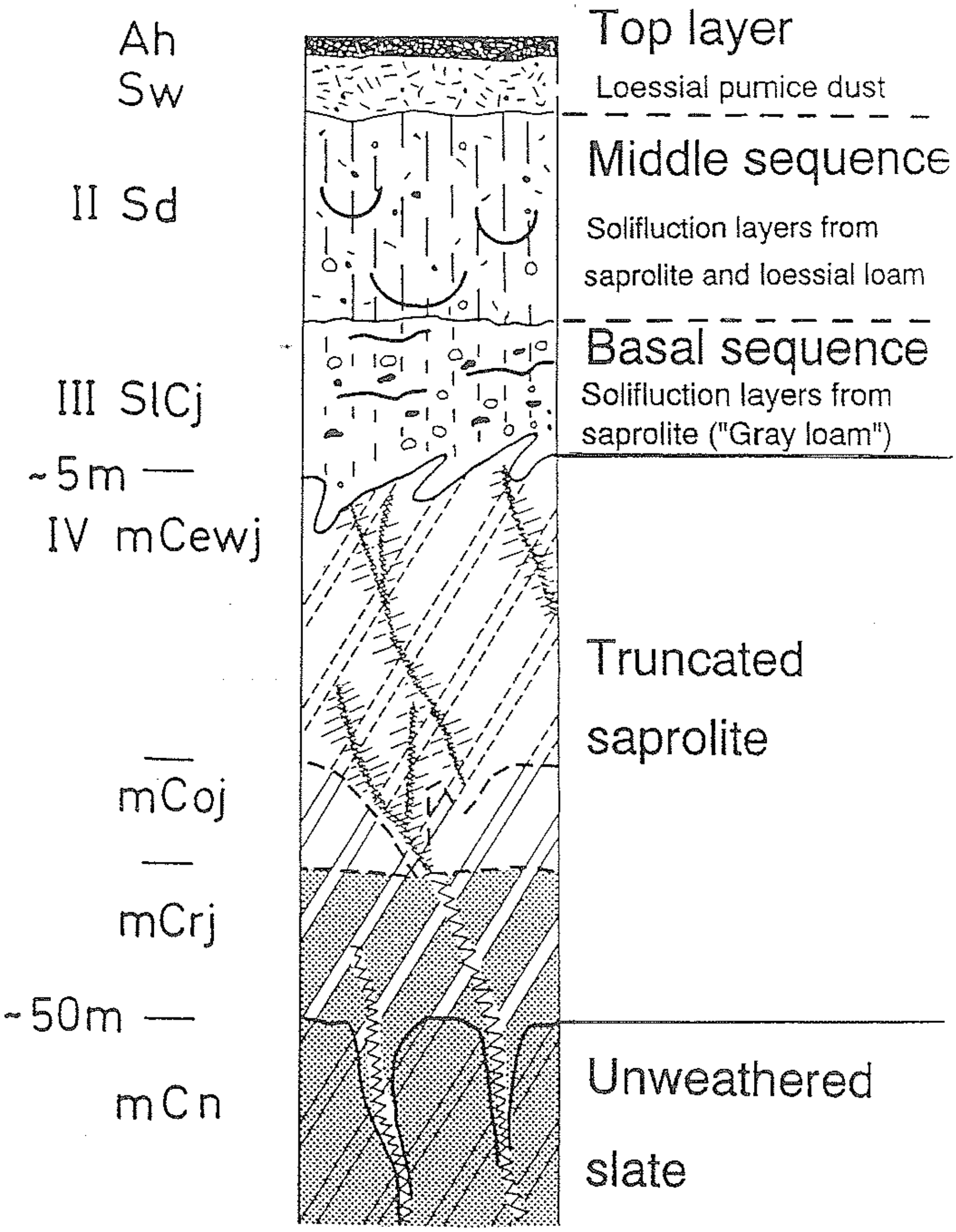


Figure 4: Vertical section of the partially eroded Mesozoic-Tertiary weathering mantle overlain by periglacial superficial layers (horizon symbols see fig.1)

Gray Loams can derive from diverse zones of the thick weathering mantle and they are not only related to the Tertiary landscape, but frequently cover slopes and bottoms of Pleistocene valleys. Therefore, the importance of Gray Loams for morphogenetic and paleoclimatic statements is rather limited. The investigated soils from the Quaternary superficial layers belong systematically to the soil types of Pseudogley (FAO : Stagnic

Luvisol or Cambisol) and Brown Earth-Pseudogley (FAO : Cambi-Stagnic Luvisol) respectively.

In the Eastern Eifel area of Quaternary volcanism, as well as more seldom in areas of Tertiary volcanism, postvolcanic activity still recently occurs. It is characterized by mofettes. Some of them raise mineralized thermal waters with a temperature between 8 - 30° C. Iron ochre in the surrounding of CO_2 springs consists of ferrihydrite and carbonates, which derive from hydrothermal alteration of the Fe-Mg-chlorites in the slates.

In these areas as well as in areas of deep tectonic faulting and of Tertiary volcanism narrowly extending zones of deep kaolinization are reaching far below the base of Mesozoic-Tertiary weathering. They developed by hydrothermal alteration due to hydrolytical activity of thermal CO_2 waters and show no mineralogical depth gradient. According to the absence of oxygene, altered slates display the same gray colour as the fresh slates. Neo-formation of smectite, kaolinite and especially of dickite from primary chlorite are the mineralogical characteristics. While primary quartz veins in the deeper parts of the alteration zones were subject to dissolution, neogenic quartz occurs as coatings in joints of sandstones near the surface. Also the Mesozoic-Tertiary weathering mantle was subject to hydrothermal alteration and characterized by the occurrence of veins of kaolinite-dickite and secondary quartz.

Quaternary basalt dikes crossing the kaolinitic saprolite frequently show characteristics of "autohydrothermal" alteration due to the transformation of basalt into pure smectite.

2 Excursion areas

The excursion area "Northeastern Eifel" (Nordosteifel) is situated in the declination zone from Northeastern Eifel to the Lower Rhine Embayment. The area encloses the territory of the Ahrberge south of Bad Neuenahr and the territory north of the lower Ahr up to Bonn. The Eastern border is the Rhine river and in the West the line between the villages Mayschoss and Meckenheim.

The excursion area "Eastern Hunsrueck" (Osthunsrück), situated in the Southeast of the Rhenish Massif, left of the river Rhine, is bordered in the South by the Soonwald, in the East by the river Rhine, in the North by the river Moselle and in the West by the ridges of Hochwald and Idarwald. The highest elevations of this flat upland area are between 450 and 500 m a.s.l.

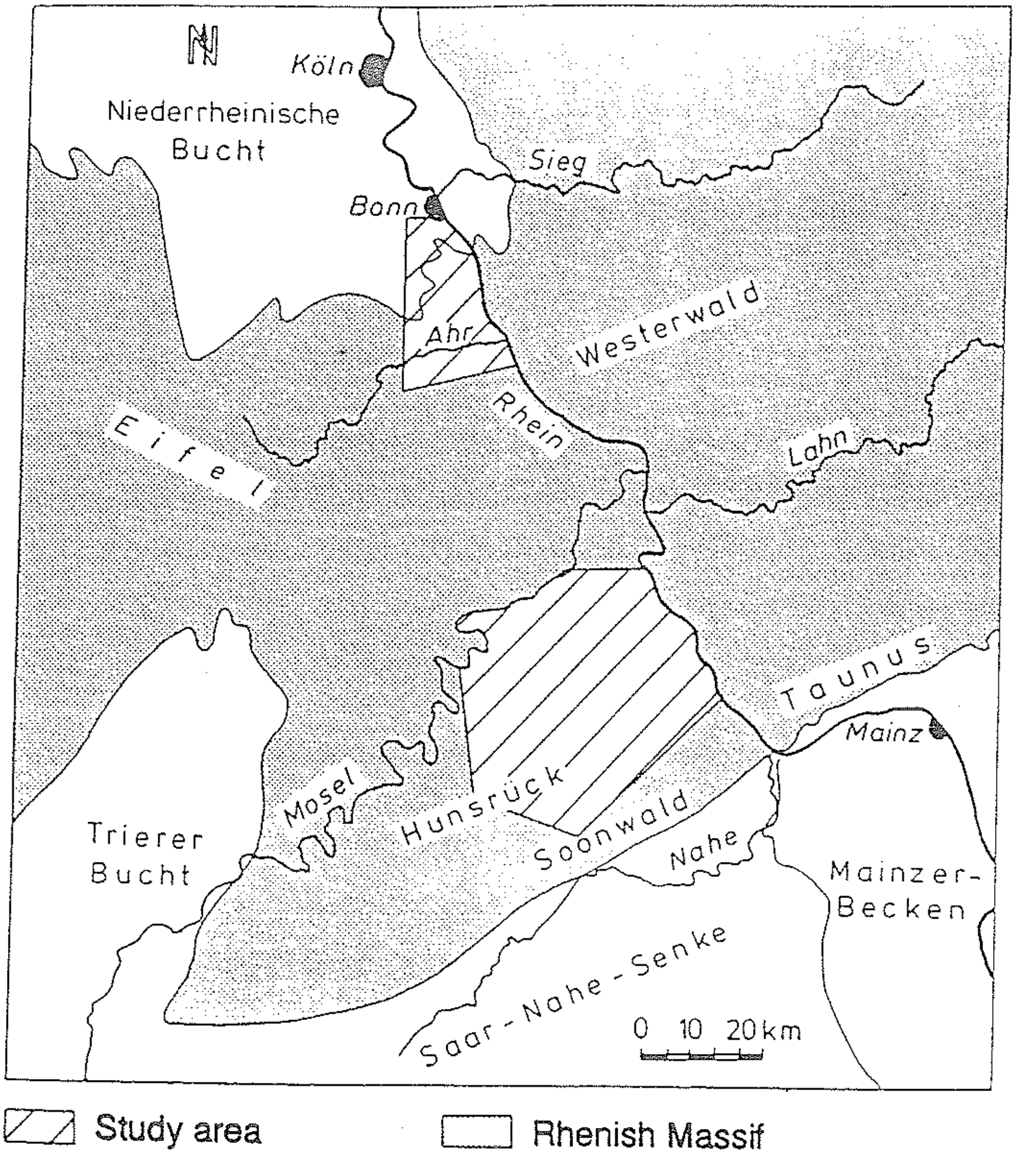


Figure 5: Excursion areas in the Rhenish Massif

2.1 Northeastern Eifel

Stratigraphically the Lower Devonian rocks of the Eifel and the Rhenish Embayment belong to the Middle and Upper Siegennian layers. Fresh Lower Devonian clay and silt slates and sandstones occur in the lower part of steep slopes of the V-shaped valleys of the Ahr and the Rhine, forming the parent rocks of vineyard soils. Their areal extent is of no importance in this territory. In the mountainous region South of the Ahr, Rankers (FAO: Dystric Leptosols) an decidic Brown Earth (FAO: Dystric Cambisols) developed from fresh rocks on higher mountains and crests where Mesozoic-Tertiary weathering relics are extensively denuded.

Exposures of the Mesozoic-Tertiary weathering mantle in the Ahr valley and the transition area from the Northeastern Eifel to the Lower Rhine were investigated.

Quitzow (1978, 1982) designated that part of the region as the "more distant Lower Rhine Embayment" and its Eastern part as the trough region of the Rhine river, which was formed by a flexure of the R1-peneplain in Upper Oligocene. Simultaneous with formation of the special flexure of the Rhine trough region, the MTV was settled. In the region between Bad Neuenahr and Lohrsdorf the bleached saprolite occur at 190 - 170 m a.s.l. Similar weathering products were found in exposures (80 m a.s.l.) in the Ahr valley near Sinzig, 6 - 8 km further East.

Block faulting with formation of tilted blocks and fault troughs has started during the Upper Oligocene. The flat up to undulated relief of the excursion area was formed by Tertiary peneplanations, filling up trough regions with Tertiary sediments, Pleistocene deposition of the main terrace of the Rhine river and processes of deposition and solifluction of loess . The fluviatile incision of rivers during the Pliocene and the Pleistocene was not very intensive.The recent relief shows only a slightly changed relief formed by peneplaination at the end of the Miocene (QUITZOW 1978). According to the low erosion activities a denudation of the weathering mantle was only slightly given.

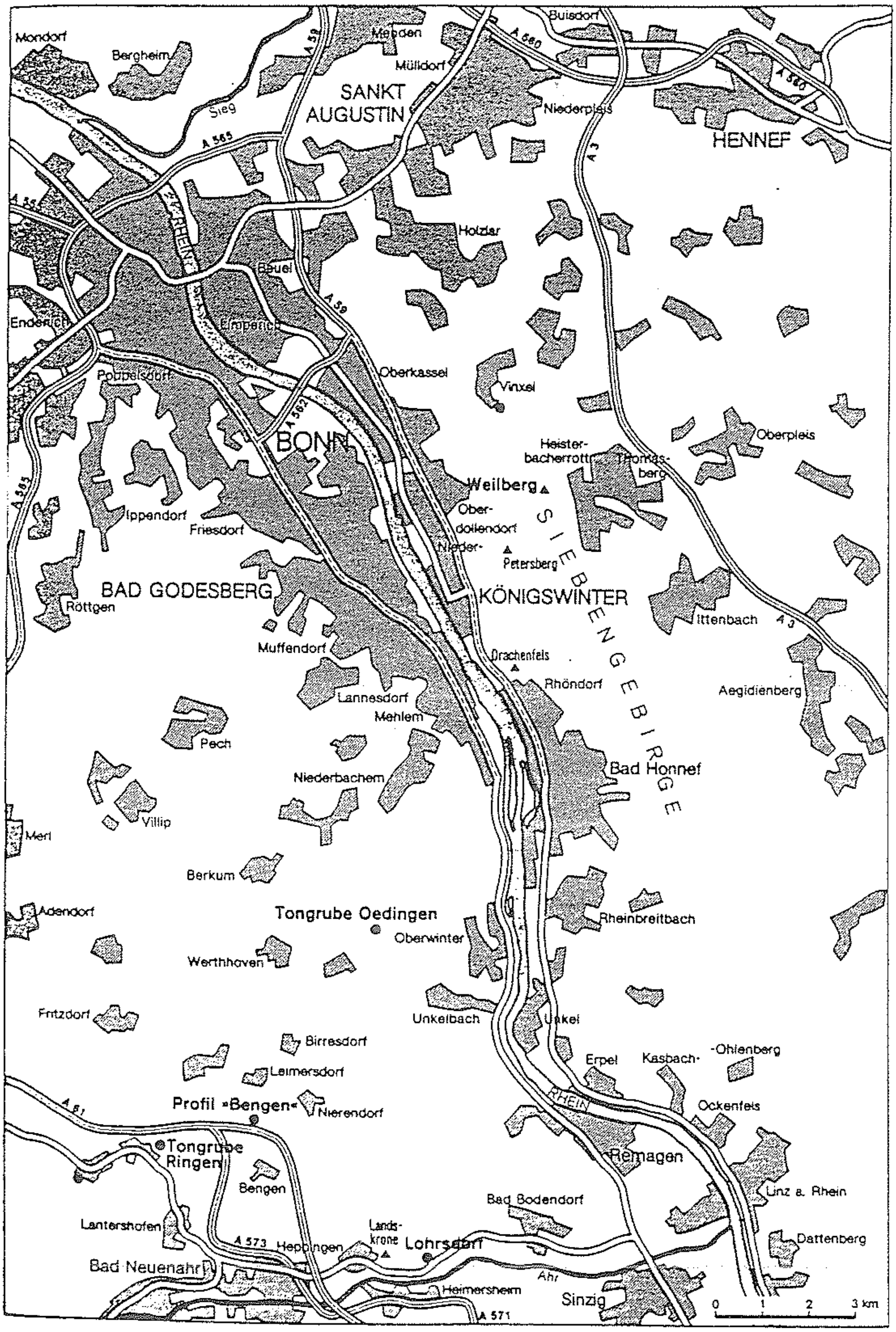


Figure 6: Excursion sites in the Northeastern Eifel

The weathering mantle is build up of kaolinized rocks, marked by bleaching. RAUFF & KEGEL (1923), EBERT (1939 a, b) and QUITZOW (1978) emphasizes the thickness of the MTV in comparison to other regions of the Rhenish Massif. Except for small areas between the villages Ringen and Lantershofen, autochthonous residuals of a Tertiary solum above the saprolite were not found. A field in the North of Niederich village was named 'Auf der roten Erde' (on red earth) (r 25 79600, h 56 07200, Bl. 5408 Bad Neuenahr-Ahrweiler), showing the relict red Tertiary surface.This is because the loess cover is absent (URBAN 1983). Primary investigations on formation and classification of a fossil autochthonous Red Plastosol from a highway exposure near Bengen were carried out by FELIX-HENNINGSEN & WIECHMANN (1985).
In the excursion area the autochthonous weathering complex is covered with Tertiary volcanic rocks and sediments, forming stratigraphical time marks. Upper Oligocene trachyte tuffs of the Siebengebirge volcanism are interfingered by clayey and gravelly Tertiary sediments (SPIES 1986), which are denudation products of the weathering mantle. Gravelly to sandy deposits were stratigraphically classified as "Vallendarschotter" (gravels), deposited from the Upper Eocene to the Lower Oligocene (QUITZOW 1978, BIBUS 1980, BOENIGK 1980,1981, MEYER 1986, SPIES 1986). Silicified gravels, named "Tertiary quartzites", are spread over a great area along the North border of the Eifel and the Siebengebirge mountainous region (RAUF & KEGEL 1923, BURRE 1939, SPIES 1986). They give evidence of semiarid climatic phases (SOLLE 1966, QUITZOW 1969). Tertiary clays were sedimented in tectonic depressions. Embedments of trachytic tuffs verify the Upper Oligocene age of the basal layers. In the Lower Miocene lignite seams were formed in overlying beds. Investigations of SPIES (1986.) on a drill core of the clay pit "Ringen", showed that the Tertiary sediments lie directly on the saprolite. Complete kaolinization of the embedded trachytic tuffs gives evidence of a syn-sedimentary weathering-intensive climate.

In the investigated area Tertiary weathering formations were overlaid by a up to several metres thick Pleistocene layer, consisting of solifluidal loessial loam and eolian loess. Dominating soil types are Parabraunerden (FAO: Luvisols), and Parabraunerde-Pseudogleys (FAO: Stagnic Luvisols), and in erosional positions Pararendzinas (FAO:Calcaric Regosols). Therefore, soil maps of the region (MÜCKENHAUSEN & WORTMANN 1958, SCHNEIDER 1983, STÖHR 1966 a) give only fragmentary informations on the range of Tertiary weathering. References to the distribution of Tertiary weathering products in this area are in the geological maps of EBERT (1939 a,b, sheet Altenahr and sheet Ahrweiler) and of AHRENS (1939, sheet Linz).

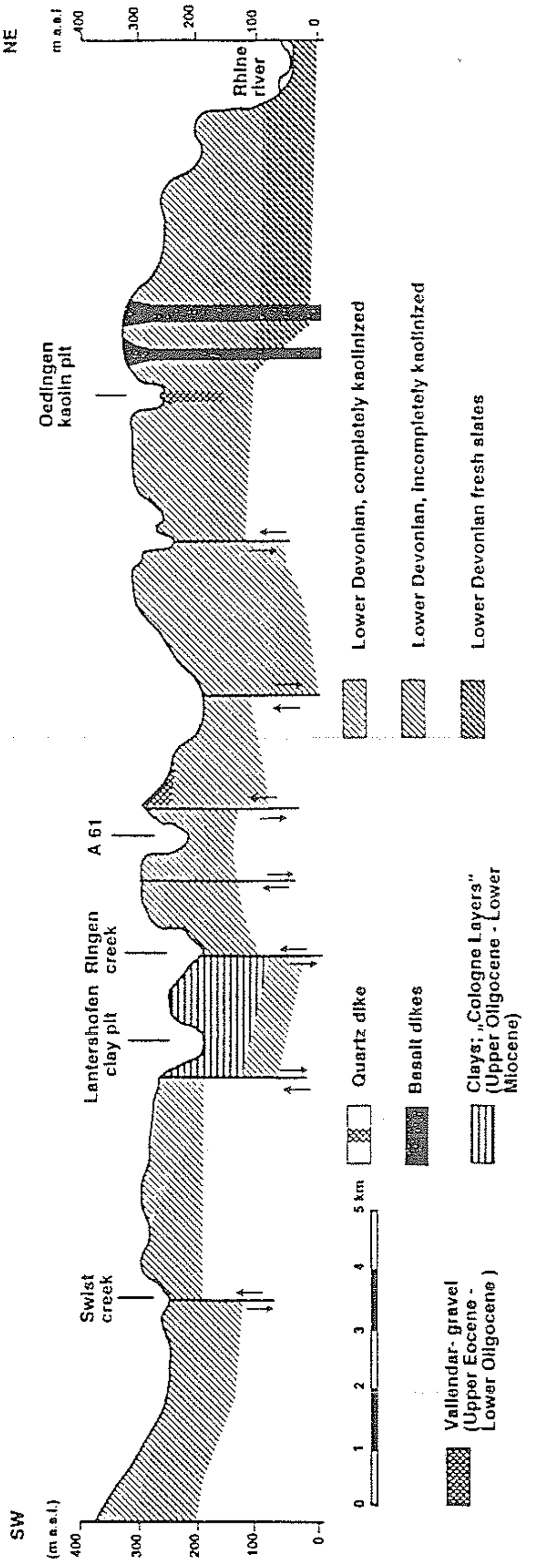


Figure 7:Landscape section of the Northeastern Eifel study area (after SPIES 1986)

In the West of the studied area kaolinized weathering products are represented on the map when the thickness of the loess cover is small. Pseudogleys (FAO:Stagnic Gleysols) and Braunerde-Pseudogleys (FAO: Stagnic Cambisols) are the typical soils of that region, because redeposited kaolinitic material forms a impermeable layer in the solum of the recent soil. MÜCKENHAUSEN et al. (1971) realized investigations on the genesis of Pseudogleys (FAO: Stagnic Gleysols) in that area. SCHULTE-KARRING & SCHRÖDER (1986) were engaged in subsoil melioration of agriculturally used soils.

Also in the adjacent Eifel mountainous area recent soils have developed in large areas in redeposited substrata of the MTV. MÜCKENHAUSEN (1950, 1951, 1953) mapped "Grey Loams" on the sheets Altenahr, Aremberg, Blankenheim and Röttgen.

In several areas of the Eastern Eifel volcanism a vertical zonation of the weathering mantle, according to decreasing rock weathering and kaolinization with increasing depth is not evident. Around recent mofettes as well as in areas of deep tectonic faulting and of Tertiary volcanism narrowly extending zones of deep kaolinization are reaching far below the base of Mesozoic-Tertiary weathering. In such situation it is questionable to assign the kaolinite by Mesozoic- Tertiary weathering processes. Investigations of SPIES (1986) showed that the alteration zones are relatively thin and linear with a width from several metres to some hundred metres. SPIES (1986) analysed the decomposed rocks from the thermal water boring "Walpurgisquelle" near Bad Neuenahr. He found kaolinitic alteration of the Lower Devonian rocks up to a depth of 345 m. In other regions of the Ahrtal decomposed, kaolinized rocks were found to depths far below the MTV base. This excursion visits a mofette area in the Wehr caldera of Middle Pleistocene age. Rock decomposition and kaolinization reaches down to more than 500 metres.

At the beginning of this century the processes of weathering and pedogenetic kaolinization were not well known. Therefore, on the basis of the geological knowledge about volcanism, post volcanic activity and alteration of rocks in the surrounding of thermal springs discussions among geo-scientists are concerned about the hydrothermal or weathering genesis of the MTV.

Recently, a lot of CO_2 springs exist in the Eastern Eifel area. The ascending water decomposes the rocks along the joints. There from a mineralization of water and the kaolinization of the rocks result. The mofettes raise mineralized thermal, carbonic acid waters with a temperature between 10° - >30° C. The temperature depends on the speed of ascent and extent of jointing of the slates respectively. CO_2 is released from magma in consequence of cooling down of volcanic chambers in some km depth and ascends within joint systems (ULRICH 1958). The contact with descending meteoric ground water in about 1 - 3 km depth leads to the formation of carbonic acid with low pH due to the high pressure. The temperature increases according to the geothermy (HUMMEL 1930). The decreased specific weight of the water leads to ascent, while the slates beside the ascent path are subject to hydrolysis and neo-formation of minerals. Therefore, the waters become mineralized, mainly with Fe and Mg as cations released from the primary Fe-Mg chlorite. Small amounts of Na and sulfate are supposed to derive from migration of saline waters in deep joint systems from marine deposits of the Lower Rhine Embayment (FRESENIUS & KUSSMAUL 1985). Carbonic acid springs are situated at the valley bottoms and basins, exploited in wells and borings (e.g. in the Ahr valley) by the mineral water industry. At some places of the Rhenish Massif dry mofettes occur beside springs for example as in the Wehr caldera. Iron dross in the surrounding of CO_2 springs consists of ferrihydrite and carbonates, which derive from hydrothermal alteration of the Fe-Mg-chlorites in the slates. Beside the unusual depth and absence of a vertical zonation, alteration zones with characteristic mineral neo-formations are recognizable. According to the absence of oxygene, altered slates display the same gray colour as the fresh slates. Neo-formation of smectite, kaolinite and especially of dickite from primary chlorite are the mineralogical characteristics. The distribution of smectite and kaolinite within the alteration zones is in accordance with the rock permeability. In less permeable parts, mainly banks of clay slates, kaolinite ocurs near the joints while smectite was formed in some distance from joints, where the exchange of the pore solutions was very slow. Beside kaolinite the 7 A mineral dickite was found. Dickite is an indicator of rock decomposition by ascending thermal water because it cannot be formed in weathering environment and it is absent in the fresh slates.

It occurs together with kaolinite of high crystallinity in white monomineralic (7 A) veins. The differences in thermal stability allow an easy discrimination between dickite and kaolinite. While the crystal lattice of kaolinite collapses at temperatures above 520° C, dickite remains stable to temperatures > 600° C. While primary quartz veins in the deeper parts of the alteration zones were subject to dissolution, neogenic quartz occurs as coatings in joints of sandstones near the surface. In the reducing environment of the alteration zones siderite and other carbonates were found.

The MTV was already formed when the postvolcanic activity in the Upper Oligocene began. In consequence a superimposition of the weathered rocks by ascending weathering processes was possible (SPIES 1986). The section selected for analysis of the MTV in this area did not reveal any action of ascending water.

2.2 Eastern Hunsrück

The basement rocks of Lower Devonian age were folded by Variszian orogeny and consist of non-calcareous silicatic rocks.

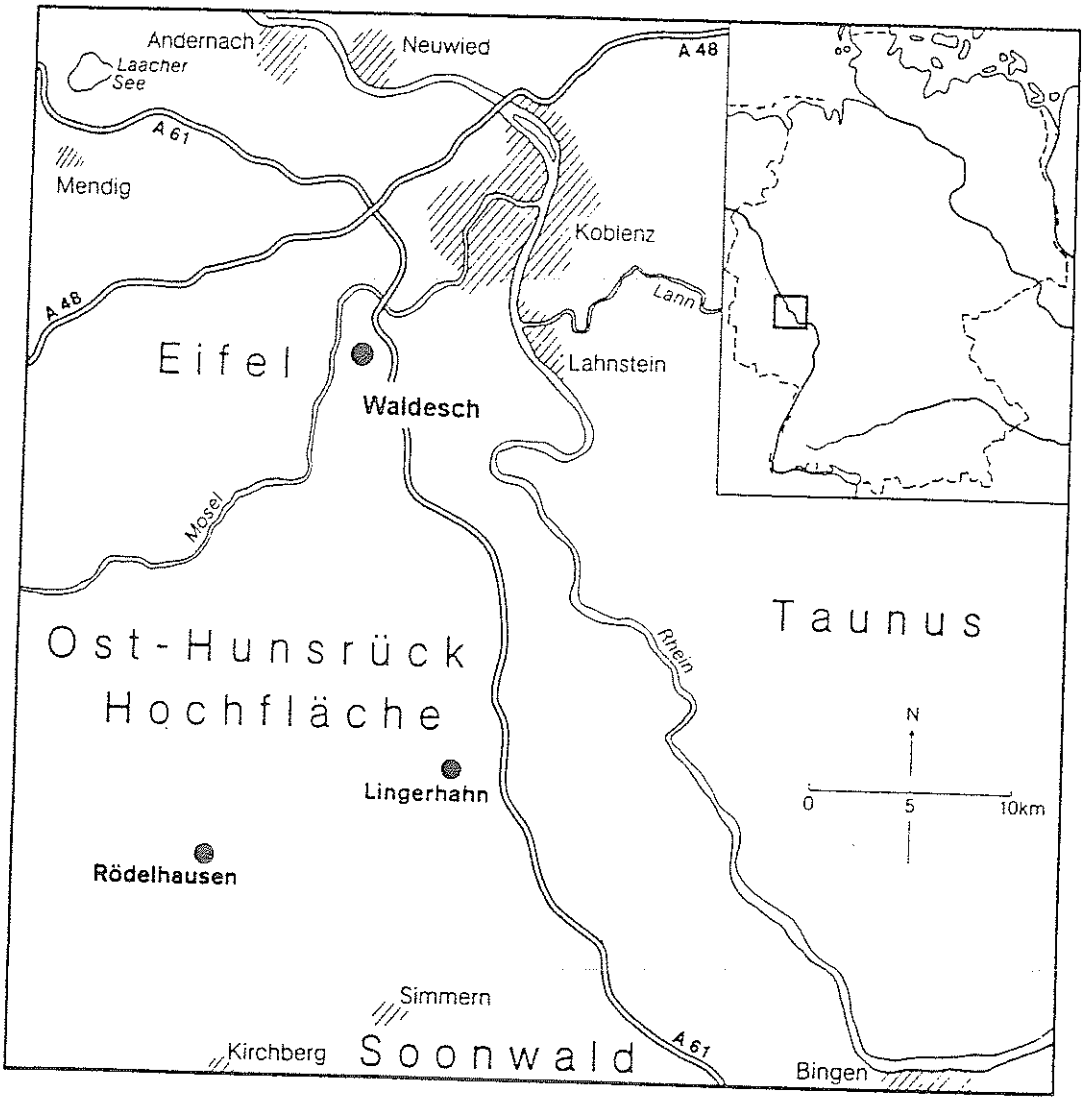


Figure 8: Excursion sites in the Eastern Hunsrück

Dark gray silt/clay slates predominate among graywackes, sandy and partly quartzitic slates and quartzites. Since Late Paleozoic these rocks have been subject to continental weathering and removal.From Upper Mesozoic to Lower Tertiary, a time of relatively less tectonic movements, a peneplain with a thick weathering mantle was formed by deep and intensive chemical weathering under tropical or subtropical climate. The kaolinization of the Devonian rocks exceeded a depth of 50 m. In the Eastern Hunsrück area relics of this kaolinized weathering mantle are widely spread and were early recognized by the mapping geologists as a separate geological formation.

In the Upper Middle Oligocene a marine transgression of short duration reworked the soil zone in the upper part of the weathering mantle. The few relics of Lower Tertiary clays, sands and gravels represent the dislocated weathering products.

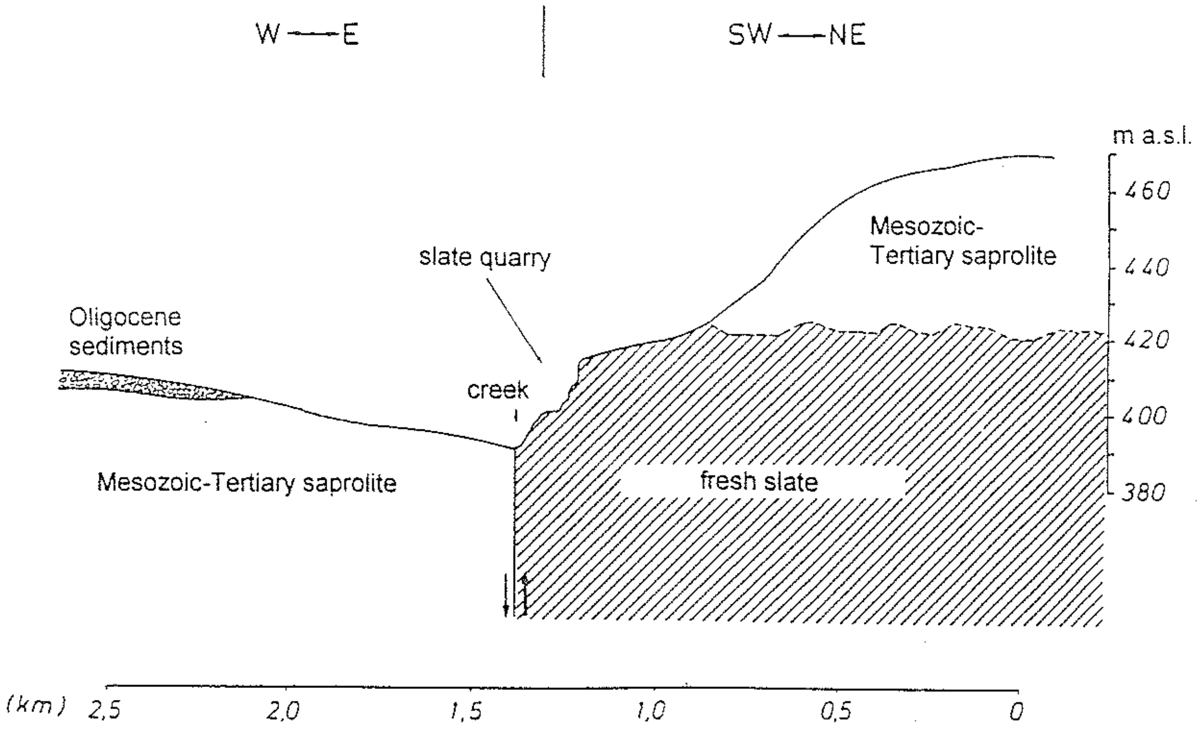


Figure 9: Eastern Hunsrück - cross section of the Alterkülz creek valley as an example for an asymmetric valley due to block faulting; at the uplifted block fresh slates are exposed which then are mined for production of roof shingles

At the end of the Lower Tertiary the uplift of the Rhenish Massif began and went on during Upper Tertiary and Quaternary till today. In the Eastern Hunsrück area warping and faulting connected with this uplift were relatively weak. The central part suffered a weak up-arching together with flexure-like bending and less fault tectonics. The perpendicular throws of the faults are mostly far below 50 m. In the Upper Tertiary the river systems of Rhine and Moselle already began to develop. In spite of increasing removal as a consequence of uplifting, the kaolinitic weathering mantle may have covered the whole Eastern Hunsrück area at the end of Tertiary, because the tropical to subtropical climatic conditions lasted up to the Pliocene and caused a permanent reformation of the partly denuded weathering zone.

With the beginning of the Pleistocene, about 2 mio. years ago, climate and morphogenesis began to change in a distinct way. The latter was considerably intensified by the strengthened and sometimes jerking uplift of the Rhenish Massif. The Eastern Hunsrück area,like the whole Rhenish Massif, was a periglacial region during ice age. The permafrost soil of the treeless tundra was subject to mechanical weathering by frost splitting. During the yearly melting periods the congelifractates were transported downhill by solifluction. That way, the big streams such as Rhine and Moselle incised deeper and deeper into the basement, the tributaries forced their way onward to the watersheds of the flat upland areas. Their V-shaped valleys undercut the old weathering mantle and dissected the formerly continuous peneplain into many smaller relic plains. In the more deeply incised valleys the fresh Devonian rock was exposed. On the relict plains the pre-Pleistocene soils were largely removed by intensive erosion and denudation, and only the more or less thick parts of the saprolite zone remained.

During the cold periods - at least during Wuerm glacial period - the whole area was covered by loess, which in the interglacial periods changed to loessial loam by soil formation. In the following cold period it was subject to redeposition by fluvial or solifluction processes. Therefore, talus deposits mostly contain a loessial component.

In the late Würm glacial period, at the end of the Alleröd interstadial, the "Laacher See"-volcano had an extremely gas-rich eruption, which was accompanied by an extrusion of pumice up to the Northern part of the Eastern Hunsrück. Due to subsequent eolian drifting of the pumice during the cold Younger Tundra Period the loessial pumice dust arose and was spread as a thin cover over the whole Eastern Hunsrück area. After sedimentation of this dust layer, it was partly redistributed by solifluction. Most of the recent soils of this area contain this layer in their uppermost 20-40 cm.

With beginning Holocene the influence of the cold ice age periods ended and the now existing landscape scenery changed only little more. Bottom clays, alluvial cones and gravel layers in the valleys are the main deposits of the latest geological past. The thin loessial pumice dust layer was removed in wide areas with the beginning of agricultural use. Nowadays it remained mainly in soils of old forest habitats.

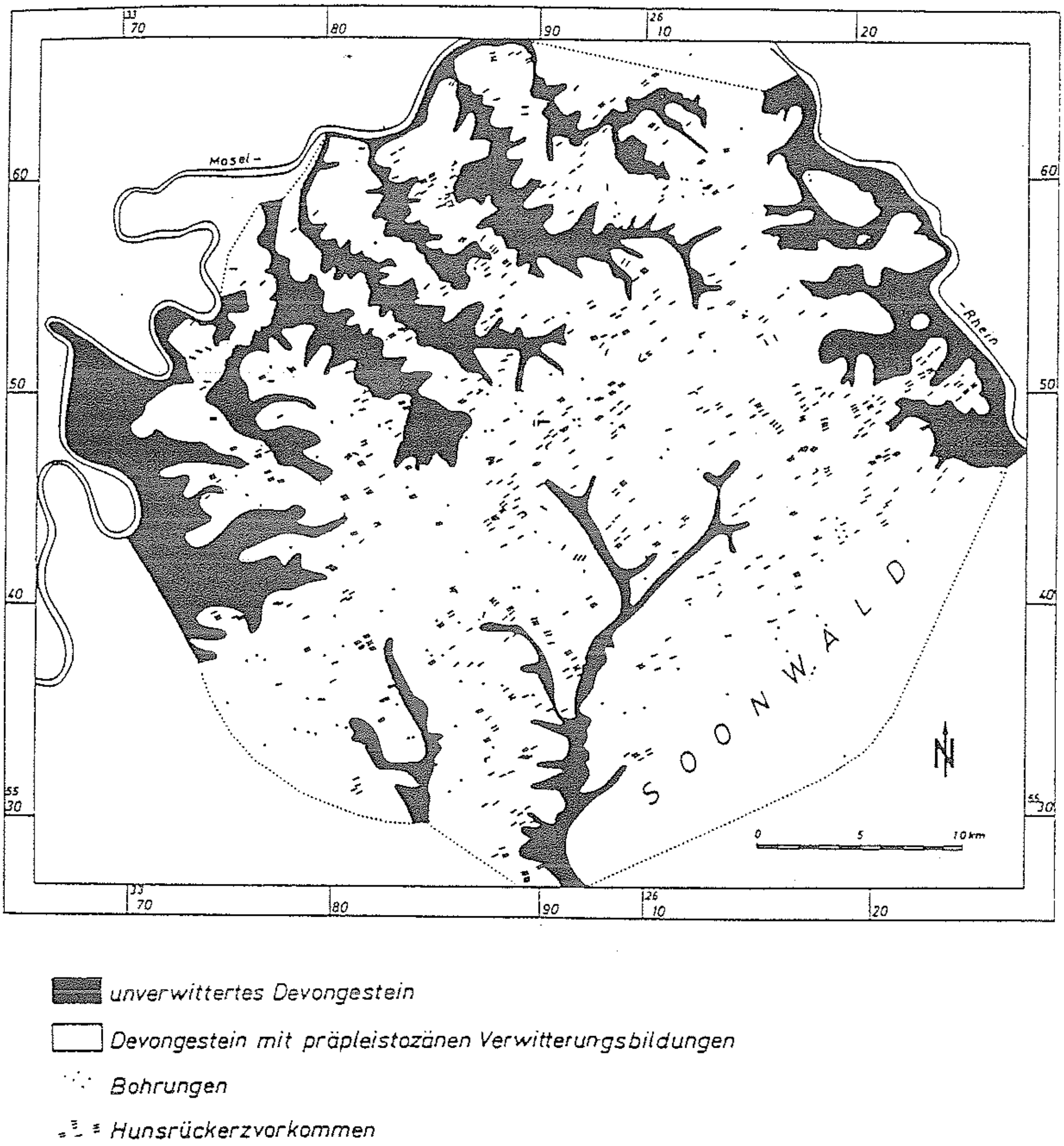


Figure 10: Range of pre-Pleistocene weathering products (without further differentiation) in the Eastern Hunsrück (SPIES 1986)

3 Climate of the Rhenish Tertiary

Investigations on palaeosoils always raise the question on climate-formation conditions. Since 1968 SCHWARZBACH evaluated all of the known inorganic and biological indicators of climate. He stated that since the Eocene the temperature curve decreases more or less regularly. Climatic oscillations were predominantly marked by arid periods. Already in the Middle Tertiary the climate was warm temperate, subtropical but very humid. The bauxitization and ferrallitization of the Miocene basalts of the Vogelsberg are not contrary to this interpretation because they were promoted by the substratum. Comprehensive investigations of EHRLICHMANN & DONGUS (1981) confirm the general decrease of temperature beginning from old to young. Three maxima of heat - in the Eocene, the Helvetian (Lower Miocene) and the Sarmatian (Middle - Upper Miocene) were identified. The latter was humid up to semihumid (GREGOR 1980) and was assigned the type "Cfa" (according to Köppen). In the Lower Sarmatian this "Virginian" climate was considerably poorer in precipitation and, possibly, even dry in winter.

At the famous fossil deposit in Rott at the Northern decline of the Siebengebirge mountainous area there is the only possibility to get more information about the climate after the deposition of the trachytic tuff mantle of the Siebengebirge volcanoes. The so-called "Rott-Formations" cover the tuff. They are deposits of a fresh-water lake. It is located only a few kilometres from the coast of the Upper Oligocene sea, coming from the Lower Rhine Embayment. The sediments are almost 30 metres thick and predominantly contain clays, "leaf coals" and brown coals. The diatomites give evidence of a supply of silicic acid from the deep weathering of trachyte tuff.

Important for the palaeoclimate are plant relics in the leaf coals. Structures like annual rings of pinus were also found in them. In consequence of this, SCHWARZBACH (1974) advocates a humid, warm temperate climate of the Upper Oligocene in Rott, as opposed to the recent climate. In his opinion the climate was about the same as it is today on Eastern borders of the continents (South-East of the USA, Japan, Central China, South-East of Australia).

4 Excursion sites

Stop 2 Lohrsdorf and Ahr valley

Site: *Vineyard path near Lohrsdorf, steep edge at 110 m a.s.l.*
TK 5409 Linz, r 25 74300 h 56 01050
Topics: *Fresh slates and weathering base of saprolite*

Summary

Above the base of weathering appears an at least 40 m thick zone with incomplete kaolinization of the primary chlorite, neo-formation of smectite and kaolinite with increasing contents upwards. Because of desilification smectite decreases in the upper zones where kaolinite dominates - partly next to residues of chlorite. Neo-formation of minerals occured in a formerly reducing environment under water saturation - joint ground water and adhesive water. In light gray, oxidized zones and dark gray zones the same contents of neo-formed minerals occur. During the Quaternary the oxidation of continous primary organic substance resulted in an olive-gray brigthening of the rock after its exposure due to valley erosion. The intensity of this process depends on the degree of weathering and the permeability of the slates. Therefore the oxidative brightening of the rock near the joints increases upwards. Some (deci-)meters within the rocks the black reduction zone is still developed without oxidation .

The intensity of the morphological and mineralogical changes of the slates and their downward advance depends on primary properties of rocks which are determined by permeability. Petrographic alternation of beds, jointing and the occurrence of quartz veins resulted in vertical boundaries between zones of different degrees of weathering, which are interlocked in the range of decameters.

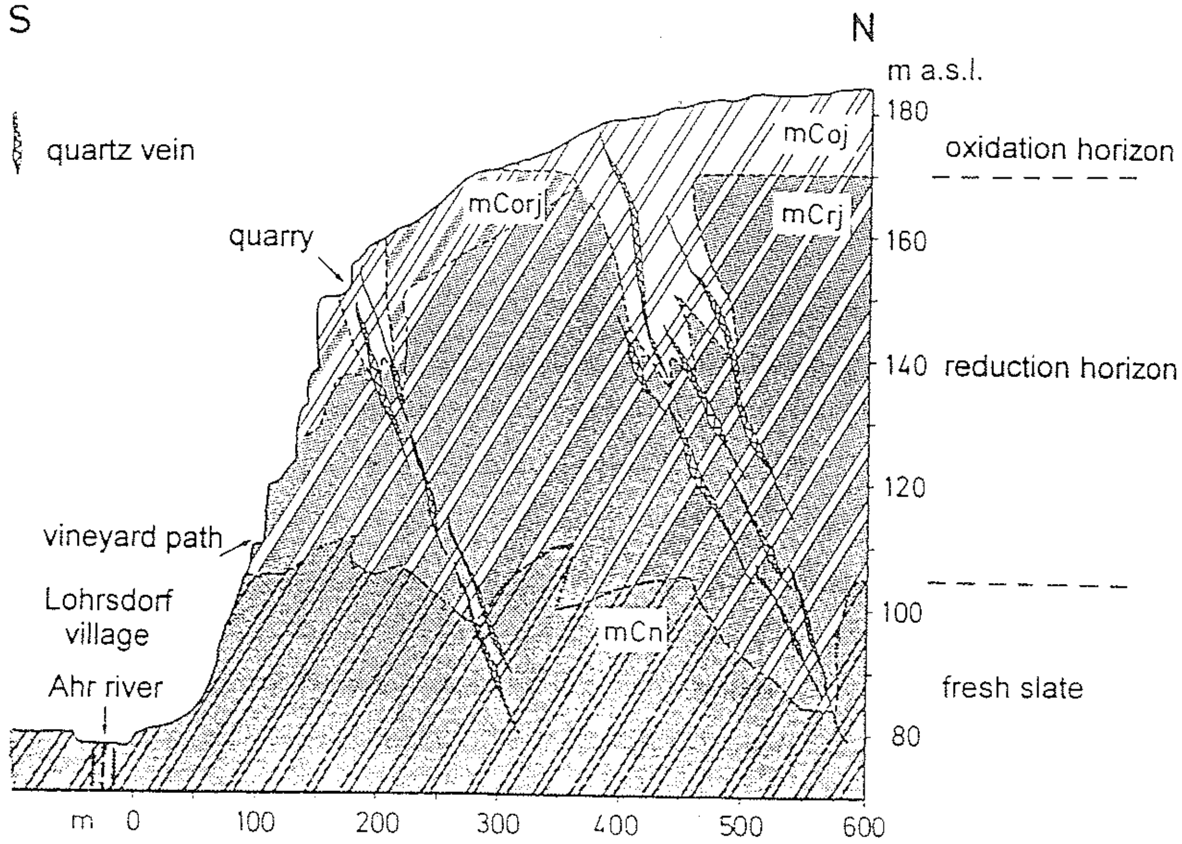


Figure 11: Ahr valley - cross section of the Northern slope near Lohrsdorf displaying the undermost saprolite zones (explanation of horizon symbols cf. fig. 1)

Description

Unweathered slates

Bulk density:

- 2,49 - 2,58 g/cm^3 in clayey slates of the Hunsrück area (Hunsrück slates), 2,67 - 2,69 g/cm^3 in slates of the Northeastern Eifel.

Specific gravity:

- 2,70 - 2,72 g/cm^3.

Qualitative mineral composition:

- muscovite: $KAl_2(AlSi_3O_{10})(OH_2)$
- Fe-Mg-chlorite (Fe-rhipidolithe): $(Mg^{2+}_{2,12}\ Fe^{2+}_{2,16}\ ME^{3+}_{1,72})\ (Si_{2,28}\ AL_{1,72})\ O_{10}\ (OH)_8$
- accessory minerals: pyrite, apatite, < 1 wt.-%
- heavy minerals: ultrastable group zircon, tourmaline, rutile

  coaly-bituminous organic matter: 0,3 - 0,5 wt.-% C

Quantitative mineral composition:

Table 1: Lower Devonian slates - approximate mineral composition (weight-%) of the clay fraction < 2 mm and the bulk sample; in sandstones the quartz content can increase up to 90 %

	clay fraction	*bulk sample*
muscovite/illite[1]	51 - 62	30 - 39
chlorite[2]	25 - 39	24 - 27
quartz[3]	8 - 12	36 - 46
feldspars[4]	traces	0 - 10

1: wt.-% K_2O x 10 (after FANNING & KERAMIDAS 1977: 208)

2: loss of weight after HCl+NaOH-extraction

3: quartz content (after TILL & SPEARS 1969)

4: feldspars as difference: 100 % - (% I/M + % Chl + % Q).

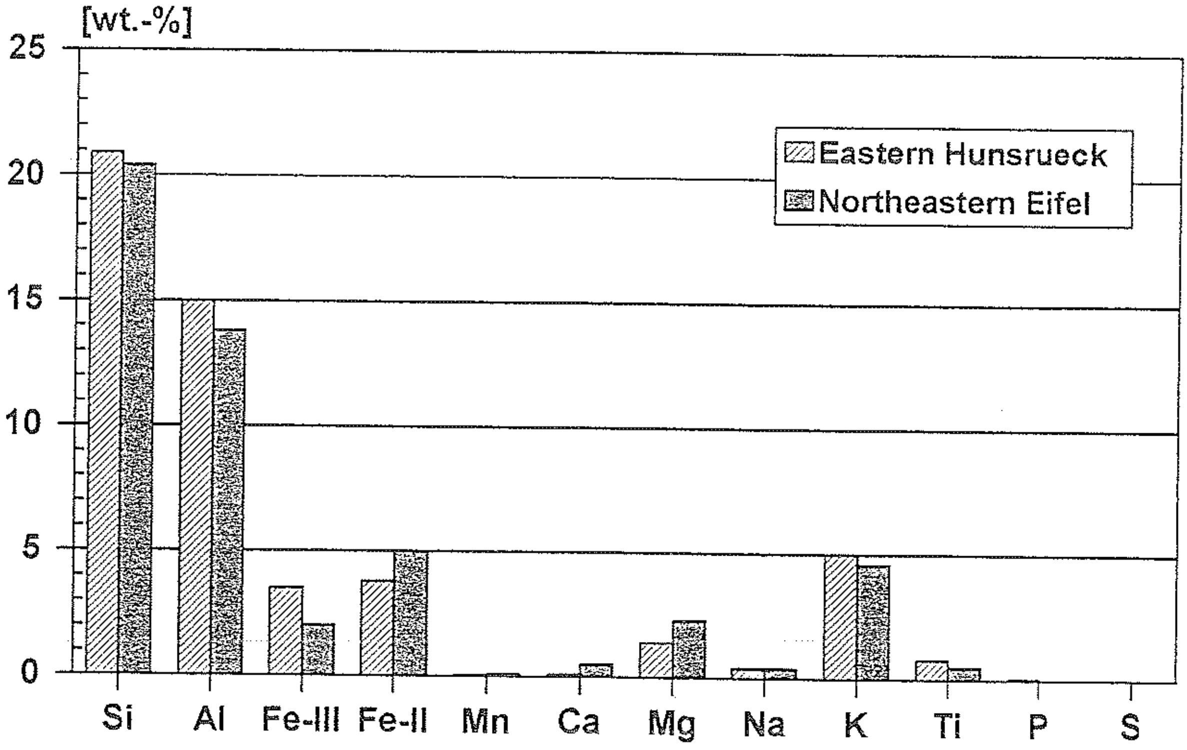


Figure 12: Fresh slates - amounts of elements of the clay fraction from fresh slates of the Northeastern Eifel and the Eastern Hunsrück (determined by XFA)

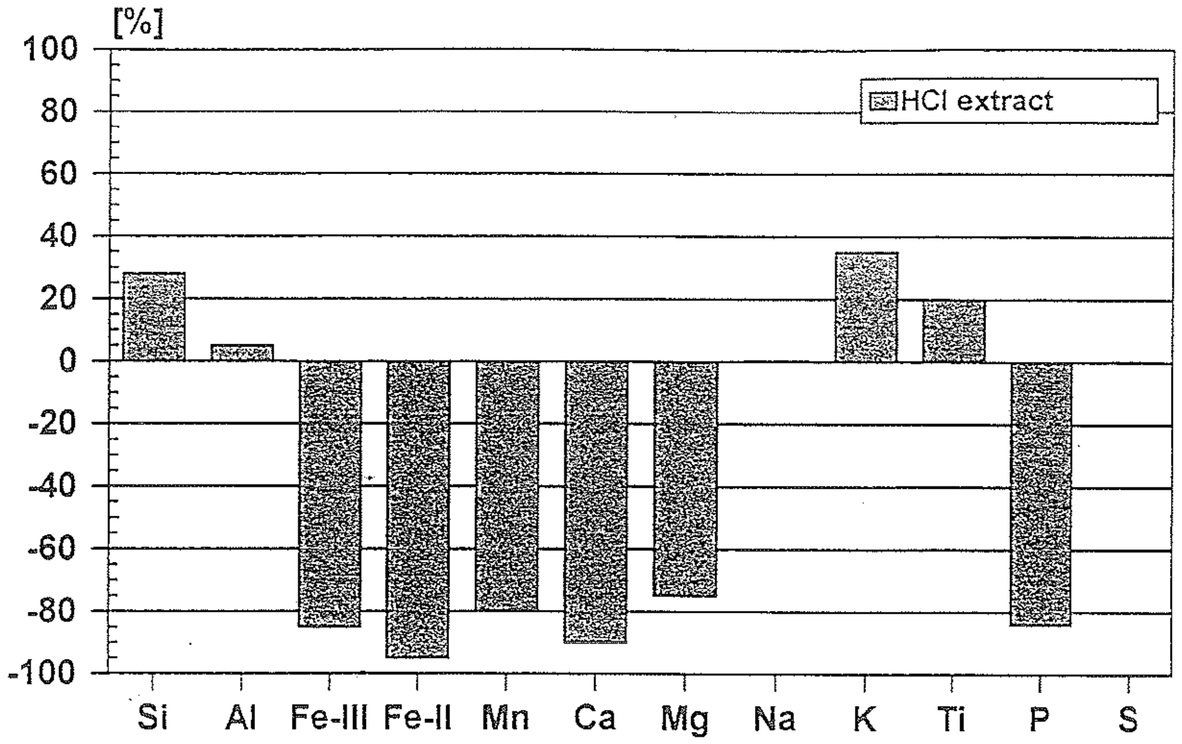


Figure 13: Fresh slates - relative differences between fresh slates and samples after HCl extraction; element losses due to extraction result from dissolution of primary Fe-Mg chlorite, element "gains" due to relative enrichment because of the mass loss of extracted chlorites

Base of weathering and reduction horizon

Morphological characteristics:

mCn and: mCrj	steep standing and slightly jointed black-gray (10 Y 4/1), fresh clay slate
mCorj:	black-gray clay slate of the reduction zone, brightening of rock by oxidative decomposition of organic matter with olive-gray (10 Y 5/2) zones, which extend just a few mm to cm from the joints into the massive slate ground mass; upwards increasing oxidation; areas with quartz veins and sandy slates are predominantly light olive-gray (7,5 Y 5/2 - 6/2) coloured, although they still show diffuse limited black-gray (7,5 Y 4/1) and olive-gray (7,5 Y 4/2) spots and zones. Slate and joint planes show some thin black and rustybrown oxide coatings. Quartz veins show solution cavities and in contrast to quartz veins of the higher oxidation zone of the saprolite, they are not incrustated with Fe-oxides.

Mineralogical changes:

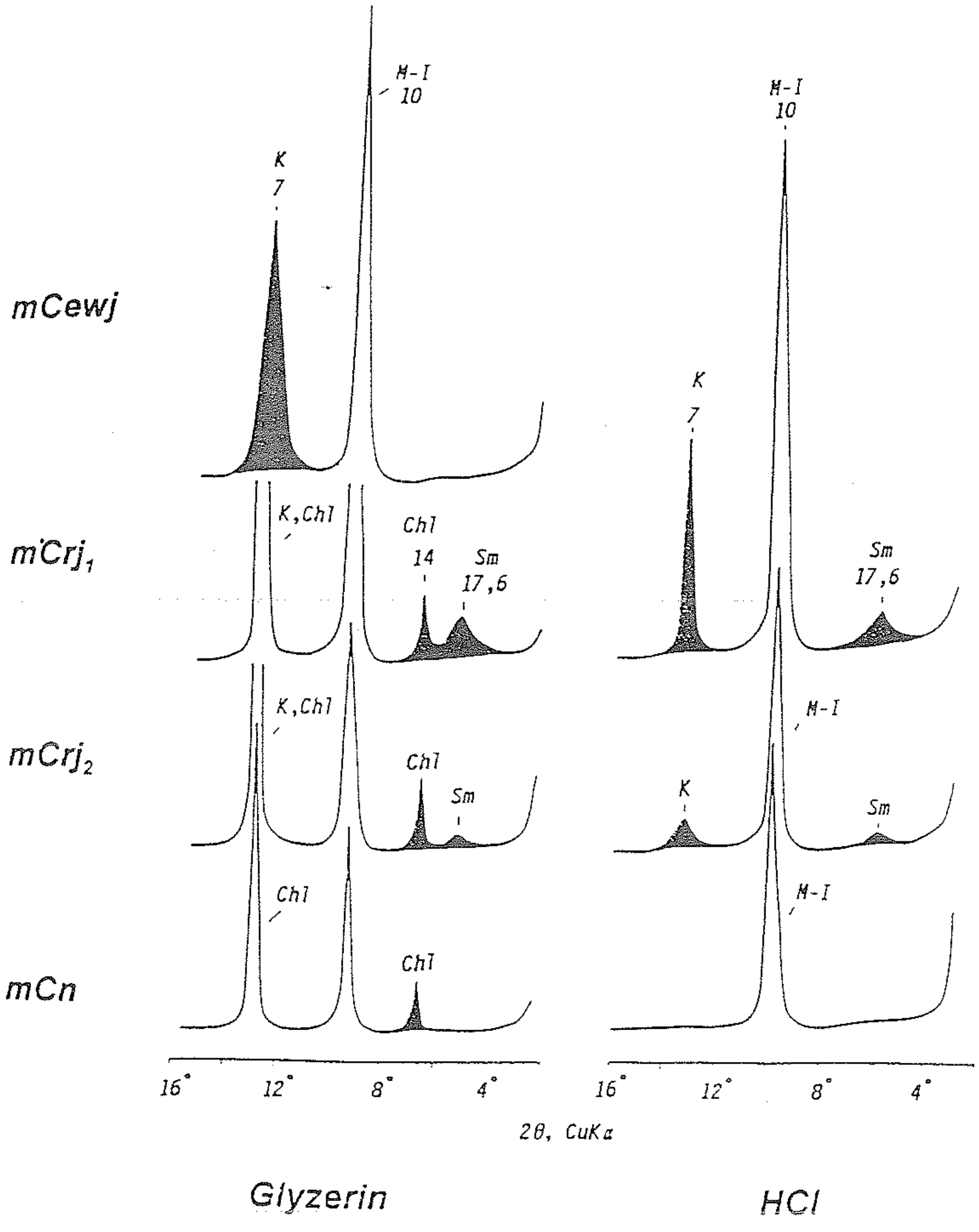


Figure 14: Mineralogical changes of the fresh slate (mCn) in the reduction zones (mCrj) and in the bleached saprolite (mCewj); example from the Eastern Hunsrück, site "Wahlbach" (K=kaolinite, M-I=muscovite-illite, Sm=smectite, Chl=chlorite)

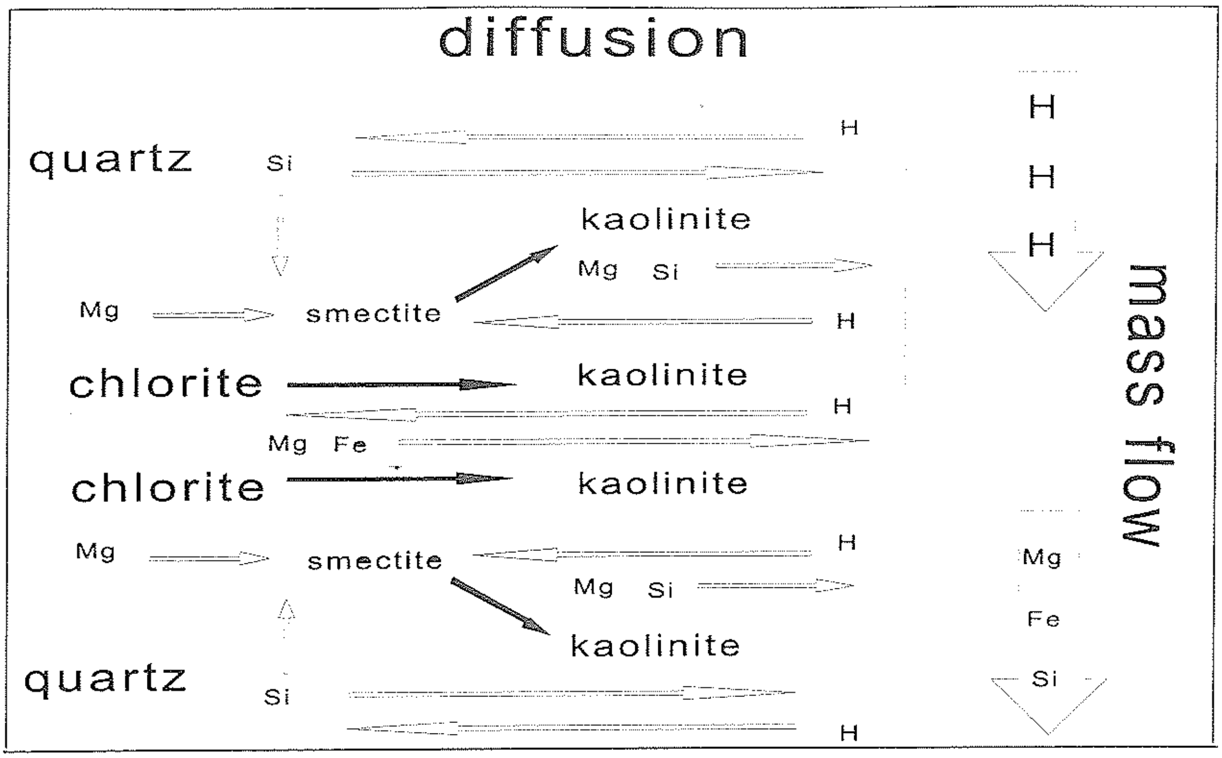


Figure 15: Scheme of the neo-formation of kaolinite and smectite in the reduction zone of the Mesozoic-Tertiary weathering mantle

Stop 3 Kaolin pit Oedingen/Oberwinter

Site: *Open kaolin mine pit of Erbslöh & Co., plant Oberwinter, 233 m a.s.l. TK 5309 Königswinter, r 25 82775 h 56 09150*

Topic: *Upper saprolite zones of the Mesozoic-Tertiary weathering mantle, transition from the reduction to the oxidation zones; genesis, geochemistry and mineralogy*

Summary

In the open mine pit of Oedingen the autochthonous saprolite is exploited for the kaolin industry. In a nearby plant in Oberwinter village at the Rhine river the saprolite is ground and dispersed in water. After sedimentation of the quartz sands the clay and silt fractions, enriched in kaolinite, are separated by filter pressing.

A big quartz dike in the saprolite of the Lower Devonian age crosses the pit. Due to the solution of quartz veins and formation of tectonic faults in silicified slates joining the quartz dike, oxidation could penetrate very deep into the saprolite with a decrease of ground water level during the Upper Tertiary. This led to the formation of a white bleached kaolinitic saprolite, because the leaching of silica, bases, and oxidizable metals already occurred under reducing conditions due to ground water saturation and migration. Isovolumetric balances show that in consequence of leaching during saprolite formation the slates nearly lost 30 % of their initial weight. Therefore, they gained a pore space in the same rate.

Kaolinite was neo-formed from primary Fe-Mg chlorite as well as from illites of the 10 A-fraction (= illite + muscovite). Leaching of potassium proves a loss of about 30 % of the initial amount of 10 A minerals. 90 % of the kaolinite is of b-axis disordered type, which directly developed from chlorite. Only 10 % are of "fireclay mineral" type, which shows an intercalation disorder, because an intercalation with Dimethylsulfoxide is not possible. Hinckley index varies with the texture of the saprolite. Kaolinites from sandstones display a higher index than those of clay or silt saprolite.

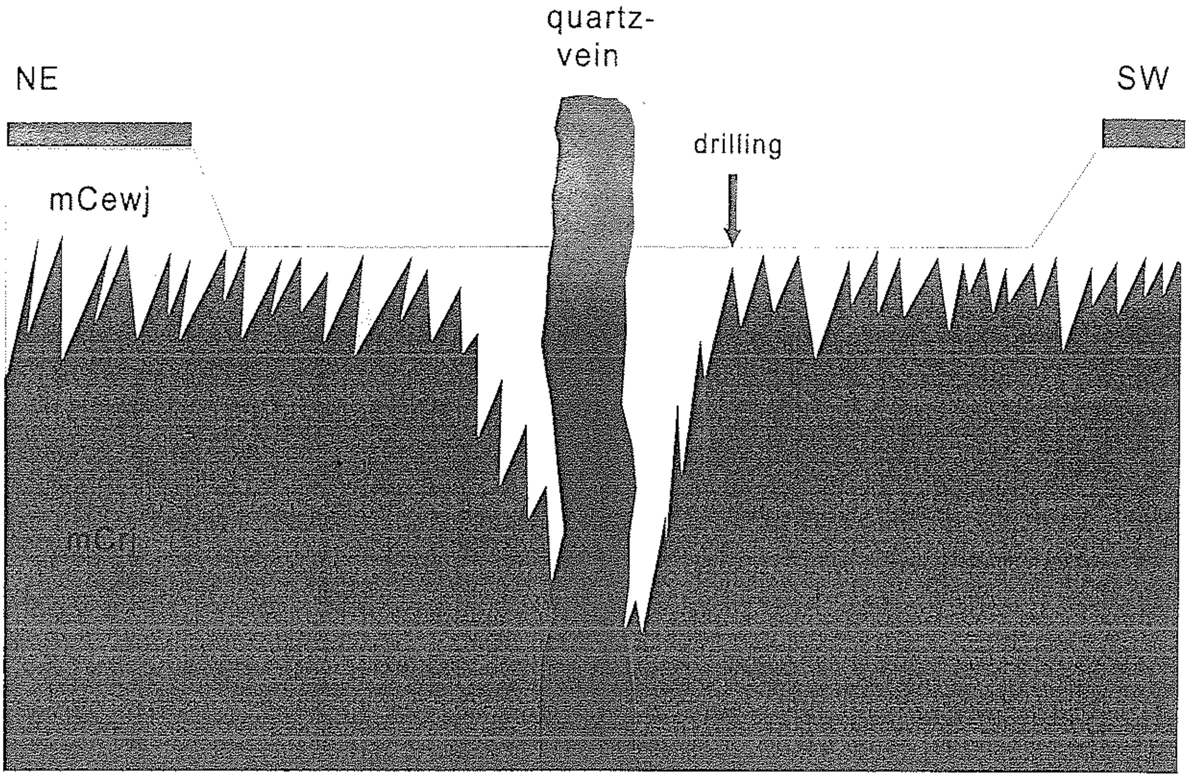


Figure 16: Schematic cross section through site Ödingen

Joints of the quartz dike and the neighbouring silicified slates are partly filled with monomineralic white kaolinite of relatively high crystallinity. Therefore, also the Hinkley index is the highest. This kaolinite only could emerge by precipitation from ground water with soluble Al ions or complexes.

Description

Morphological features:

Oxidation horizon of the saprolite, bleached zone ("Weißverwitterung"):

mCewj: white (N 8/0) clay-, silt slates and sandstones, soft, friable; partly moderate mineralized red to brown sandstone banks (mCsj,mCmsj) appear.

Reduction horizon of the saprolite, upper reduction zone with complete kaolinization of the primary chlorite:

mCrj: black (N 3/0) to dark gray (N 4/0) silty clay slates and clay slates, soft, friable; within the reduction zone quartz veins show distinct solution features.

Petrographical characteristics:

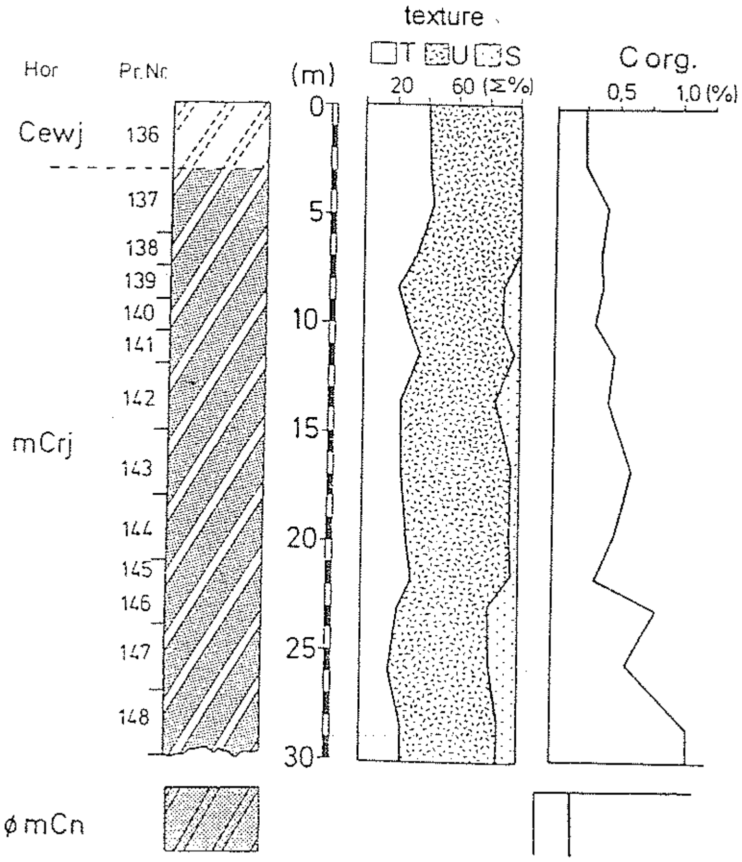


Figure 17: Oedingen drill core - particle size distribution and content of organic carbon (Pr.Nr.=sample code)

Mineralogical and geochemical characteristics:

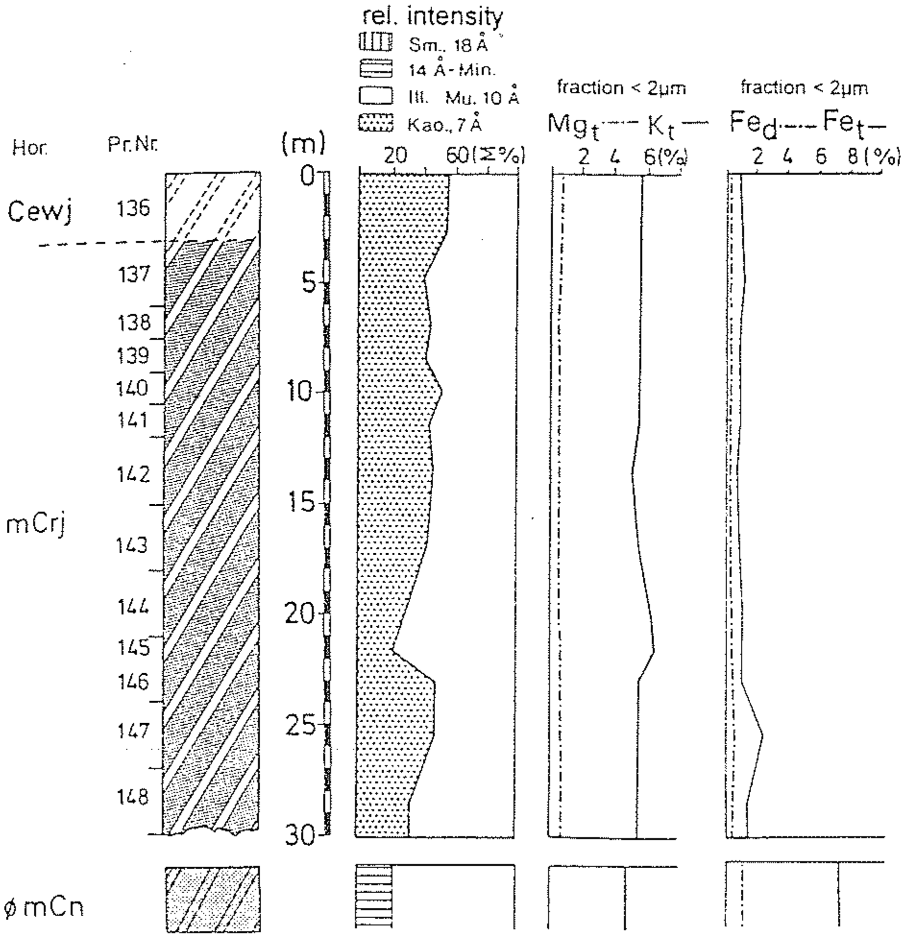


Figure 18: Oedingen drill core - clay mineral distribution (relative intensities), total amounts of Mg, K and Fe, as well as free iron oxides ($Fe_d = Fe_{CBD}$, Pr.Nr.=sample code)

Isovolumetric balances:

Element-wt.% x bulk density g/cm^3 = element-weight by volume in g/100 cm^3 rock result in the element contents per volume unit. Compared with the parent rock element gains and losses can be balanced. With regard to that it is presupposed that rock and saprolite had been petrographical homogeneous. It can be tested for example by quotients of weathering resistant minerals or leaching resistant elements, in this case Ti/Zr-ratio.

Table 2: *Isovolumetric balance of a saprolite profile (site "Wahlbach", Eastern Hunsrück). I. Weight by volume (g/100 cm^3) of element oxides of fresh slates (mCn) and differences of the weights by volume (g/100 cm^3) of saprolite samples (mCrj = lower reduction zone, mCorj = upper reduction zone, partly oxidized, mCewj = bleached zone, K = kaolinite, Sm = smectite, GLV = ignition loss, RG = bulk density, rest = MnO+CaO+Na$_2$O+P$_2$O$_5$+SO$_3$, in g/100 cm^3)*

zone	*mCn*	*mCrj*	*mCorj*	*mCewj*
minerals		*(K) Sm*	*K,Sm*	*K*
SiO_2	153,1	-18,1	-12,1	-38,0
Al_2O_3	50,0	-0,8	-5,4	-7,5
Fe_2O_3	21,8	-2,3	-4,0	-14,7
MgO	6,3	+0,4	-1,1	-4,7
K_2O	9,4	+0,3	-0,3	-3,0
TiO_2	2,5	-0,1	-0,1	-0,3
GLV	13,0	-0,5	-1,0	-3,0
rest	2,0	-0,6	-2,0	-1,7
sum (=RG)	258,0	-24,0	-35,0	-73,0

Table 3: *Isovolumetric balance of a saprolite profile (site "Wahlbach", Eastern Hunsrück). II. Relative composition of mass losses in % relating to the total mass loss of the samples (mCrj = lower reduction zone, mCorj = upper reduction zone, partly oxidized, mCewj = bleached zone, K = kaolinite, Sm = smectite, GLV = ignition loss, RG = bulk density, rest = MnO+CaO+Na2O+P2O5+SO3, in g/100 cm3)*

zone	*mCn*	*mCrj*	*mCorj*	*mCewj*
minerals		*(K),Sm*	*K,Sm*	*K*
SiO_2	0	80,2	61,0	52,1
Al_2O_3	0	3,5	15,5	10,3
Fe_2O_3	0	10,4	11,4	20,2
MgO	0	1,7	3,0	6,4
K_2O	0	-1,5	1,0	4,2
TiO_2	0	0,4	0,6	0,6
GLV	0	2,0	3,0	4,1
rest	0	3,3	4,5	2,1
mass loss	0	100,0	100,0	100,0

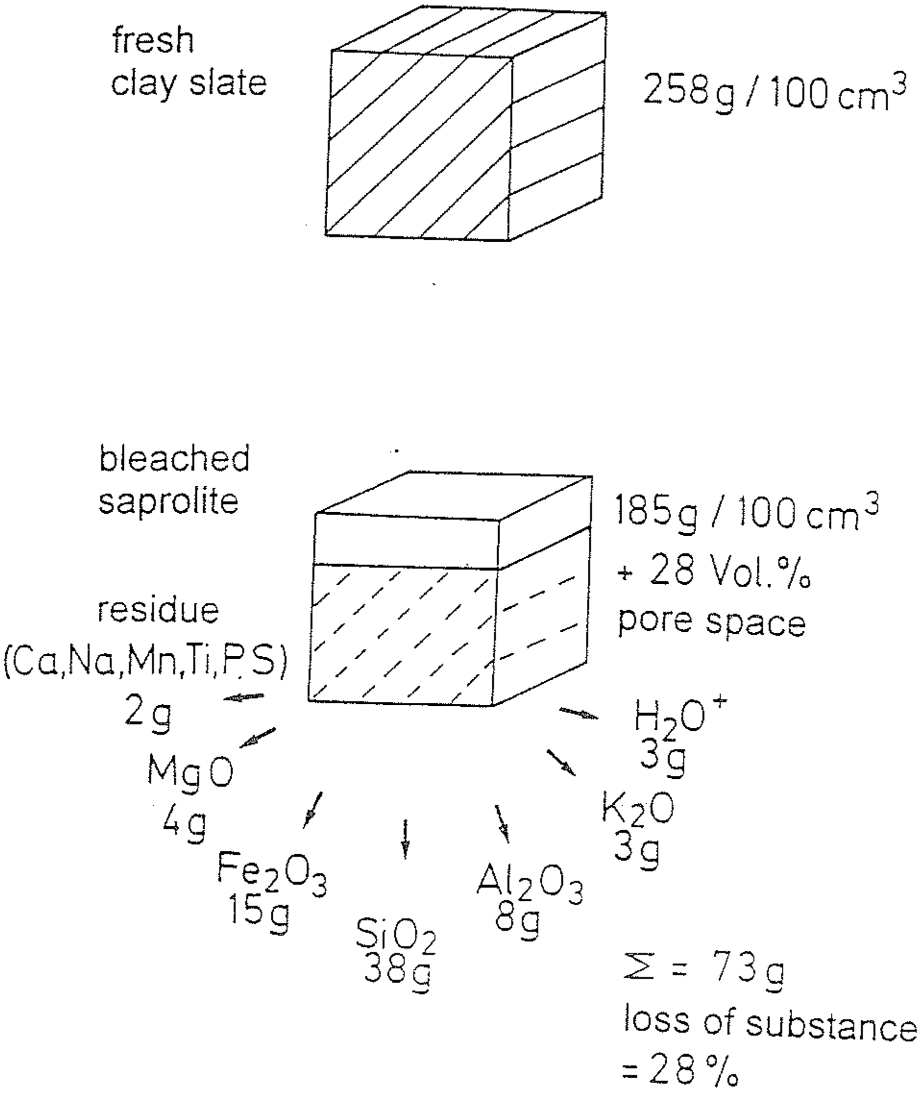


Figure 19: Element loss and gain of pore volume of the bleached saprolite compared with unweathered slate

Origin of the silica acid:

Table 4: SiO2 : Al2O3 molar ratio of chlorite and neo-formed minerals (WEAVER & POLLARD 1973)

Fe-Mg-chlorite (n = 11)	1,99
kaolinite (original form)	2,00
smectite (n=8)	5,12

Table 5: Quartz content and quartz losses in a saprolite profile (site "Wahlbach", Eastern Hunsrück) (analysis after TILL & SPEARS 1969; mCrj = lower reduction zone, mCorj = upper reduction zone, partly oxidized, mCewj = bleached zone, K = kaolinite, Sm = smectite)

zone	*mineral neo-formation*	*quartz* [weight-%]	*quartz* [g/100 cm^3]	*loss in quartz* [g/100 cm^3]
mCewj	K	40	74	16 = 18 %
mCorj	K, Sm	35	78	12 = 13 %
mCrj	(K) Sm	35	82	8 = %
mCn	-	35	90	0

Kaolinite content and kaolinite crystallinity:

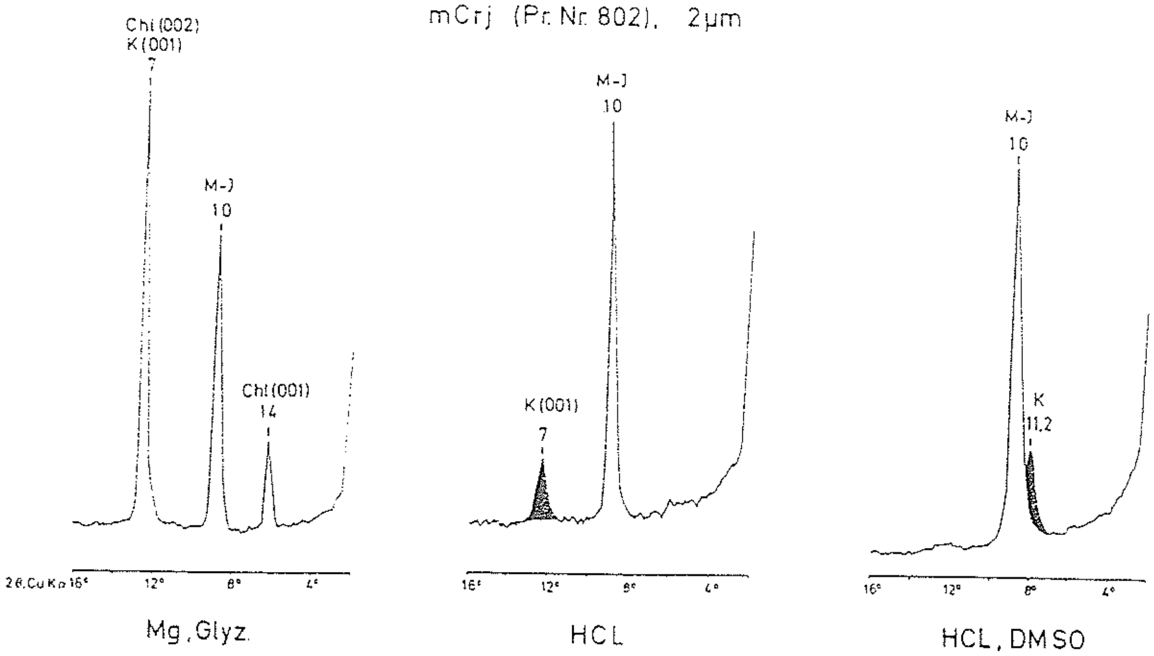


Figure 20: XDA plots of the clay fraction (orientated specimen) from the bottom zones of the saprolite with incomplete kaolinitization of primary Fe-Mg chlorite. The latter is easy soluble in HCl, so that the kaolinite is visible at 7 A. The kaolinite is of b-axis disordered type and DMSO intercalation is possible, resulting in a shift of the kaolinite peak from 7,2 to 11,2 A (K=kaolinite, M-I=muscovite-illite, Sm=smectite, Chl=chlorite, Pr.Nr.= sample code)

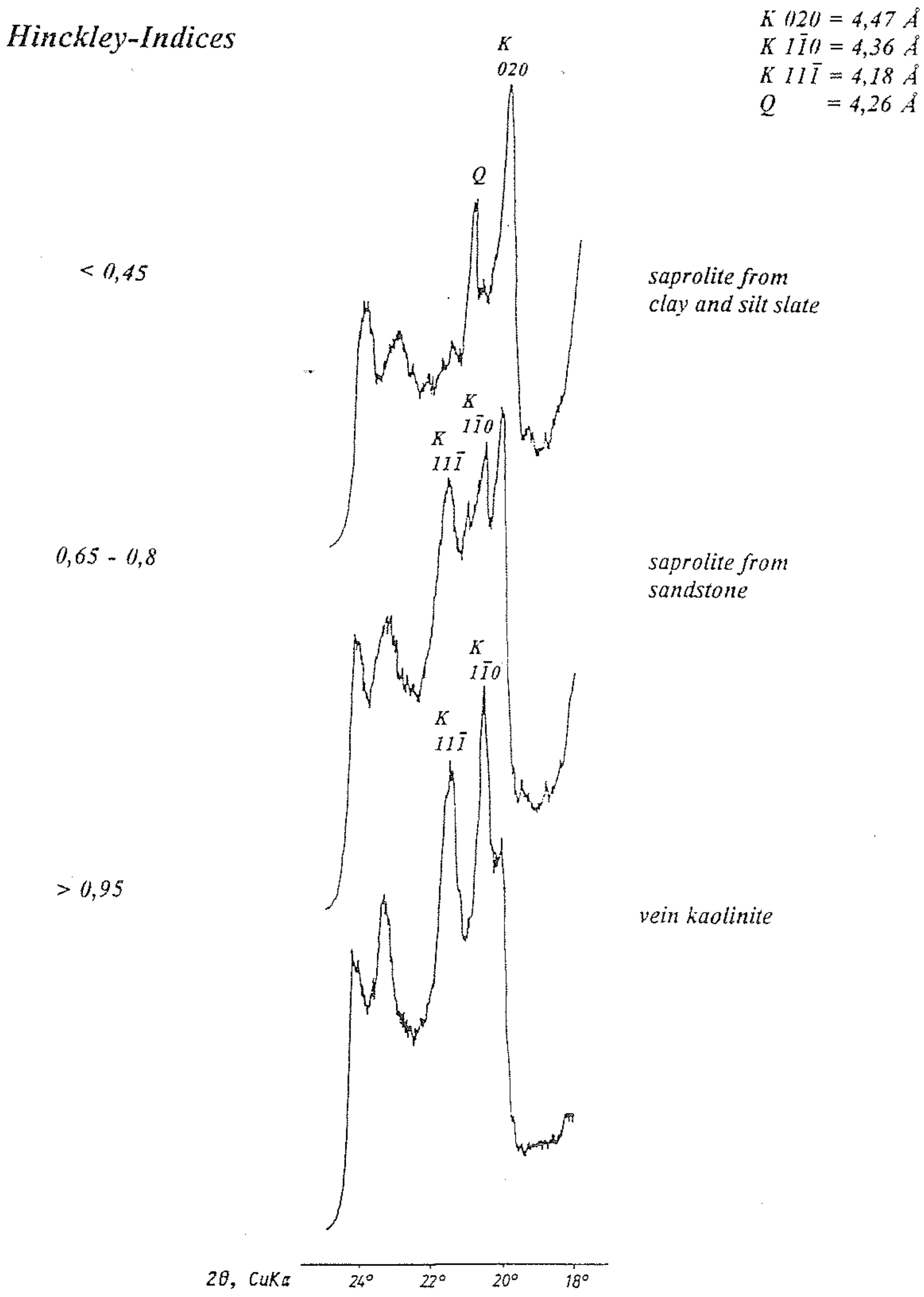


Figure 21: XDA plots of lower order peaks of kaolinites from the clay fraction (powder specimen) of saprolites with different texture (K=kaolinite, Q=quartz)

Kaolinite content (analysis after ISLAM & LOTSE, 1986):

bleached saprolite derived from clay silt slates: 20 - 25 wt.-% bleached saprolite derived from sandy slates and sandstones: 15 - < 10 wt.-%

Kaolinite crystallinity:

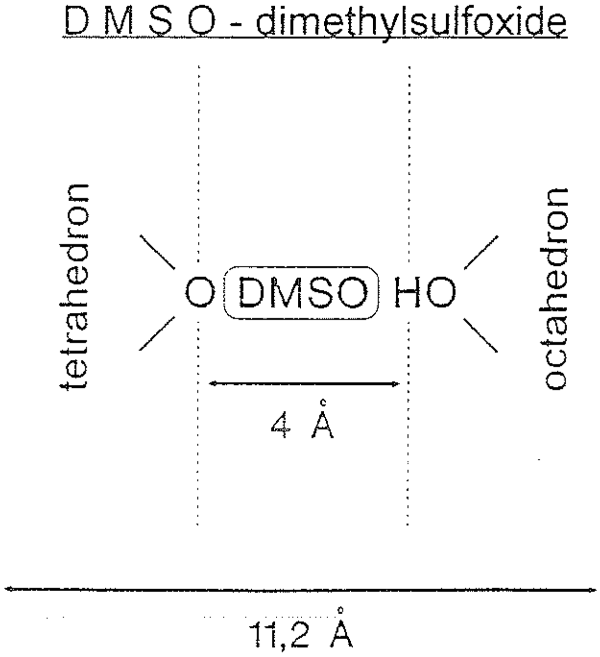


Figure 22: Principle of the expansion of kaolinite with dimethylsulfoxide (DMSO)

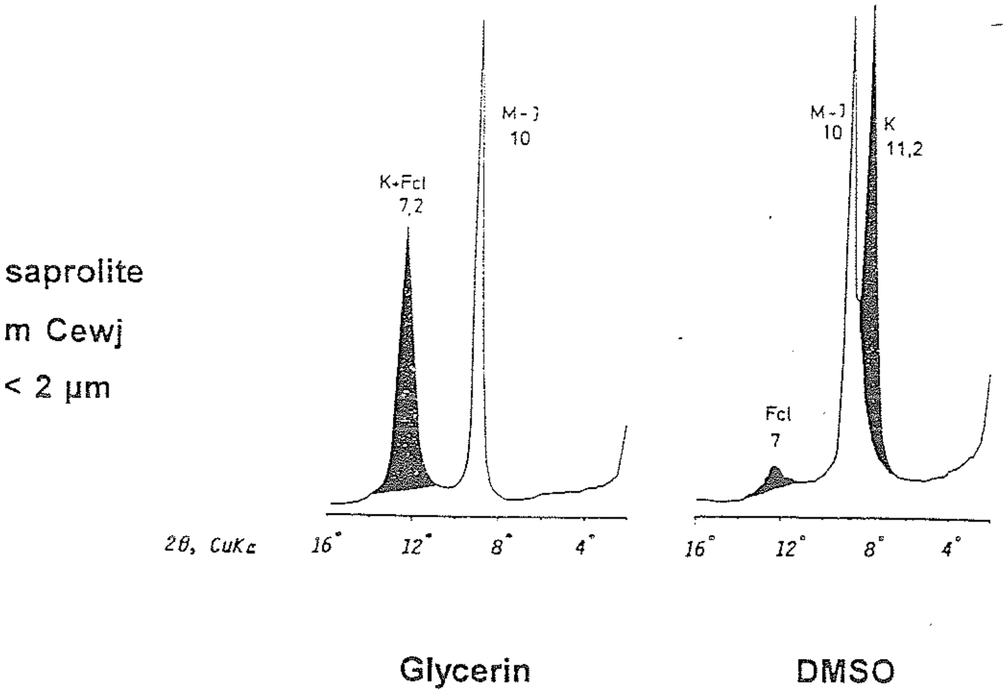


Figure 23: X-ray diagrams of the clay fraction from the bleached saprolite (mCewj). In all saprolite zones b-axis disordered kaolinite (expandable with DMSO from 7 to 11,2 Å) dominates, contents of fireclay (not expandable with DMSO) up to 10 disordered kaolinite) % (K=kaolinite, M-I=muscovite-illite, Fcl=intercalation

Table 6. : Oedingen saprolite - amounts of total main element oxides and trace elements

		Black S.	*Brown S.*	*White S.*
SiO_2	%	65,22	68,78	68,09
Al_2O_3	%	21,43	16,68	20,08
Fe_2O_3	%	0,84	4,25	0,75
MnO	%	0,01	0,01	0,01
MgO	%	0,63	0,46	0,51
CaO	%	0,18	0,15	0,17
Na_2O	%	0,16	0,08	0,14
K_2O	%	4,07	2,94	3,78
TiO_2	%	1,04	0,94	0,98
P_2O_5	%	0,07	0,05	0,06
SO_3	%	0,00	0,00	0,00
H_2O^+	%	5,15	4,58	4,61
H_2O^-	%	0,74	0,52	0,63
Sum M. E.	%	99,55	99,45	99,82
Sum (ME+TE)	%	99,76	99,67	100,03
Ba	mg/kg	567	426	521
Ce	mg/kg	162	125	144
Co	mg/kg	10	10	0
Cr	mg/kg	146	135	160
Cu	mg/kg	14	87	0
Ga	mg/kg	24	23	22
La	mg/kg	119	87	112
Nb	mg/kg	21	19	19
Nd	mg/kg	54	39	41
Ni	mg/kg	22	51	10
Pb	mg/kg	56	40	39
Rb	mg/kg	188	129	163
Sr	mg/kg	103	92	115
Th	mg/kg	19	19	14
U	mg/kg	12	12	5
V	mg/kg	132	116	117
Y	mg/kg	52	42	42
Zn	mg/kg	91	134	37
Zr	mg/kg	240	259	235

Stop 4 Ringen paleosol

Site : *Road ditch near the village of Ringen, exposure of a red paleosol, TK 5408 Bad Neuenahr, r 52 80000, h 56 04940, 178 m a.s.l.*

Topics: *Pre-Upper Oligocene, polygenetic paleosol from saprolite; mineralogical and geochemical changes with the transition from the saprolite to the solum*

Summary

Autochthonous paleosols of the Mesozoic-Tertiary weathering mantle are very rare due to severe erosion in the course of the tectonically and climatically induced relief formation of the Rhenish Massif during the Upper Tertiary and the Pleistocene. Remnants of paleosols only can be found in former depressions, where they were covered by Tertiary fluvial sediments. Because of their relief position most of the soils represent gleyic soil types. Such a soil, exposed in a nearby highway road cut, was investigated in detail by FELIX-HENNINGSEN & WIECHMANN (1985) and FELIX-HENNINGSEN (1990 a). The paleosol at this excursion stop is similar to that investigated soil, which developed from bleached saprolite.

The horizonation and micromorphological characteristics represent a Plinthic Acrisol rich in clay. The kaolinite content of the clay fraction increases from 25 % in the saprolite up to 90 % in the upper soil horizons, due to the kaolinitization of muscovite, which remained stable in the saprolite. Because the saprolite from silt and clay slates is interbedded with sandstones, the sand fraction of the soil consists of quartz.

The distribution of pedogenic oxides displays a maximum of Fe and Mn oxides in the uppermost concretionary horizon. This reflects a soil genesis under the influence of a high ground water table. In phases of a deeper ground water table leaching was possible. Therefore the distribution of amorphous (NaOH soluble) Al and Si oxides characterizes the beginning of a ferrallitic stage in the uppermost horizon.

The mineralogical properties of kaolinite of the solum differ in a typical way from that of the saprolite. Kaolinites of the soil horizons are characterized by high amounts of "fireclay minerals" (see RANGE et al. 1969, LAGALY 1981), representing kaolinites with an intercalation disorder. The amount varies with the particle size fraction. The silt fraction of the soil horizons and the saprolite displays the same high amounts of b-axis disordered kaolinite (shift to 11,2 A, see BRINDLEY 1961, BAILY 1963, RANGE et al. 1969). It shows that the saprolite was the parent material of the soil and the kaolinite of the saprolite was incorporated to the soil horizons. In the soil horizons the amounts of intercalation disordered kaolinite represent an increasing tendency from the saprolite to the top horizons as well as from the coarse clay fraction to the fine clay fraction (< 0,2 mm, FELIX-HENNINGSEN 1990 b). That gives evidence, that the formation of intercalation disordered kaolinite is typical for the solum, in which processes of congruent dissolution of primary saprolitic kaolinite and precipitation of secondary kaolinite,occurred as well as the neo-formation of kaolinite from muscovite. Due to soil formation under desilication and the low Si content of muscovite, the secondary kaolinite and the kaolinite after muscovite respectively, precipitated in an environment of a relative Si deficit of the pore solutions. This is indicated by the NaOH-soluble Si and Al, extracted from amorphous clay minerals and fine grained kaolinites. The intercalation disordered kaolinites display an isomorphic substitution of tetrahedral Si by Al. For charge balance foreign ions, as H^+ or K^+ are irregularily distributed in the crystal lattice. Bending of the silicate layers leads to domains with a decrease of distance between octahedral and tetrahedral layers, with the consequence of an increase of binding forces between the silicate layers. They cannot be overcome by the polarizing forces of the DMSO. Another possibility for the formation of intercalation disordered kaolinite may be the isomorphic substitution of Al^{3+} by Fe^{3+} (HERBILLON et al. 1976). Because of the bigger ion diameter of Fe^{3+} a shortening of the bindings between tetrahedral and octahedral layers leads to an increasing binding energy. On the other hand there is no difference of the amounts of intercalation disordered kaolinite between white bleached mottles of the plinthic horizon and the red hematitic parts.

Summarizing the genesis of the paleosol, the morphological and pedochemical characteristics of the soil horizon display a formation under the influence of a high ground water table. The thickness of the plinthic horizon may reflect the seasonal fluctuations while the bleached horizon was ground water saturated. The fact that the saprolite below the paleosol has a 40 m thick white bleached oxidized horizon indicates the polygenesis. The oxidation of the primary coaly bituminous organic matter of the saprolite was only possible under aeration in consequence of descent of the ground water table. This obviously started in the Upper Oligocene with the tectonical uplift of the Rhenish Massif, simultanously with the regression of the North Sea and the beginning of sedimentation of kaolinitic clays from eroding land surfaces in depressions of fault troughs. Additional, silcrete formations of the period give evidence of a dryer, possibly semiarid climate.

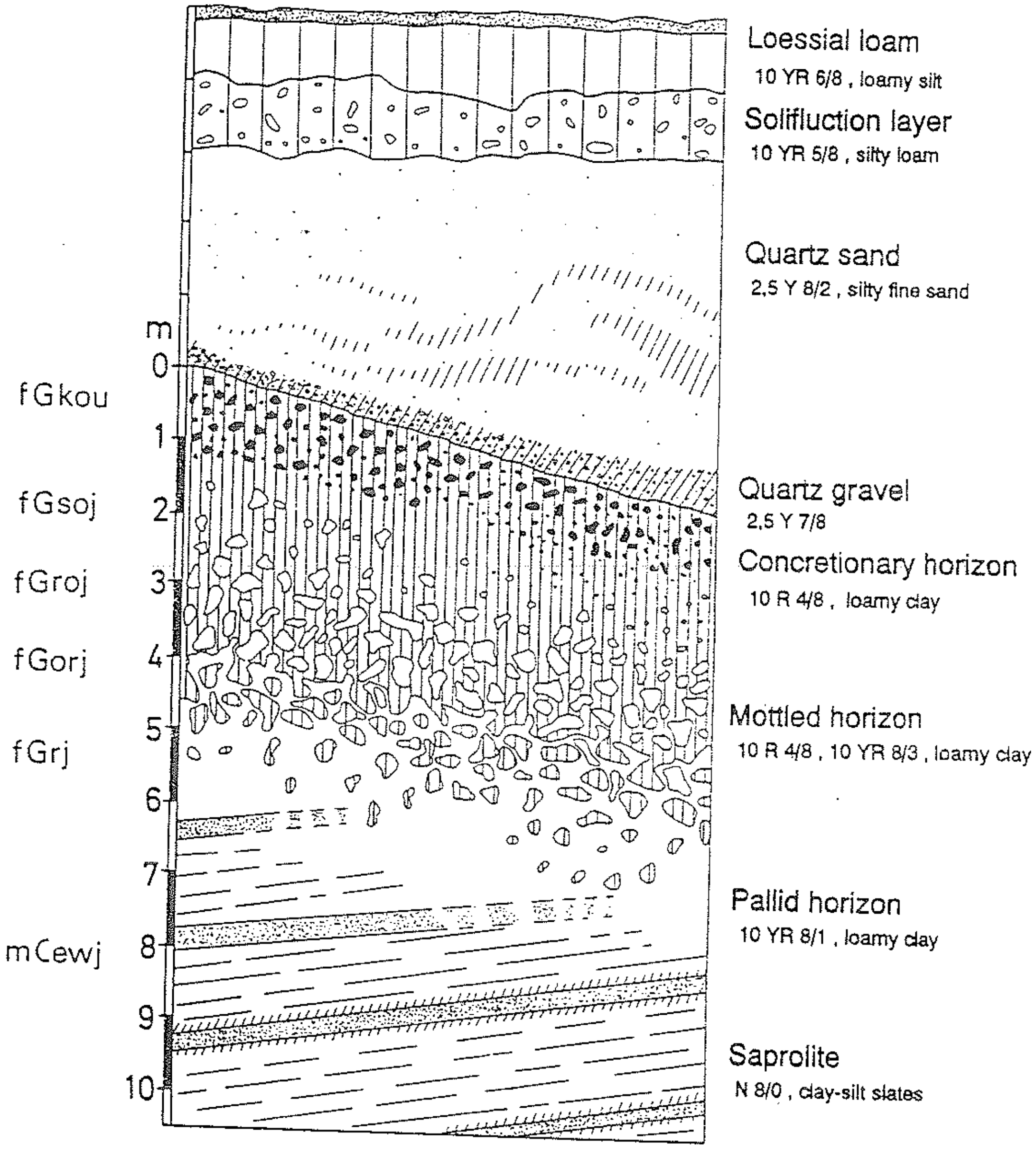


Figure 24: Profile Bengen - autochthonous fossil pre-Upper Oligocene Gleyic Acrisol exposed at a highway (A 61) cut exposure near Bengen village

Description

Superficial periglacial layers:

0 - 2 m:	Stagnic Luvisol from loess over loessial solifluction with fragments of bleached saprolite and red clayey soil relics
2 - 5 m:	White medium textured quartz sand with silty layers and well rounded quartz gravels

Fossil soil:

Concretionary horizon

fGkou	0.- 120 cm: and white mottles, rounded red Fe oxide concretions with up to several cm red loamy clay (10 R 3/6 - 4/8) with small yellowish diameter and oxide incrustated fragments of sandstone layers, gliding transition to

Plinthic horizon:

fGsoj 120 - 500 cm:	red loamy clay (10 R 3/6 - 4/8) to the depth fGroj increasingly mottled with rounded white
fGorj	spots (10 YR 8/3), single Feoxide concretions and oxide incrustated sandstone fragments, gliding transition to

Pallid horizon:

Grj 500 - 630 cm:	white loamy clay (10 YR 8/1), at 600 cm beginning of slate structure, gliding transition to

Saprolite:

mCewj > 630 cm:	bleached, white saprolite from clayey silt slates (N 8/0), soft and friable, with slate structure

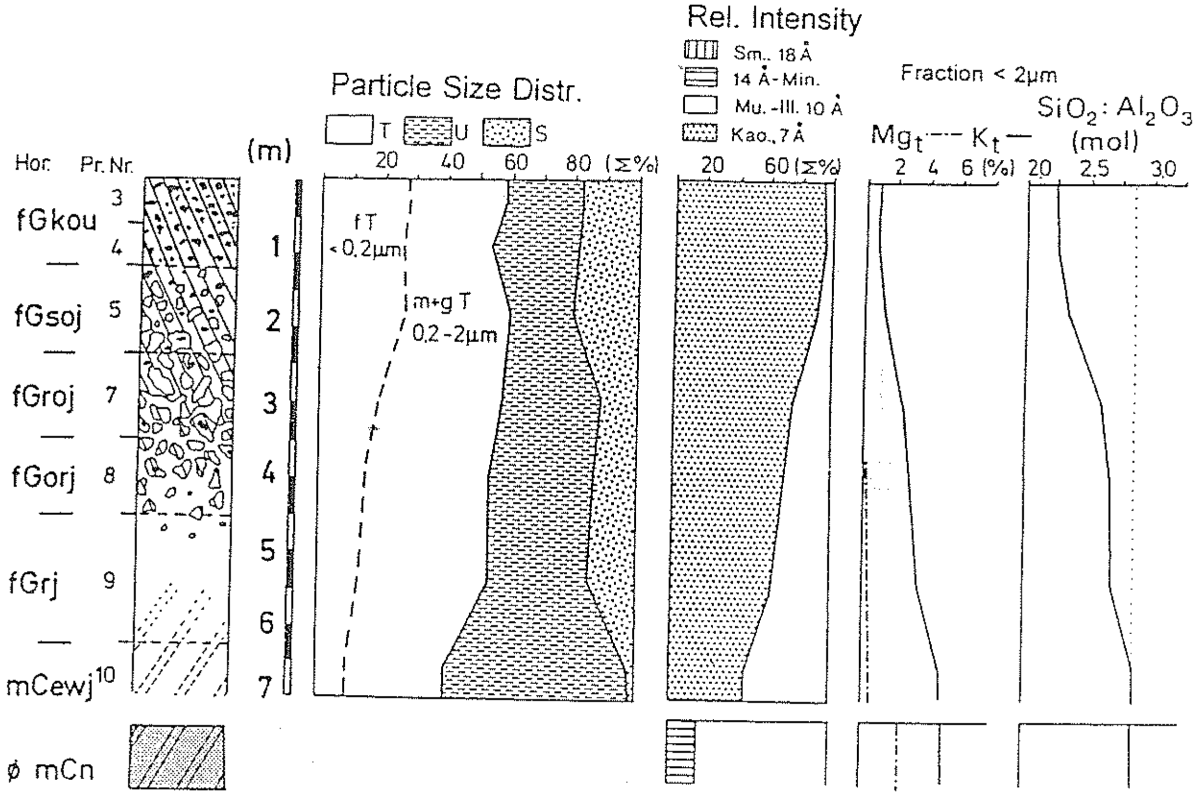


Figure 25: Profile Bengen - particle size distribution, clay mineral distribution (relative intensities), total amounts of Mg and K, and SiO2:Al2O3 molecular relations of the clay fraction (Pr.Nr.=sample code)

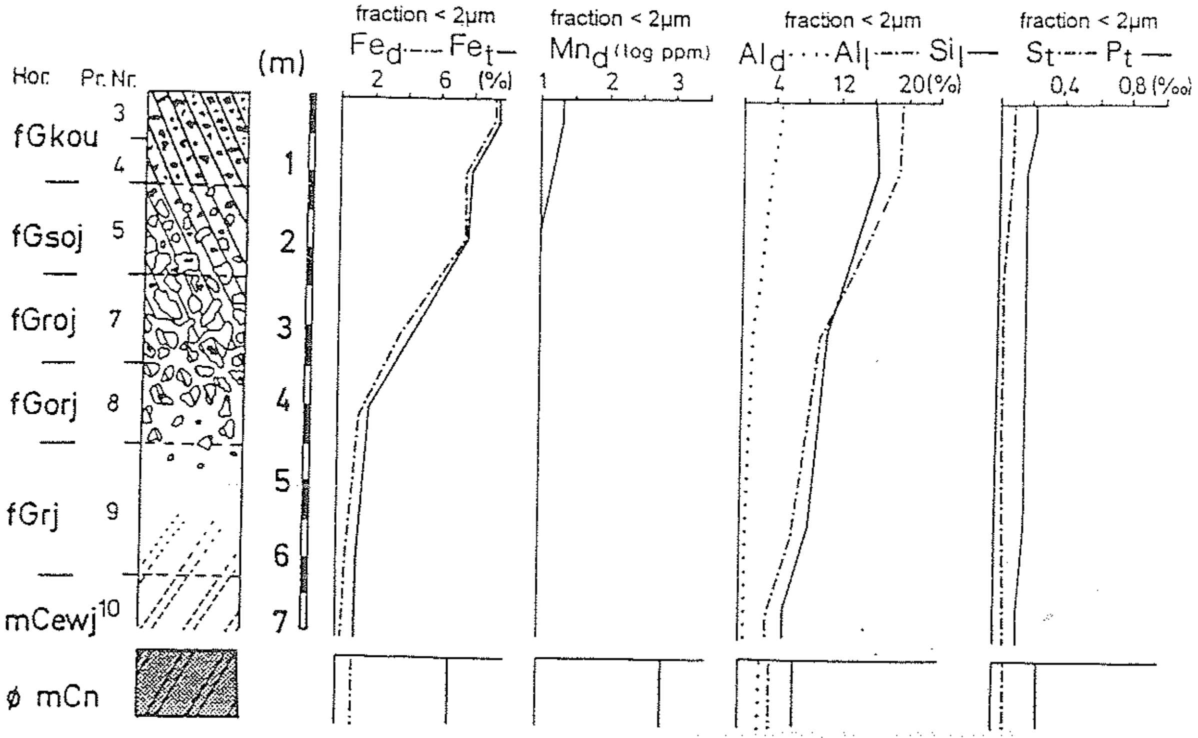


Figure 26: Profile Bengen - total amount of iron, silica and phosphate as well as pedogenic oxides (Fed,Mnd, Ald = FeCBD, MnCBD, AlCBD, Pr.Nr.=sample code)

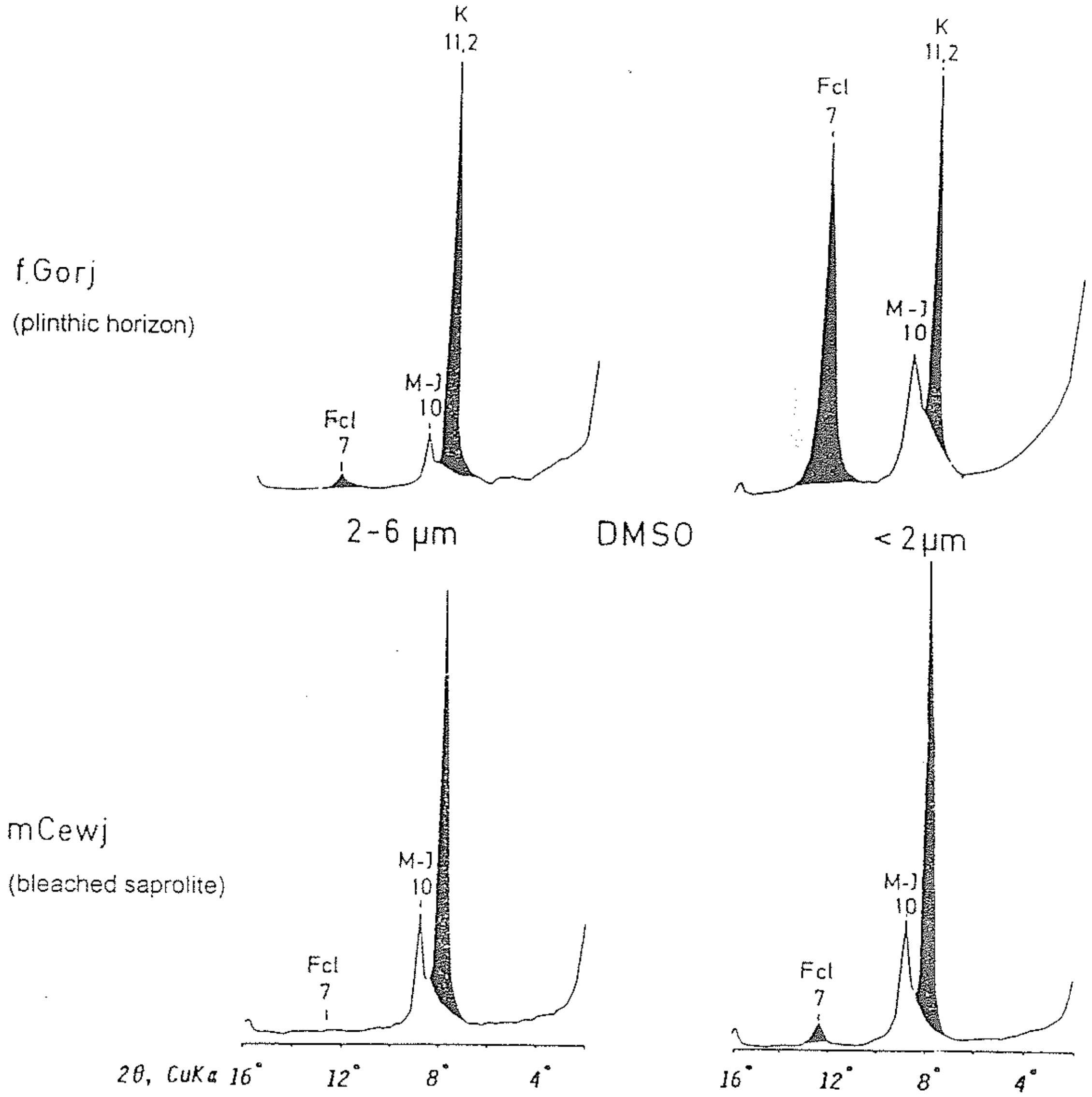


Figure 27: Profile Bengen - distribution of muscovite-illite (M-I), b-axis disordered kaolinite (K), andCBD (Fcl) in the fine silt (6 - 2 mm) and clay fraction (< 2 mm) of the plinthic horizon (fGorj) and the saprolite (mCewj). Neoformation of intercalation disordered kaolinite increases in the clay fraction of the soil horizons by kaolinitisation of muscovite-illite and congruent dissolution of 'primary' kaolinite which was incorporated from the saprolite

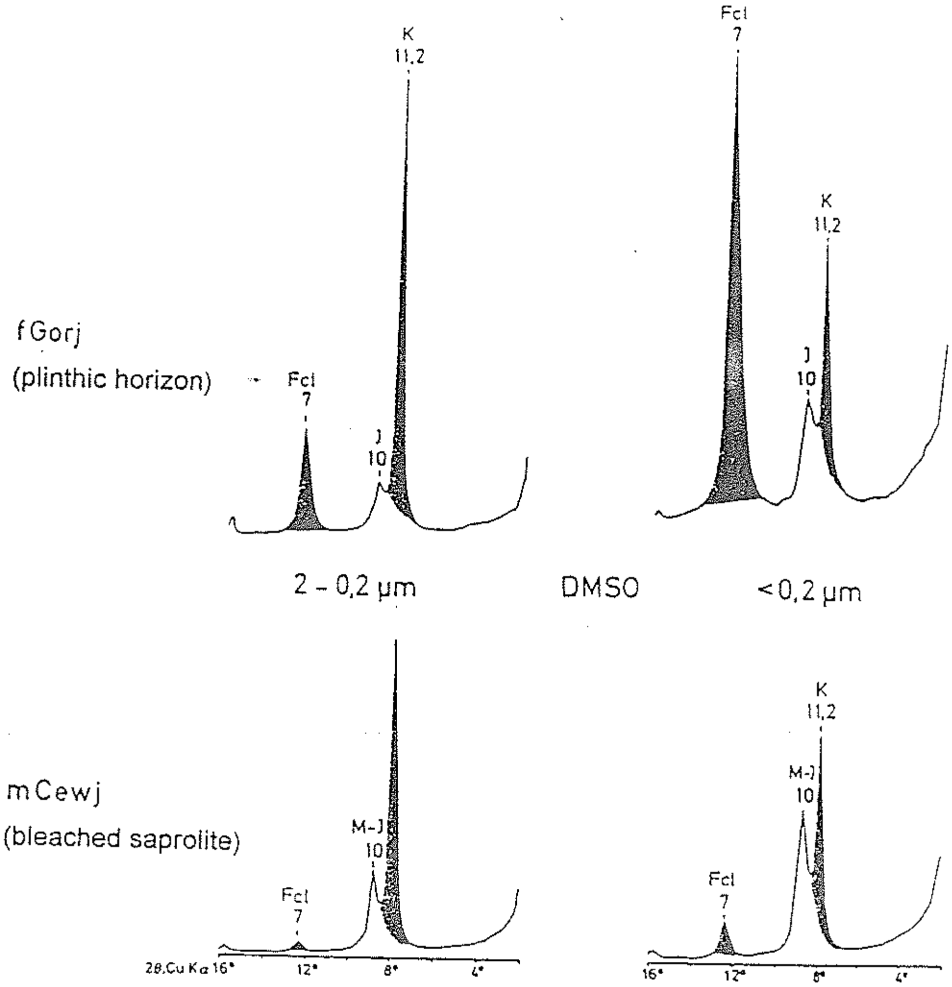


Figure 28: Profile Bengen - distribution of b-axis disordered kaolinite (K) and intercalation disordered kaolinite (Fcl) in the coarse (2 - 0,2 mm) and fine (< 0,2 mm) clay fractions of the plinthic horizon and the saprolite (M-I: muscovite-illite). Although in soil and saprolite the amount of intercalation disordered kaolinite increases with decreasing particle size, this is much more pronounced in the soil horizons. It indicates general differences of pedochemical conditions in soils and saprolites, under which neo-formation of kaolinite occurred

Stop 5 Ringen kaolin clay deposit

Site: *Ringen village, kaolin clay open mine pit, 197 m a.s.l. TK 5408 Bad Neuenahr, r 25 78170 h 56 04500*

Topics: *Upper Oligocene and Miocene clay sediments: Mineralogy and landscape development during Mid-Tertiary*

Summary

Below 10 m thick Pleistocene sediments consisting of loesses, loessial solifluction, and loessial basalt tuff, follow about 60 m Tertiary clay sediments. They were deposited in a fault trough and cover saprolite from Lower Devonian slates. The sediments derive from erosion of the pre-Upper Oligocene soils and white bleached saprolite, due to the tectonical uplift of fault blocks during Upper Oligocene. A basal gravel is covered by clay and silt layers, in which completely kaolinized banks of trachyte tuff are intercalated, which were erupted during the volcanic event of the "Siebengebirge" mountaneous area East of Bonn. They display a stratigraphical time mark (see SPIES 1986). Coaly layers within the sediments stratigraphically belong to the Lower Miocene ("Cologne Layers")

Only a few upper metres of the saprolite below the clay sediments display characteristics of pre-sedimentary bleaching and oxidation. The deeper saprolite zones are of black colour due to primary coaly bituminous organic matter. The shallow oxidation of saprolite is also typical for other clay deposits in fault troughs of the Rhenish Massif (SPIES 1986). This characteristic gives evidence, that the lowering of the Oligocene ground water table and the deep oxidation of the kaolinitic saprolite occurred simultaneously with the tectonical uplift of the Rhenish Massif.

The clay fraction of the sediments shows predominance of kaolinite, of which the greater part is of intercalation disordered type while the underlying saprolite typically shows the b-axis disordered kaolinite. This proves, that the clay sediments derived from erosion of the pre-Upper Oligocene soils. Alternating proportions of b-axis disordered kaolinites in different layers display the contribution of saprolitic material to the sediments.

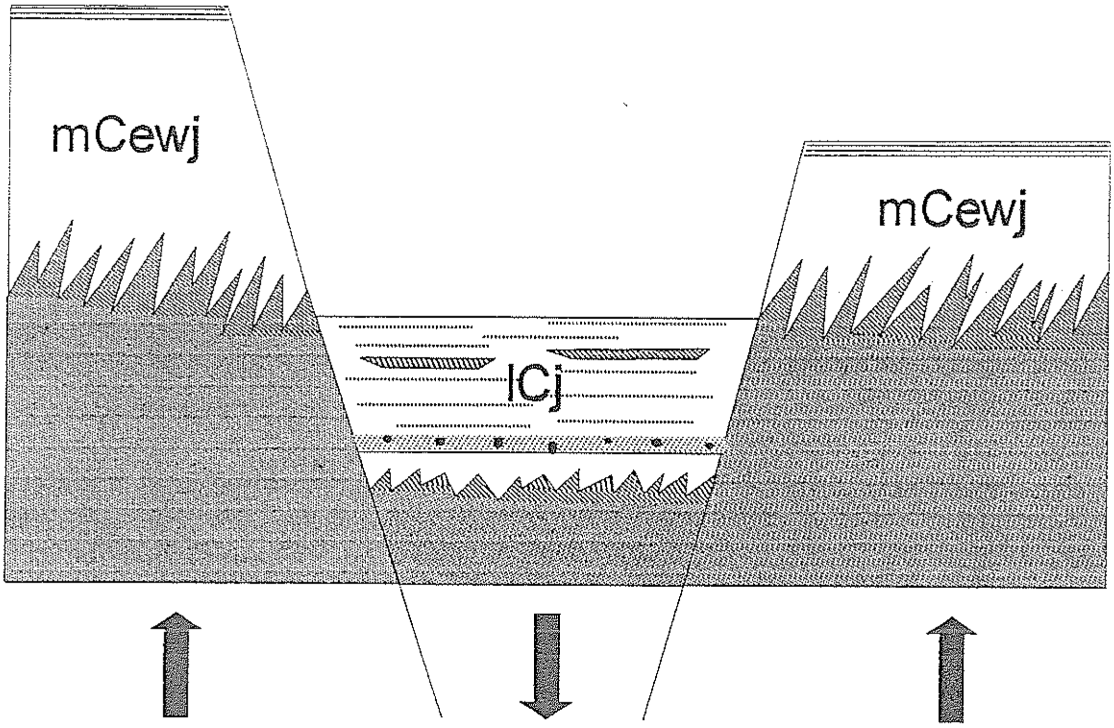


Figure 29: Kaolin clay deposit Ringen - scetch of a cross section (without scale), displaying upliftet blocks and fault troughs, which were sedimentary basins (mCewj=bleached saprolite)

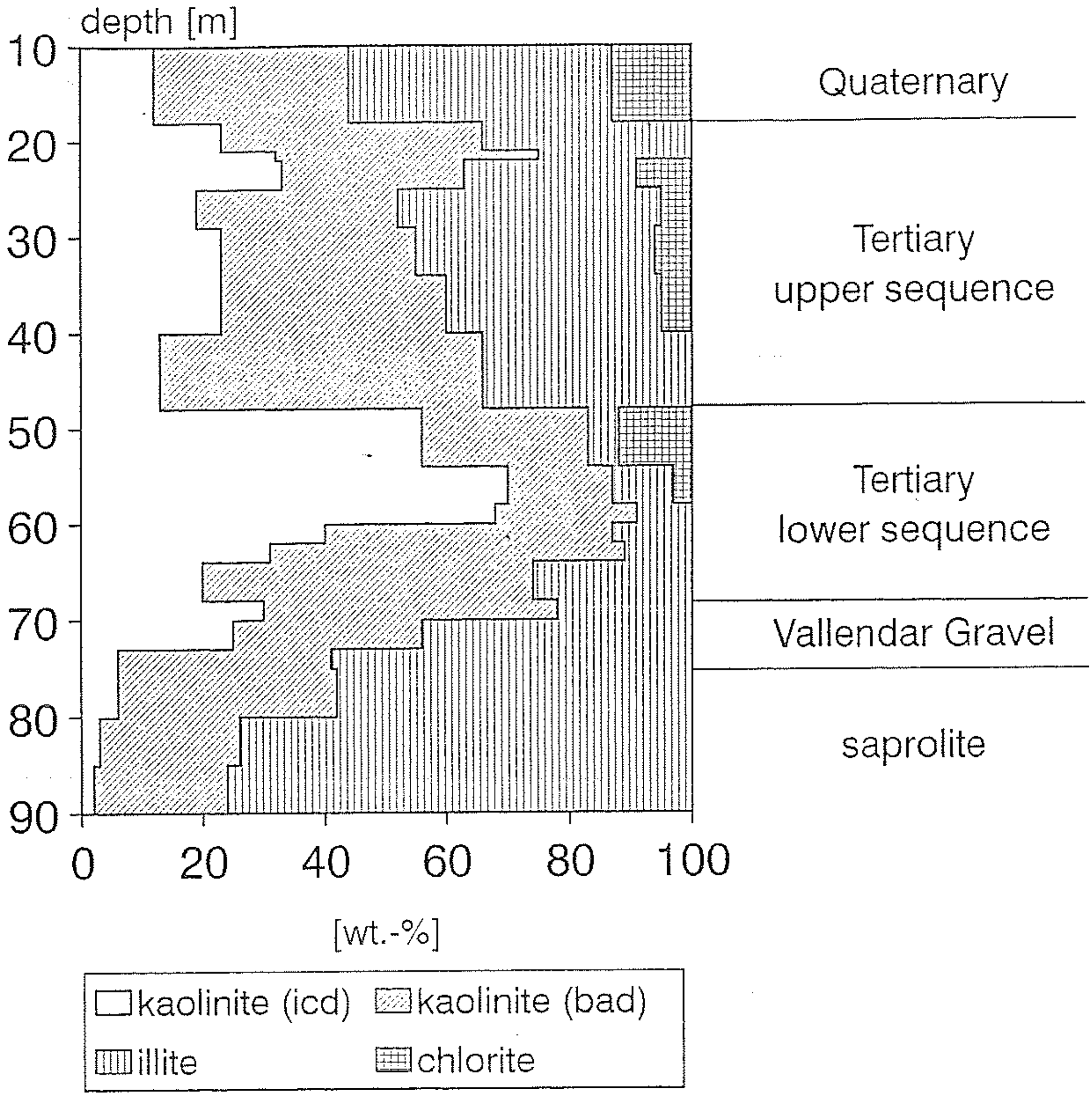


Figure 30: Kaolin clay deposit Ringen - horizonation and layers of a prospect drill

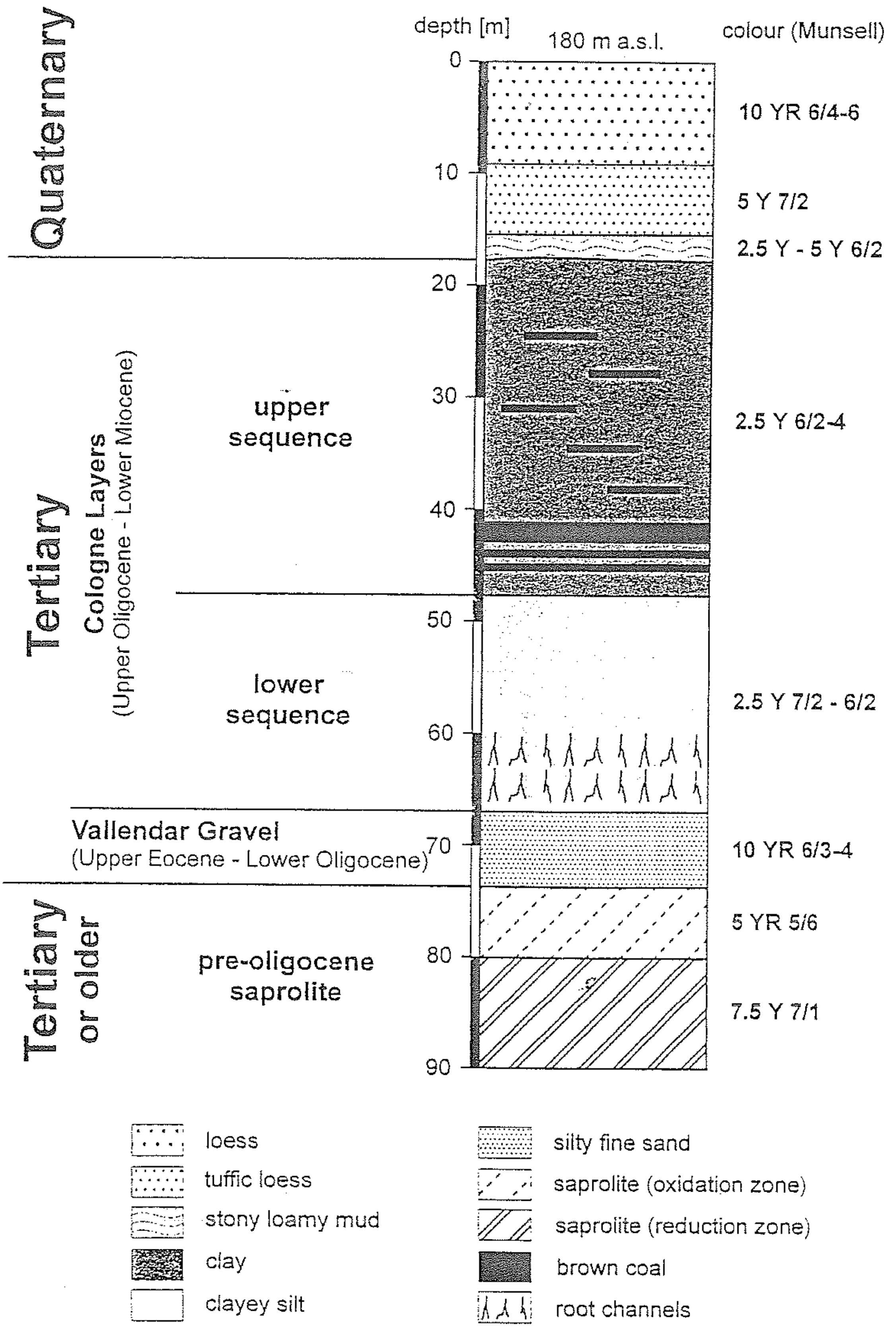


Figure 31: Kaolin clay deposit Ringen - distribution of clay minerals in samples of the prospect drill core (icd-kaolinite = intercalation, disordered kaolinite, "fireclay minerals"; bad-kaolinite = b-axis disordered kaolinite)

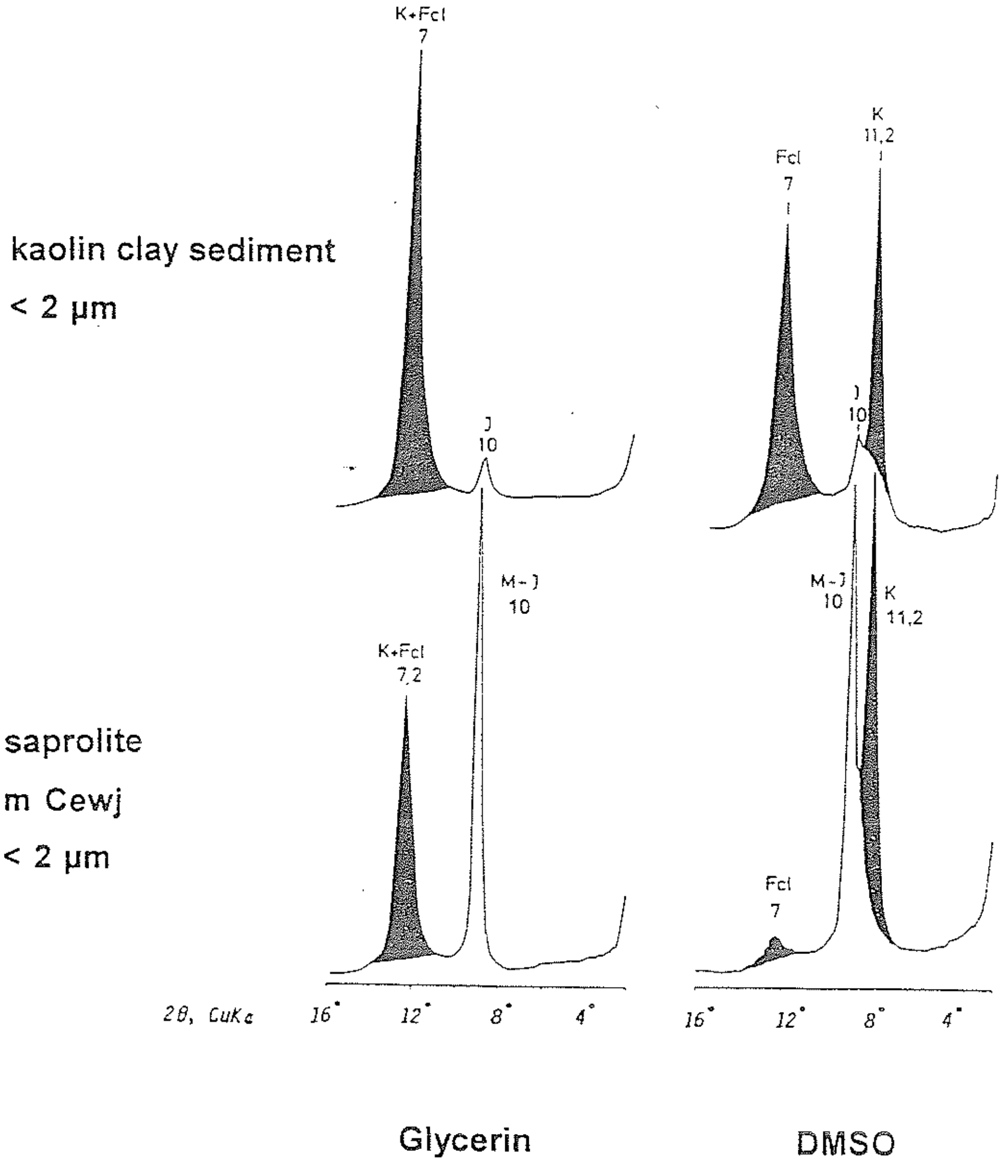


Figure 32: Kaolin clay deposit Ringen - XRD-diagrams of DMSO treated clay sediment and saprolite from the prospect drill core (K=kaolinite, M-I=muscovite-illite, I=illite, Fcl=intercalation disordered kaolinite)

Stop 6 Wehr caldera

Site: *East of Wehr village, CO_2- mofette, 297 m a.s.l.*

TK 5509 Burgbrohl, r 25 86600 h 55 89050

Topics: *Hydrothermal alteration and kaolinization of Lower Devonian rocks below the base of weathering, precipitation of ferrihydrite from a CO_2 spring, dry reductomorphism of adjacent soils*

Summary

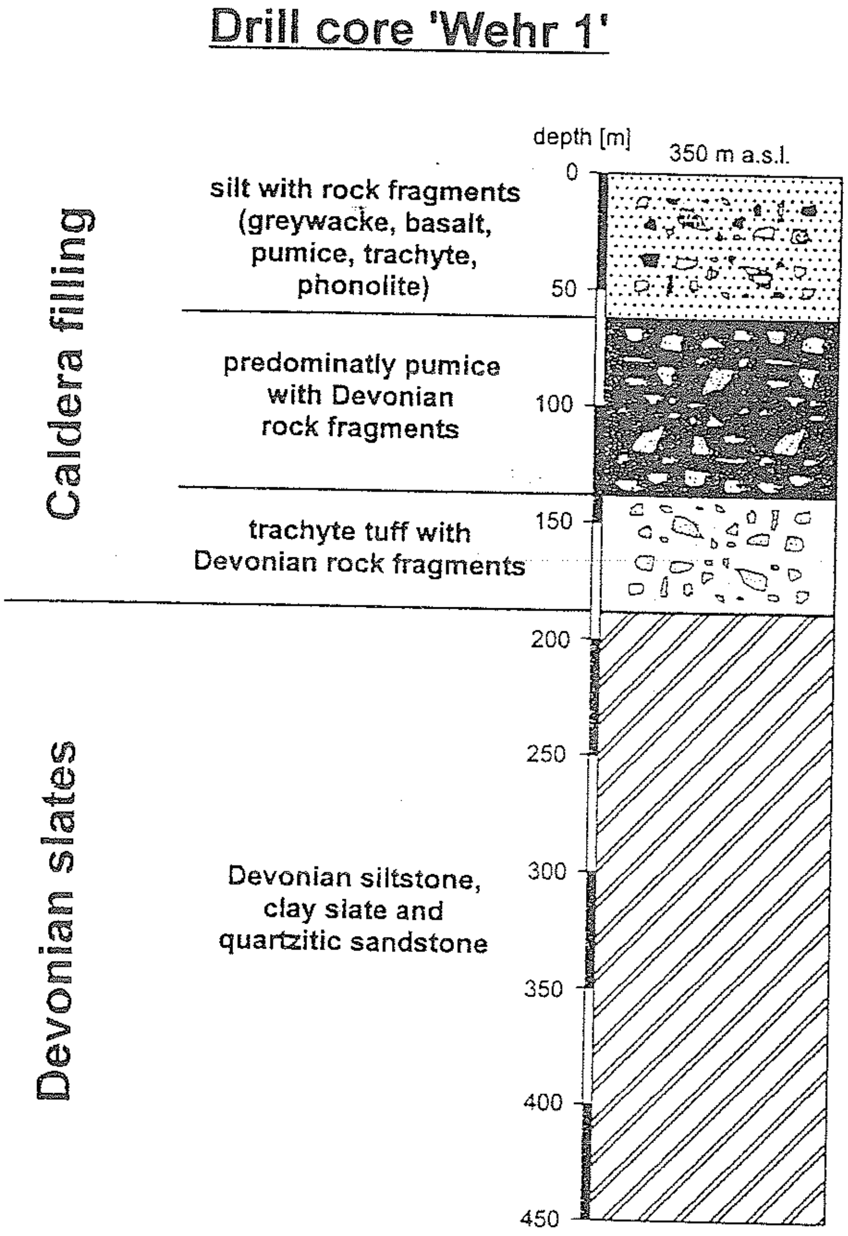
The Wehr caldera with a diameter of about 2.000 m and an elevation of 279 m a.s.l. of the caldera bottom, belongs to the East Eifel volcanic area. The age of eruption is assumed Middle Pleistocene, about 220.000 years b.p. (WINDHEUSER 1978, WINDHEUSER et al. 1982). The oldest pumice deposits of the Wehr eruption, were found in the middle terraces of the Rhine river. The caldera is filled with about 150 m pyroclastics, Pleistocene solifluction deposits, loessial sediments and Holocene lake deposits in the deepest parts.

Below this caldera as well as 2.000 m below the Laacher See caldera a magmatic chamber is existing. CO_2 is released from magma in consequence of cooling down of volcanic chambers and ascends within joint systems (ULRICH 1958). The contact with descending meteoric ground water in about 1 - 3 km depth leads to the formation of carbonic acid with low pH due to the high pressure and with an increased temperature according to the geothermy (HUMMEL 1930). The decreased specific weight of the water leads to ascent, while the slates beside the ascent path are subject to hydrolysis and neo-formation of minerals. Therefore the waters become mineralized, mainly with Fe and Mg as cations. Small amounts of Na and sulfate are supposed to derive from migration of saline waters in deep joint systems from marine deposits of the Lower Rhine Embayment (FRESENIUS & KUSSMAUL 1985). Carbonic acid springs, having their source at valley bottoms and basins, are exploited in wells and borings (e.g. in the Wehr caldera and the Ahr valley) by the mineral water industry. At some places of the Rhenish Massif dry mofettes occur beside springs as in the Wehr caldera. Deposits of red iron ochre in the surrounding of CO_2 springs consist of ferrihydrite and Fe-, Ca- and Mg- carbonates, which derive from hydrothermal alteration of the Fe-Mg-chlorites in the slates. For a short period at the beginning of this century the iron ochre was mined.

Material of a > 500 m deep well drilling in the Wehr caldera was investigated with respect to characteristics of hydrothermal alteration. The autochthonous slates are friable like Mesozoic-Tertiary saprolite. According to the absence of oxygene, altered slates display the same gray colour as the fresh slates. Neo-formation of smectite, kaolinite and especially of dickite from primary chlorite are the mineralogical characteristics. The distribution of smectite and kaolinite within the alteration zones is in accordance with the rock permeability. In less permeable parts, mainly banks of clay slates, kaolinite and dickite occur near the joints, while smectite was formed mainly in banks of clay slates in greater distance from joints where the exchange of the pore solutions was only slow.

Dickite is a typical 7 A mineral of hydrothermal alteration zones. It often occurs together with kaolinite of high crystallinity in white monomineralic (7 A) veins . The differences in thermal stability allow the easy discrimination between dickite and kaolinite. While the crystal lattice of kaolinite collapses at temperatures above 520° C, dickite remains stable to temperatures > 600° C (fig. 36 see Stop 7 Waldesch). While primary quartz veins in the deeper parts of the alteration zones were subject to dissolution, neo-genic quartz occurs as coatings in joints of sandstones near the surface.

Every year several areas of the Wehr caldera show depressions of plant growth due to the ascent of dry CO_2 to the root zone. The soil profiles display an increase of bleached mottles due to increasing reduction with depth, although the physical soil properties as well as the elevated position of the area gives no evidence for influence of ground water or logging of surface water. Comparative investigations of the soil air composition display normal amounts of CO_2 at the vegetated areas, while the root zones of the areas free of vegetation contain soil air enriched in CO_2, partly with more than 60 % vol. of CO_2 (see fig. 35)



CO_2-discharge: ca. 4.000 kg/h
minimum water discharge: ca. 30 m^3/h

Figure 33: Wehr caldera - sketch of the lithological sequence in a deep drilling

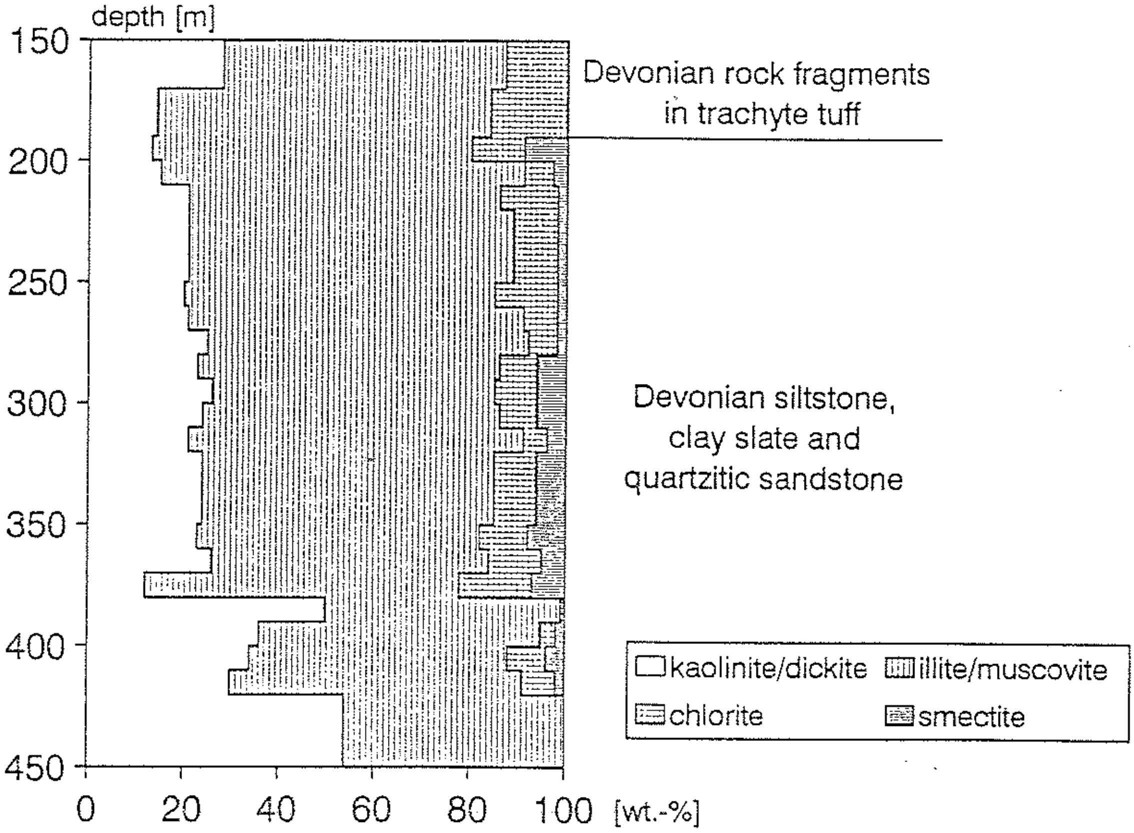


Figure 34: Wehr caldera - distribution of clay minerals (18A = smectite, 14 A = Fe-Mg chlorite, 10 A = illite/muscovite, 7 A = kaolinite and dickite)

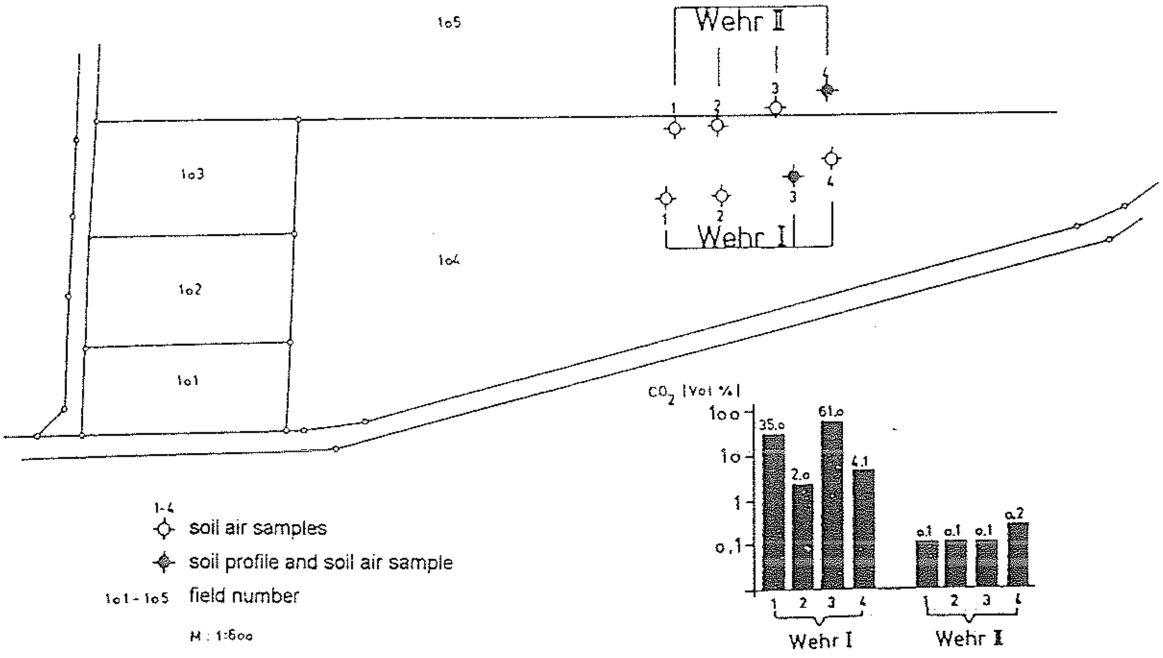


Figure 35: Wehr caldera - amounts of CO_2 in the soil air in 1 m depth at the basis of the rooted soil (BERNS 1988; Wehr I=non-vegetated areas, Wehr II=neighbouring vegetated areas, M=scale)

Table 7: Wehr caldera - total elements of iron ochre from the CO_2 spring, compared with the mean element contents of saprolitic "Hunsrück" iron stones" (n = 18, see stop 8 "Lingerhahn") and of fresh slates (n = 6), determined by XFA (main elements in weight %, trace elements in mg/kg)

	Wehr iron ochre	*iron stones*	*fresh slates*
SiO_2	3,95	41,60	60,36
Al_2O_3	0,45	8,79	18,64
Fe_2O_3	52,89	38,11	7,55
MnO	0,09	0,37	0,11
MgO	2,08	0,43	2,41
CaO	1,26	0,09	0,26
Na_2O	0,34	0,12	0,42
K_2O	0,29	1,50	3,56
TiO_2	0,03	0,48	0,96
P_2O_5	0,19	0,50	0,15
SO_3	0,01	0,02	0,04
H_2O^+	17,59	6,38	4,45
H_2O^-	10,82	0,70	0,50
S	99,99	99,09	99,41
Ba	727	417	537
Rb	12	75	139
Sr	560	49	102
Co	0	52	41
Cr	59	171	137
Cu	0	74	26
Ni	118	204	75
Pb	24	138	35
V	104	116	134
Zn	295	322	110
Zr	312	193	213

There are marked differences in the element distribution between the Wehr iron ochre and goethitic-hematitic iron stones of the bleached Mesozoic-Tertiary saprolite (see stop 8 Lingerhahn). The latter developed during descent of the Tertiary ground water table by infiltration of iron and accompanying elements into kaolinitic saprolite along joints and weathered quartz veins due to a redox gradient. Therefore, beside iron and manganese oxides they consist of elements of the silicatic matrix.

Untypical for iron stones of the saprolite, the Wehr iron ochre shows high amounts of basic ions as Ca, Mg, Na, Ba, Sr. On the other hand many heavy metals as Co, Cu, Cr, Pb obviously were rather immobile and therefore they could not be enriched in the iron ochre. Remarkable is the high amount of Zr of the iron ochre, which is believed to be very immobile in a weathering environment.

Stop 7 Waldesch quarry

Site: *Quartzite quarry at the "Horstkopf" ridge, 350 m a.s.l.*

TK 5711 Boppard, r 33 94250 h 55 68200

Topics: *Hydrothermal alteration of the Mesozoic-Tertiary weathering mantle, neoformation of hydrothermal minerals*

Summary

Since the beginning of this century the question has been discussed whether kaolinization of rocks is a weathering process or a consequence of ascending, post volcanic or hydrothermal solutions. For most of the kaolinized rocks of the European hill countries a genesis by weathering has been proved. Locally, however, indications exist for an ascendent genesis or at least a participation of ascending solutions in the kaolinization. In the Rhenish Massif this often occurs in tectonically strongly stressed areas with Tertiary and Quaternary volcanism.

The locality "Waldesch" is situated only few km South of the volcanic fields of the Eastern Eifel and single Tertiary basaltic dykes are known in the surroundings. Partly thermal hydrogene carbonate waters, which occur today in a vicinity of 6 - 8 km (Rhens village on the Rhine and Winningen village on the Moselle) are looked upon as a sign of continuing post-volcanic activity of Quaternary volcanism.

The Horstkopf quarry is situated some km South of Waldesch village upon the ridge of a small relic of a mountain chain. This ridge of quartzite juts out of the old peneplain about 50 - 100 m, as the height of the correlated Tertiary sediments proves. Therefore, this relic of a mountain was exposed to the intensive pre-Pleistocene weathering and a huge part of the thick saprolite zone is preserved. At the steep walls of the quarry,standing up to 15m high, 0,5 - 2 m thick banks of quartzite, interbedded with 0,1 - 2 m thick layers of saprolite from sandy silt slates,are cropping out. Quartzite and slates are bleached and their chlorite content is completely kaolinized. Along joints oxides in the form of hematite and goethite are infiltrated into the bleached rock, forming hard crusts. Predominantly within the joints of the slates, white monomineralic infillings of dickite, up to 1 cm thick, occur. Joint planes within the quartzite are often covered with fresh quartz crystals, unaffected by weathering, partly overlain by fibrous brown iron ore from well crystallized goethite. Here the pre-Pleistocene saprolite seems to have been superimposed by ascendent post-volcanic solutions. The processes of lateral secretion led to the mineral new-formation of dickite, quartz, hematite and goethite. The mineral phases precipitated from hot waters, which were mineralized by rock-water interaction processes, probably by rapid cooling. These mineral phases do not occur within the Mesozoic-Tertiary saprolite of the Hunsrück flat upland area, which is situated far away from a possible post-volcanic influence.

Beside the neo-formation of dickite, fibrous goethite and quartz, the occurrence of sericite, which covers all joint planes of the sandy and quartzitic saprolite layers may be an indicator of hydrothermal alteration. Compared to bleached saprolite from Hunsrück slates the Waldesch saprolite is enriched in the elements Ba and Sr. Additional the hematitic oxide accumulation zones are enriched in the elements Mg, Na, P, Cr, Pb, V and Zr, compared to the bleached saprolite as well as to the mean of Hunsrück iron stones (see Stop 8 Lingerhahn). Compared to the iron ochre from the CO_2 spring of the Wehr caldera the enrichment of basic main and trace elements is similar, while the enrichment of Cr and Pb, as well as the missing of Zn may be due to strong acid thermal waters.

Isotope analyses using the $^{18}O/^{16}O$ fractionation of neo-formed quartz and dickite as a geothermometer as well as the internal oxygene isotope fractionation of dickite led to the assumption of a temperature of mineral neo-formation of about 270 °C (investigations by S. HOERNES, Univ. Bonn)

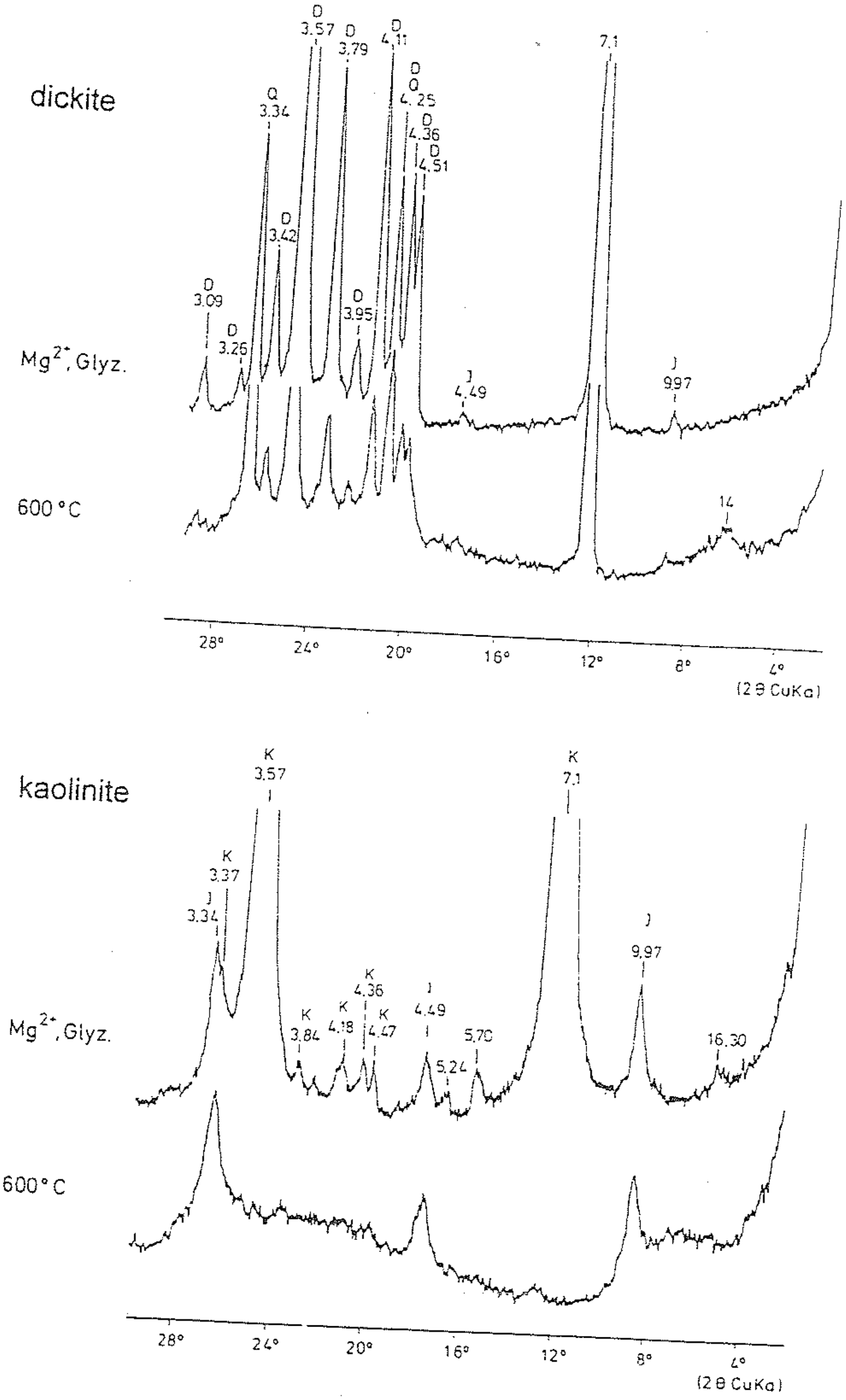


Figure 36: XRD-diagrams (glycerol-air dry and 600 °C heated specimen) of dickite (veins of Waldesch quarry) and kaolinite (veins of Oedingen kaolin pit)(D=dickite, K=kaolinite, I=illite, Q=quartz)

Table 8: *Waldesch quarry - total elements of bulk samples of bleached saprolite and iron oxide accumulations (determined by XFA), main elements in weight %, trace elements in mg/kg*

	mean of bleached saprolite *n = 33*	*W.esch bleached saprolite*	*mean of Hunsrück iron stones* *n = 18*	*W.esch, red purple ferricrust*	*W.esch hematite with sericite*
SiO_2	68,08	71,92	41,6	56,79	41,42
Al_2O_3	19,40	17,11	8,79	11,26	21,84
Fe_2O_3	1,39	0,98	38,11	21,01	23,15
MnO	0,01	0,01	0,37	0,01	0,03
MgO	0,61	0,72	0,43	0,71	0,72
CaO	0,18	0,19	0,09	0,04	0,11
Na_2O	0,15	0,01	0,12	0,26	0,35
K_2O	3,77	4,54	1,50	3,47	4,27
TiO_2	0,99	1,04	0,48	0,89	1,28
P_2O_5	0,05	0,05	0,5	0,13	0,13
SO_3	0,02	0,03	0,02	0,02	0,02
H_2O^+	4,82	2,98	6,38	2,84	-
H_2O^-	0,36	0,48	0,70	3,40	-
S	99,83	100,04	99,09	100,82	-
Ba	554	1385	417	1176	1170
Rb	174	179	75	118	133
Sr	101	215	49	108	232
Co	22	14	52	0	0
Cr	131	106	171	470	229
Cu	17	10	74	4	24
Ni	23	26	204	6	15
Pb	40	9	138	143	175
V	121	111	116	221	170
Zn	39	29	322	0	0
Zr	256	311	193	200	560

Stop 8 Lingerhahn

Site: 300 m behind the Eastern exit of Lingerhahn village at a forest edge, *TK 5911 Kisselbach, r 33 98380 h 55 52050, 487 m a.s.l.*

Topics: *Mesozoic-Tertiary saprolite with "Hunsrück iron stones " and soil formation in Quaternary superficial layers*

Summary

During Mesozoic and Tertiary the Lower Devonian slates of the Hunsrück weathered some 10 m deep under the influence of a subtropical to tropical climate.The slates changed to a soft kaolinitic saprolite, which preserved the undisturbed rock structure. From this saprolite a clay-rich and kaolinitic soil developed, several metres thick, with gray, red or mottled colours, according to the ground water level. Such autochthonous Tertiary fossil soils above a saprolite and covered by Tertiary and Pleistocene sediments were exposed at some locations in the Rhenish Massif (JARITZ 1966, FELIX-HENNINGSEN & WIECHMANN 1985, see stop 4 "Ringen"). According to their argillaceous texture and the colour these paleosoils are designated as Red or Gray Plastosols according to the German soil systematics (MÜCKENHAUSEN 1958). Morphology and properties are similar to fersiallitic or siallitic hydromorphic soils of the recent tropics (MÜCKENHAUSEN 1978). From Upper Tertiary to Lower Pleistocene this soil zone was removed by areal degradation. Below the Pleistocene superficial layers the kaolinitic saprolite follows directly.

In extended areas of the Eastern Hunsrück the basal layer of Pleistocene surface strata, from which the recent soil has developed, consists of saprolite material redistributed by solifluction processes. The relictic structure of the saprolite was disturbed with consequence of formation of a gray argillaceous layer, which is designated as "Gray Loam" (STÖHR 1967). It is covered by talus deposits and eolian sediments in different amounts (v. ZEZSCHWITZ 1970). Thus, in wide areas of the Rhenish Massif morphology and properties of the recent soils are strongly influenced by relics of the old weathering mantle. This has been discussed in several papers by MÜCKENHAUSEN.

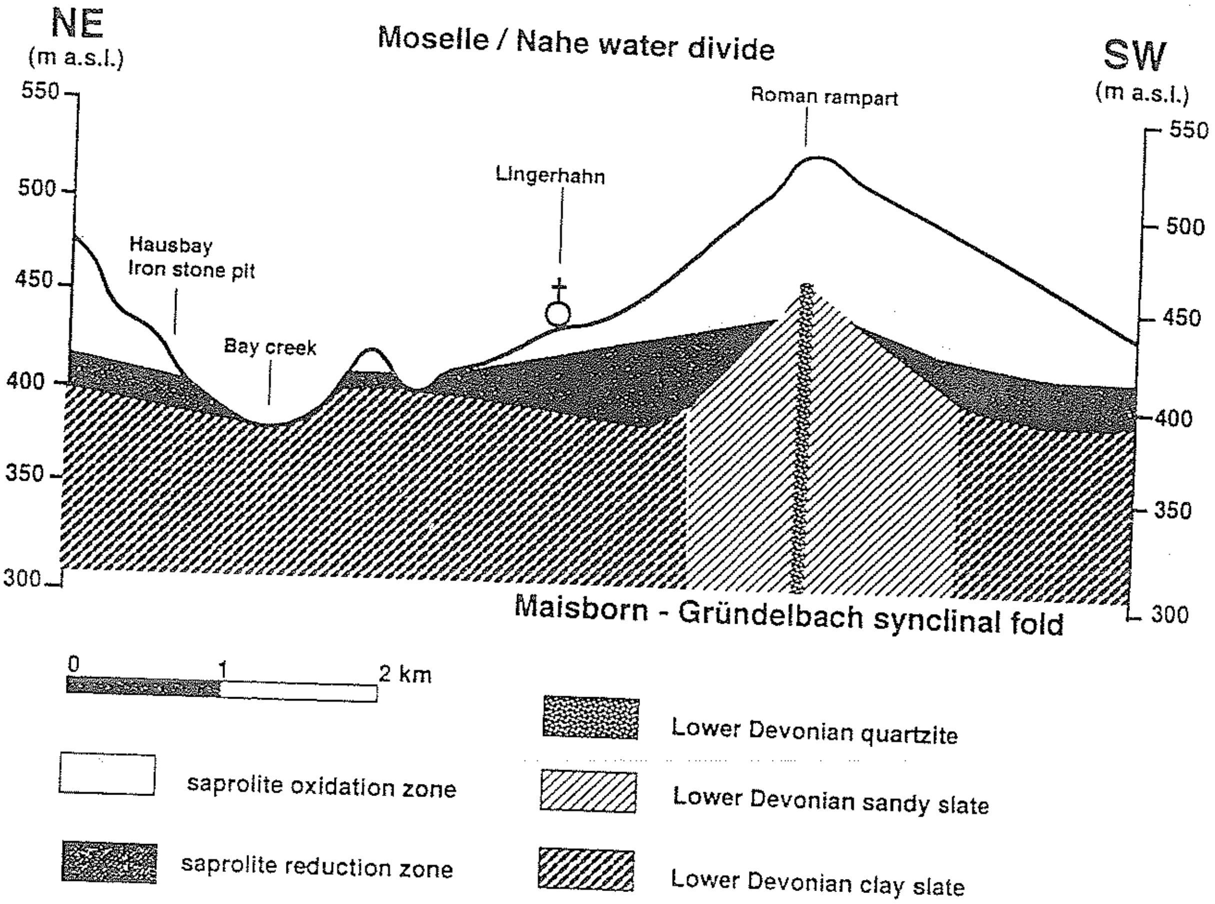


Figure 37: Cross section of the landscape around Lingerhahn village

Description

Description of the deep drilling core

The mineralogical and geochemical properties of the saprolite zone have been investigated on the core of a 50 m deep drilling near Lingerhahn village, which did not reach the completely unweathered slate.

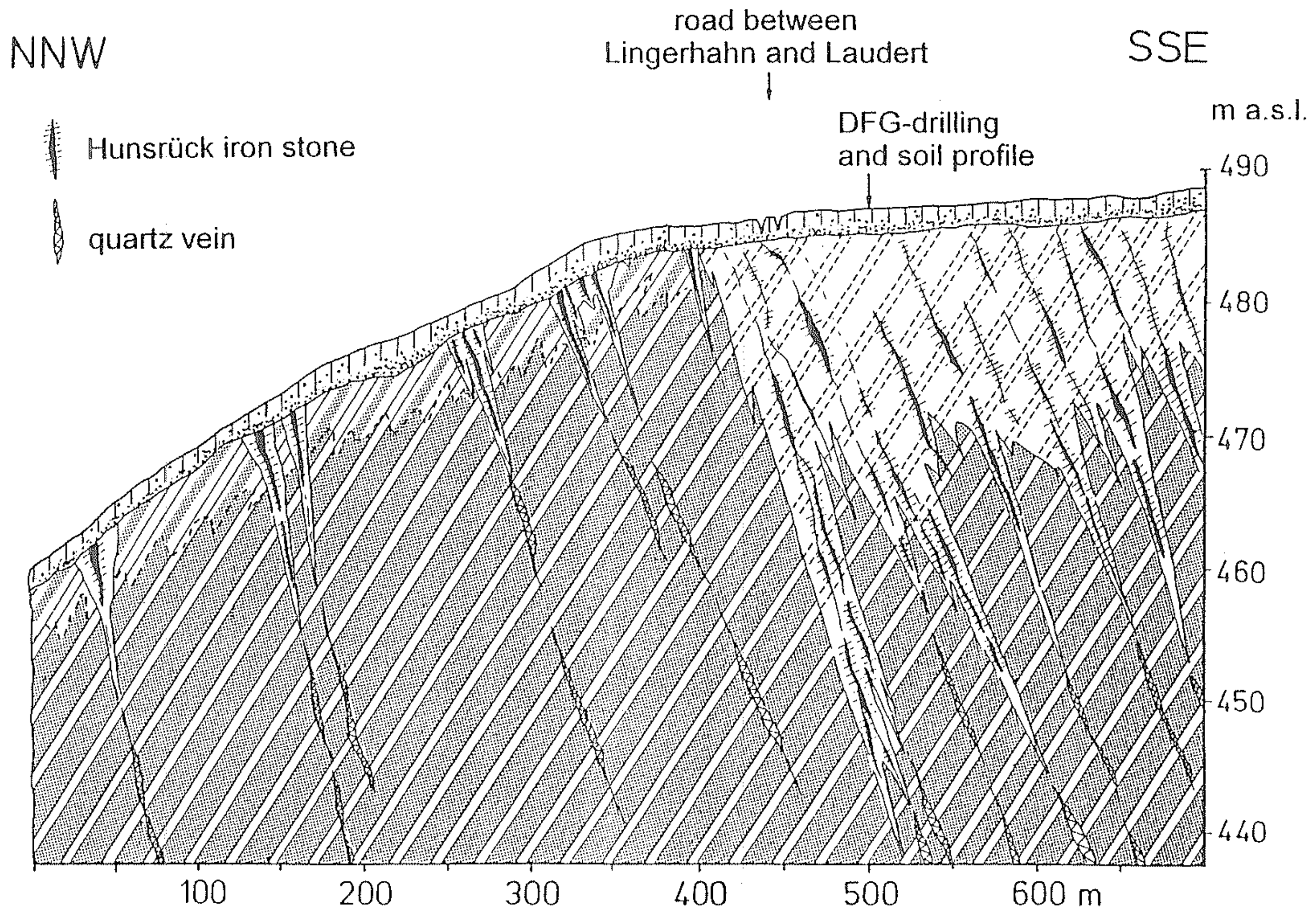


Figure 38: Cross section of the area East of Lingerhahn village (black = reduction horizon of saprolite; white = oxidation horizon of saprolite)

Stratigraphy and morphology:

0 - 1.30 m: Pleistocene superficial layers: Solifluction layers from softened saprolite material (gray loam), loessial loam and loessial pumice dust.

1,3 - 22m: Saprolite from clay slates, predominantly yellowish white (7,5 Y 8/1), with some irregular reddish gray, yellowish and red-brown zones of relatively weak oxide enrichment.

22 - 30 m: Saprolite from clay slates, narrowly interbedded with sandy silt slates, dark gray to black gray (N 4 - 3/0) by coaly-bituminous organic matter.

30 - 43 m: Saprolite from clay and silt slates, strongly pervaded by quartz veins, red (10 - 2,5 R 4/3) to yellowish brown (7,5 YR 5/8) by accumulation of Fe oxides with a narrow changing intensity, from more or less infiltrated slates up to an alteration of quartz veins to solid ferricrusts. The boundaries of this subzone are predominantly following the nearly vertical standing cleavage plains (fig. 38). From the vertical section of this zone by the drilling results a great apparent thickness. Its real thickness is about 2 m. 43 - 50 m: Black gray, coaly-bituminous saprolite like 22 - 30 m.

Generally this saprolite can be divided into two parts:

0 - 22 m: Bleached white saprolite,

22 - 50 m: Gray black, coaly-bituminous saprolite with deep penetrations of bleached and partly iron oxide enriched zones, boardering the quartz veins (see fig 38).

In the upper meters of the bleached saprolite the relic slate structure is only weakly preserved while it is of increasing distinctness toward the depth. The compactness of the bleached and the coaly-bituminous saprolite is low. The slates are soft, friable or easy to break by hand. Only zones with strong oxide enrichment are harder. The formation of ferricrusts and oxide infiltration of the boardering saprolite is bound to quartz veins, which primarily penetrate the slates. These quartz veins, which are compact and close in the unweathered stage,were subject to partial dissolution. Therefore, they show fine fissures, solution channels and caverns which, in a secondary process, were filled up and cemented by iron oxides (see formation of Hunsrück iron stones).

Geochemistry and mineralogy:

The mobilization of elements, especially of Fe and Mg, and the neo-formation of kaolinite was a result of the complete decomposition of primary chlorite minerals, which participate in total samples of unweathered slates with an amount of about 30 %, beside muscovite (40 %) and quartz (30 %) (MOSEBACH 1954). The kaolinization of chlorite had intermediate stages of smectite or chlorite-vermiculite mixed-layer minerals as occurring in the lowest parts of the saprolite. While the clay fraction from the bleached saprolite of Lingerhahn drilling shows a complete kaolinization of the chlorite, the coaly-bituminous saprolite contains kaolinite beside chlorite and chlorite-vermiculite mixed-layer minerals, which indicate a lower intensity of leaching due to a relatively high clay content. Weathering and neo-formation of minerals was accompanied by solution of quartz and desilification. In all depths of the saprolite only the muscovite remained nearly stable.

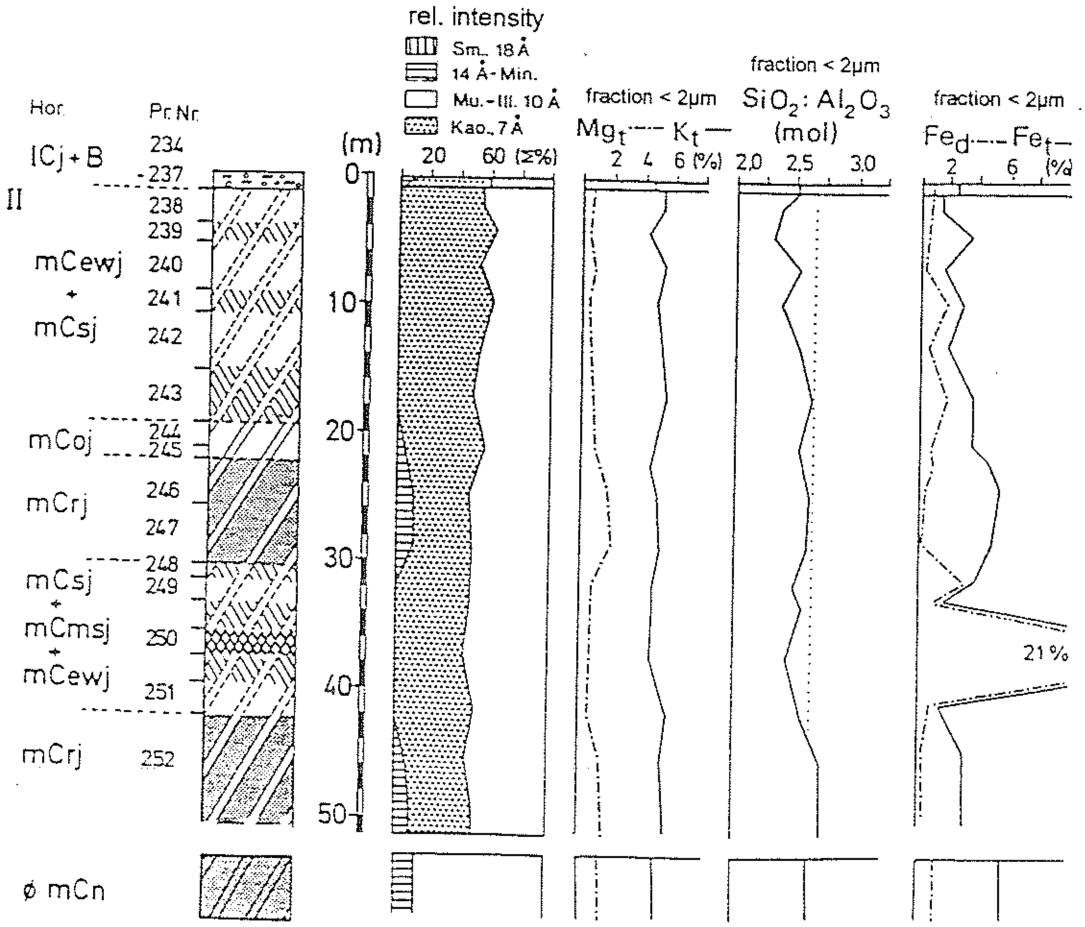


Figure 39: Drill core Lingerhahn - mineralogical and geochemical composition of the clay fraction < 2 mm (legend of clay mineral distribution: relative intensities of sm = smectites, 14 Å Min = chlorites, Mu-Ill = muscovite/illite, Kao = kaolinite; total amounts of Mg, K and Fe, $SiO_2{:}Al_2O_3$ molecular relations as well as free iron oxides,Fed= FeCBD, Pr.Nr.=sample code)

Hunsrück iron stones

Hunsrück iron stones are massiv Fe oxide accumulations of the Mesozoic-Tertiary weathering mantle, dissecting the up to 40 m thick bleached, oxidized saprolite as stonelike and sharply bordered banks. They display a width of 10 - 40 cm and the Fe content is always > 10 %. These iron stones occur in all areas of the Rhenish Massif. Especially in the Hunsrück they were mined in prospecting trenches already at Roman times as well as in periods of scarce ore supply until the first world war. VIERSCHILLING (1910) was the first, who described and mapped the more than 1.000 deposits of the Eastern Hunsrück (see fig. 10). He already noticed the relationship between the bleaching of the saprolite ("Eluvium") and the formation of the banks of iron stone. Because fragments of such iron stones are enriched in skeleton of periglacial superficial layers, they were sometimes paleoclimatically interpreted as "laterite crusts" and indicators of a humid tropical climate.

The genesis of the iron stones is combined with the genesis of the bleached saprolite. The accumulation of oxides occurred in the close surrounding of joints and vugs of tectonical fractured zones as well as in the close surrounding of dissoluted quartz veins. Cavities were completely filled with oxides. Because the bleached saprolite was leached under ground water saturation but afterwards oxidized due to the Upper Oligocene ground water descent, it can be assumed that the jointed rock parts and the dissoluted quartz veins lost the water saturation at first, due to water outflow, while the finer pores of the saprolite matrix stored adhesive water over a long period of time. Along this pathways air penetrated the saprolite and led to oxidizing conditions in the surrounding.

Reduced Fe, Mn and other heavy metals occur in small concentrations in the pore solutions as well as elements, which were adsorbed to the primary organic matter of the slates and released by increase of the redox potential.These elements migrated by diffusion over long distances (partly several meters.) in direction of the oxidized rock parts, which displayed the lowest concentration of reduced elements. During a long period of time the accumulation resulted in a concretionary oxide enrichment filling the pore spaces and impregnating the surrounding saprolite matrix.

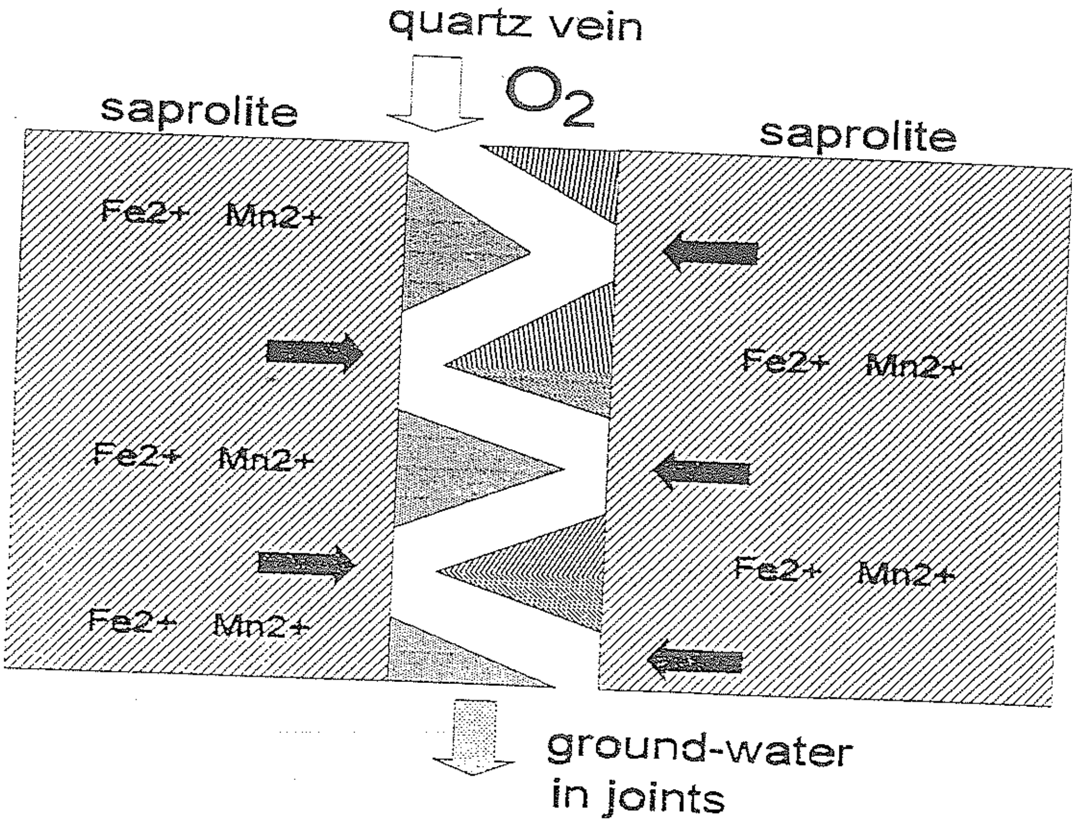


Figure 40: Formation of Hunsrück iron stones along a dissoluted quartz vein due to descending ground water table with consequence of aeration of the saprolite and migration of reduced elements from the water saturated saprolite matrix along a redox gradient by diffusion

In the deeper parts of the bleached saprolite the iron stones consist of pure goethite, frequently accompanied by discrete concretions of Mn oxide (cryptomelane, lithiophorite, see fig. 43). In direction to the former land surface the portion of hematite increases in typical way, that goethitic iron stones have an outer margin of red to purple hematitic iron oxide (see fig. 41). In the uppermost zones of the bleached saprolite, the iron stones completely consist of goethite intermixed with hematite without spatial differentiation.

The Al substitution of goethite from pure goethitic iron stones (determination according to FITZPATRICK & SCHWERTMANN 1982) varies between 5,5, and 11 mole %. Goethite from hematitic iron stones shows an increasing Al substitution with increasing hematite content (see fig. 42), which reflects the gradient of increasing Al availability and acidity respectively, from deeper to upper zones of the saprolite.

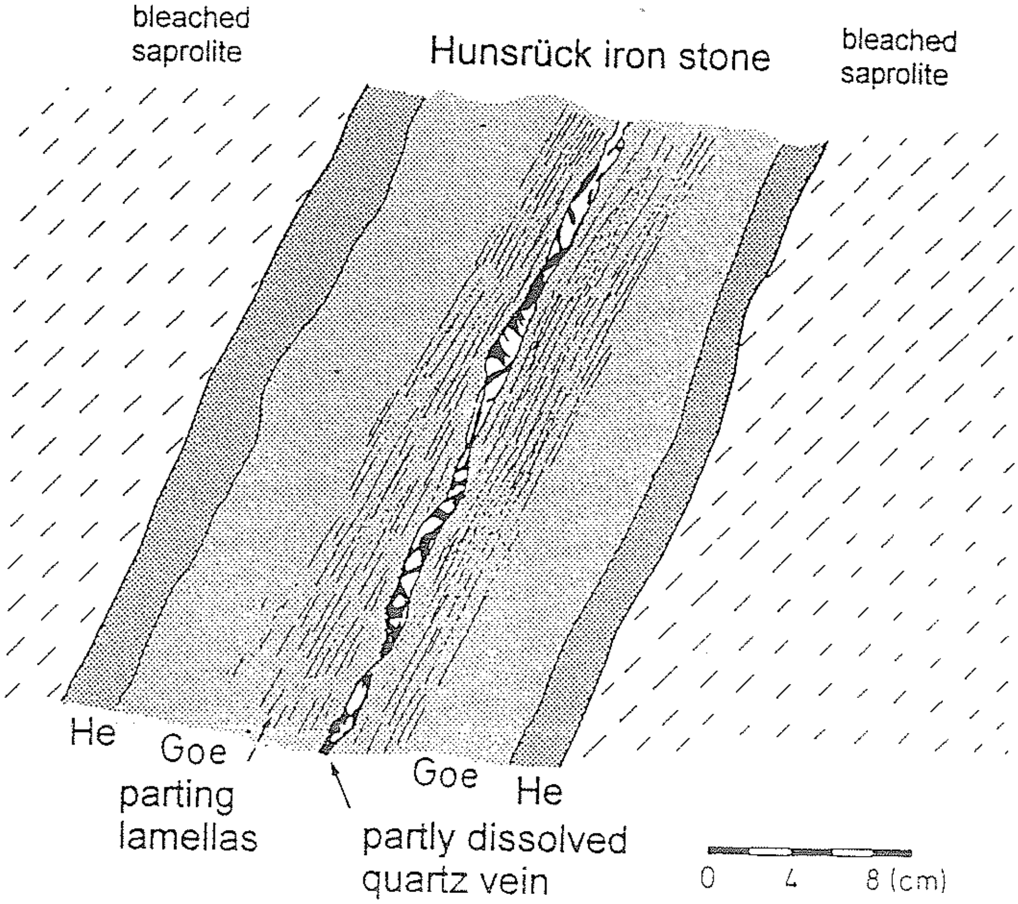


Figure 41: Hunsrück iron stone from accumulation of goethite (Goe) around a dissoluted quartz vein and with an outer margin of hematitic goethite (He)

The enrichment of Fe_{CBD} amounts up to 60 weight %. Some other elements migrated together with the Fe^{2+} ions, were precipitated with the oxides or adsorbed. Due to narrowly changing conditions in redox potential and acidity within the saprolite, the element composition of the iron stones varies widely. The Mn content for example varies between 10 - 10.000 mg/kg. As a rule the pure goethite iron stones display stronger accumulations of Mn, P, Ni and Zn compared to hematitic iron stones. The latter contain higher amounts of the element S, which indicates the participation of sulfates, possibly from the oxidation of pyrite. Inter-element correlations (see tab. 12) indicate, that a high amount of trace elements is bound to the accumulation of Mn oxides, for example Ba, Co, Ni in lithiophorite. Together with iron predominantly Zn accumulated.

The silicatic matrix of the oxide impregnated iron stones always consists of muscovite-illite, kaolinite and quartz. This indicates that the iron stone formation occurred in the saprolite after the complete kaolinization of the primary chlorite. Quantitatively the amount of kaolinite decreases within the clay fraction and the bulk sample of iron stones, compared to the neighbouring bleached saprolite. Additional, the kaolinite reflex intensities of the Fe_{CBD} free matrix are negatively correlated ($r = - 0,97^+$, n = 23) with the Fe_{CBD} content. Ore microscopic investigations prove that the accumulation process was combined with the metasomatic replacement of silicates by iron oxides. According to AMBROSI et al. (1986) H^+ ions evolve from the formation of ferrihydrite by hydrolysis of Fe^{3+} ions during the oxidation process. Mass balances show that 1 cm^3 ferrihydrite may replace about 1,5 cm^3 of kaolinite. The dissolution of kaolinite may have been one source for the Al substitution in Fe oxides.

Table 9: Hunsrück iron stones - total elements of bulk samples of bleached saprolite and Hunsrück iron stones from goethite and hematitic goethite (determined by XFA), main elements in weight- %, trace elements in mg/kg

	mean of bleached saprolite n = 33	*mean of iron stones, goethite n = 14*	*mean of iron stones, hematite n = 9*
SiO_3	68,08	39,69	45,73
Al_2O_3	19,40	9,47	8,09
Fe_2O_3	1,39	38,37	37,29
MnO	0,01	0,52	0,06
MgO	0,61	0,36	0,36
CaO	0,18	0,06	0,05
Na_2O	0,15	0,11	0,05
K_2O	3,77	1,53	1,62
TiO_2	0,99	0,46	0,57
P_2O_5	0,05	0,57	0,28
SO_3	0,02	0,02	0,03
H_2O^+	4,82	6,85	5,39
H_2O^-	0,36	0,77	0,44
Σ	99,83	98,78	99,96

	mean of bleached saprolite n = 33	*mean of iron stones, goethite n = 14*	*mean of iron stones, hematite n = 9*
Ba	554	462	294
Rb	174	70	106
Sr	101	56	30
Co	22	68	1
Cr	131	164	226
Cu	17	70	59
Ni	23	276	6
Pb	40	83	256
V	121	122	113
Zn	39	411	20
Zr	256	163	293

Table 9: *Hunsrück iron stones - significant interelement correlations (Pearson) of FeCBD and MnCBD from iron stones of goethite and hematitic goethite (CBD-Fe: mean = 27,5 %, sd.= 11,5, cv= 41,8 %; CBD-Mn: mean = 2.287 mg/kg, range = 10 - 10.000 mg/kg)*

CBD-Fe	*goethite (n=10)*	*hematite (n=13)*
P	+ 0,44^{+}	
Ni	+ 0,59^{+}	
Zn	+ 0,86^{+++}	
Al$_{CBD}$		+ 0,86^{+}
S		+ 0,80^{+}
CBD-Mn		
Fe$_{CBD}$	- 0,65^{++}	
K	+ 0,72^{+++}	
Ba	+ 0,96^{+++}	
Sr	+ 0,75^{+++}	
Co	+ 0,81^{+++}	
Cu	+ 0,66^{++}	
Ni	+ 0,87^{+++}	

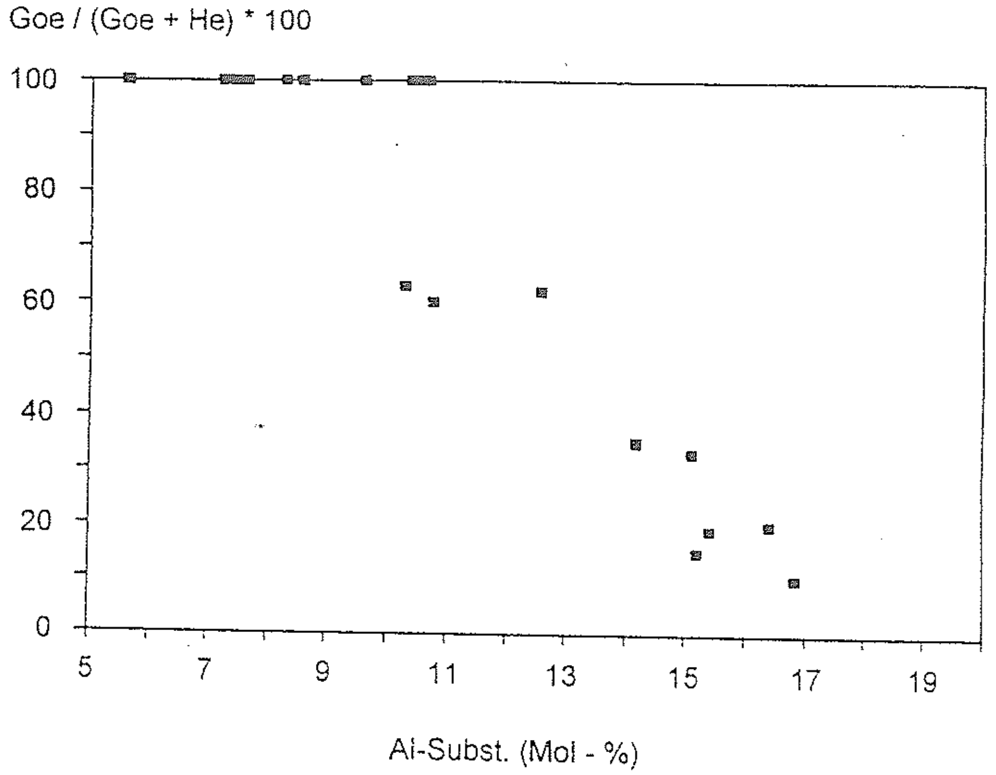


Figure 42: Hunsrück iron stones - Al substitution in goethite in relation to the amount of goethite (Goe=goethite, He=hematite)

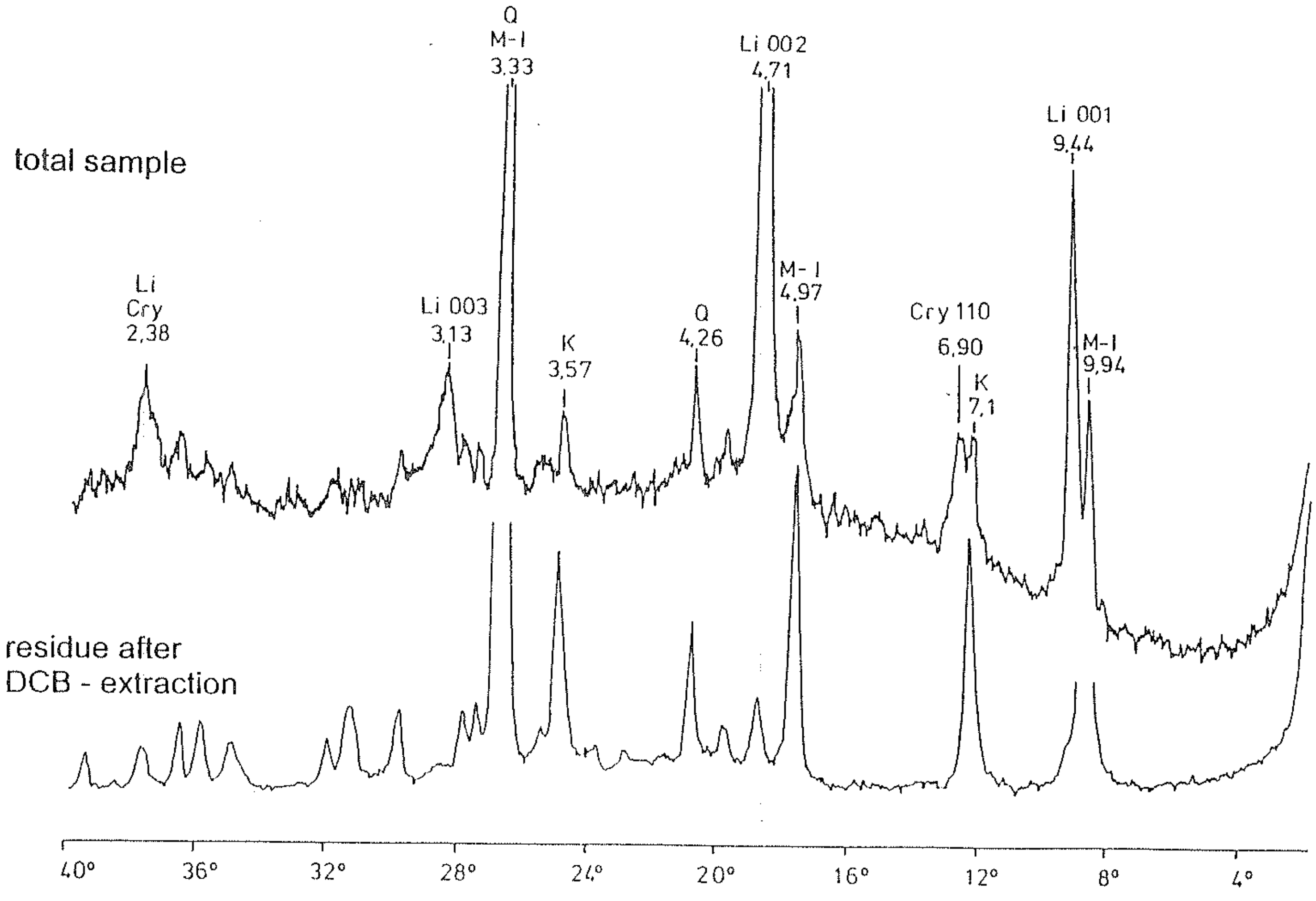


Figure 43:Hunsrück iron stones - XRD diagrams of Mn concretions consisting of lithiophorite (Li) and cryptomelane (Cry) impregnating the silicatic matrix of the saprolite (M-I = muscovite - illite, K = kaolinite, Q = quartz) and of the silicatic matrix after CBD extraction

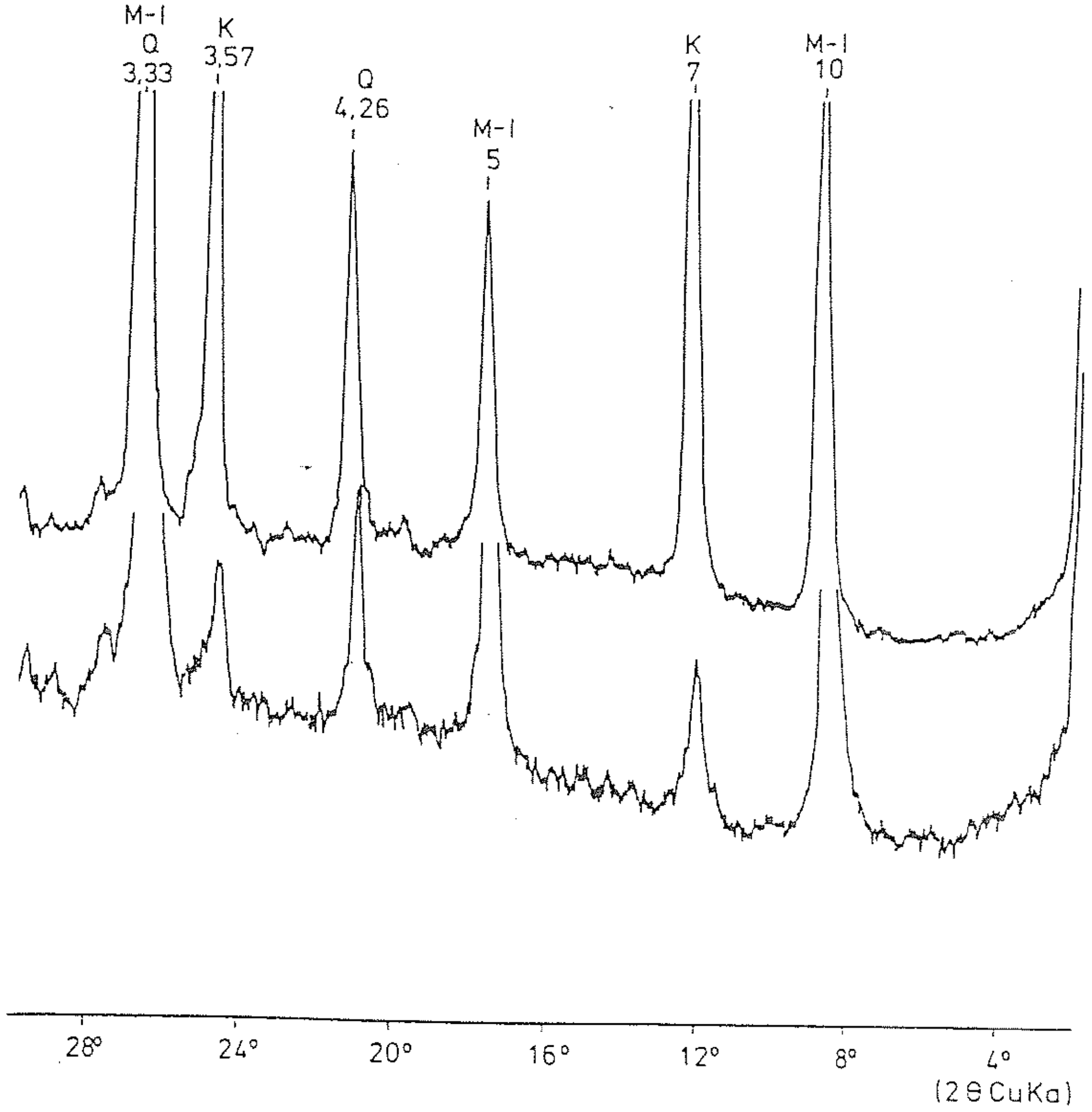


Figure 44: Hunsrück iron stones - XRD diagrams of the silicatic matrix of a hematitic goethite iron stone after CBD extraction compared to the silicatic matrix of the directly neighbouring saprolite (M-I = muscovite - illite, K = kaolinite, Q = quartz)

Description of the soil profile

Near the Lingerhahn drilling location the recent soil, developed from Pleistocene superficial layers, is exposed in an excavated pit. The profile is described as follows:

Locality:	300 m behind the Eastern exit of Lingerhahn village at a forest edge, TK 5911 Kisselbach, h 55 52050 r 33 98380
Relief:	plateau
Altitude:	487 m a.s.l.
Annual precipitation:	700 mm
Mean annual temperatur:	7° C
Land use:	Mixed forest
Parent materials:	Solifluction layers from bleached Mesozoic-Tertiary saprolite, loessial loam and loessial pumice dust
Soil type:	(Relic Para Brown Earth) Brown Earth - Pseudogley
FAO:	(relic Luvisol) Stagnic Cambisol
USDA:	Aeric Ochraquult

Ol	5 - 2 cm:	beech leaves
Of	2 - 0 cm:	fermented leaves
Ah	0 - 5 cm:	dark gray (10 YR 3/2-2/2) silty loam, humous, crumb structure, gliding transition to
SwBv	5-30 cm:	yellowish brown (10 YR 6/4), silty loam, slightly stony and rooted, weak polyhedral structure, black and rusty mottled, roundish black and dark brown concretions up to 1cm in diameter; skeleton: angular fragments of vein quartz, quartzite and Hunsrück iron stones; geogenesis: solifluction layer from loessial pumice dust, upper sequence
BvSw	30 - 50 cm:	yellowish gray (2,5Y 7/3) silty loam, stony, polyhedral

structure, slightly rooted, rusty brown spots (10 YR 6/4-8), black and dark brown concretions - 1 cm in diameter, irregular lower boundary; skeleton: as SwBv; geogenesis: lower part of the solifluction layer from loessial pumice dust, upper sequence

II rBt-Sd 50 - 130 cm: yellowish brown (7,5-10 YR 5/6-8) with yellowish gray (5 Y 7/2) mottles, silty loam, stony, poly-hedral-prismatic structure with black and brown oxide coatings on ped surfaces, single fine roots. In the lowest 20 cm strong skeleton accumulation forming irregular pocket-like intrusions into the underlying horizon; skeleton: fragments of vein-quartz, Hunsrück iron stones and bleached slate saprolite; geogenesis: solifluction layer from loess with intermixed softened saprolite material, middle sequence

III SlCj 130 - 170 cm: light gray matrix (2,5 Y 8/2 - 7,5 Y 7/1-2), yellowish orange to brown (10 YR 6/3-6) mottled clayey loam, stonly and gravelly, prismatic structure with grayish brown clay cutans on ped surfaces; skeleton: fragments of vein-quartz, ferricrusts and bleached saprolite, some rounded quartz gravels; geogenesis: solifluction layer from softened bleached saprolite (=gray loam) without visible intermixing of loess, basal sequence

IV mCewj >170 cm: softened saprolite material from silt slates (texture = silty loam), yellowish gray (2,5 Y 6/1 - 5 Y 5/1) with diffuse orange mottles, ped surfaces and root channels with clay cutans; geogenesis: periglacial disturbance of saprolite material by outcrop bending at the basis of the superficial solifluction layers.

Micromorphology:

Matrix: Only the matrix of the SwBv horizon (4 - 37 cm) shows a subdivision in roundish aggregates with an intertextic micro fabric. This marked aggregation is a typical character of the Dystric Cambisols from pumice bearing loess. In the deeper horizons the clayey - loamy textured matrix is of higher density with pores and fissures. In the II Bt-Sd horizon the homogeneous clayey ground mass contains small fragments of bleached saprolite in an irregular and dense bedding. due to mixing by solifluction.

Cutans:

While the SwBv horizon is free of oriented clay cutans within the pores, the underlying BvSw horizon contains only thin pore standing undisturbed clay cutans.

The II rBt-Sd horizon has only single and thin undisturbed cutans within the recent pores. But fragments of thick cutans, which are spread in the matrix, give evidence for the redeposition of an interglacial Bt horizon by solifluction processes during theUpper Pleistocene.

Mottles and concretions:

Down to a depth of 50 cm the horizons contain well rounded, sharply boardered allochthonous concretions, which often show inclusions of oriented clay cutans. Also micro-fragments of oxide impregnated slates and ferricrusts are occurring. In consequence of logging surface water, the finely dispersed Fe oxides of the clayey matrix were partly redistributed, so that oxide accumulations, especially in the surrounding area of open pores, occur beside diffuse boardered, light gray bleached zones.

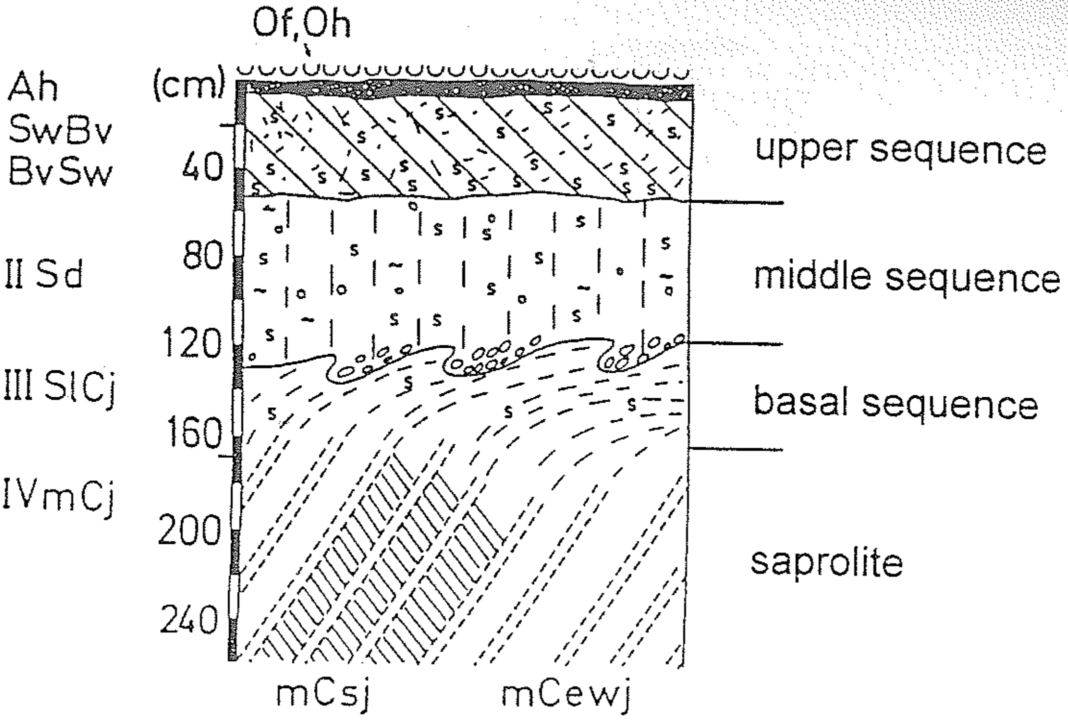


Figure 45: Soil profile Lingerhahn - superficial layers and horizonation (mCsj=accumulation zone of sesquioxides, mCewj=bleached saprolite)

Distribution of heavy minerals:

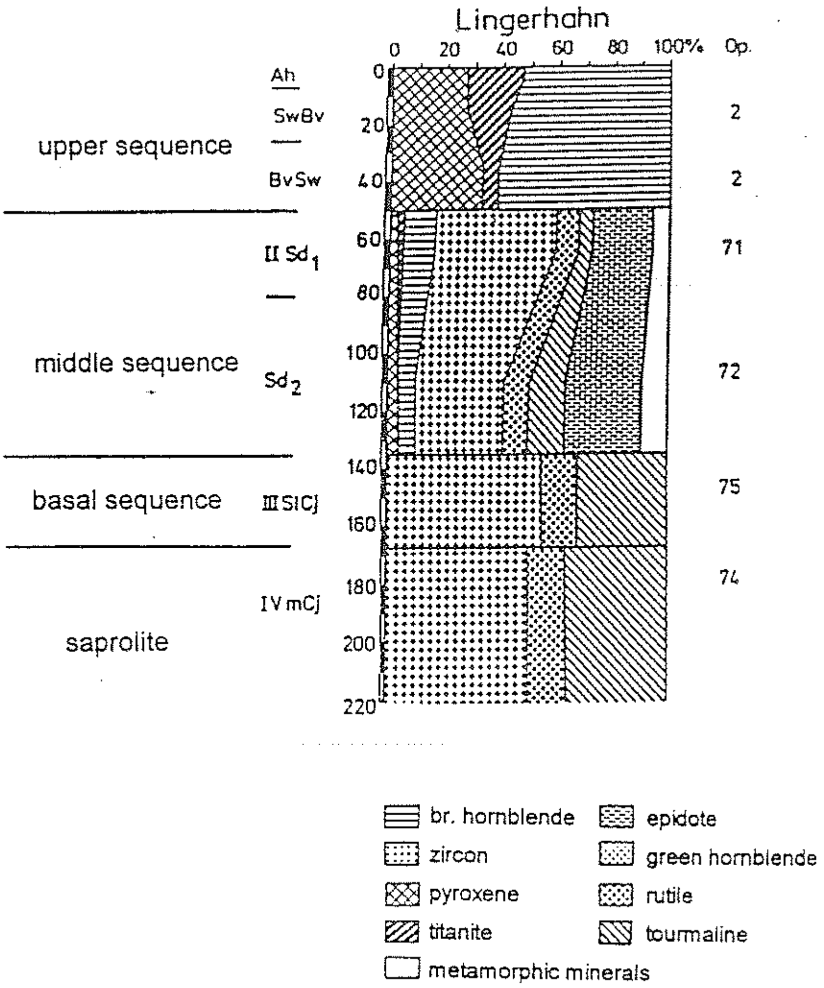


Figure 46: Soil profile Lingerhahn - distribution of heavy minerals of saprolite and superficial layers (in weight % of the summarized transparent heavy minerals of the fraction 30-400 mm; Op.= % opaque minerals)

The distribution of heavy minerals reflects the stratigraphy of solifluction layers of different ages and the source of the materials:

- the upper sequence with an absolute dominance of the volcanic minerals assemblage, which is typical for the loessial pumice dust of the Late Pleistocene age (Younger Tundra Period).
- Sd horizon with an instable and metamorphic mineral assemblage, which is characteristic for the loess deposits of this region, beside the stable spektrum of the saprolite material.
- basal sequence and saprolite with the stable spectrum of Lower Devonian sedimentary rocks with a high amount of opaque minerals.

Texture and pore volume:

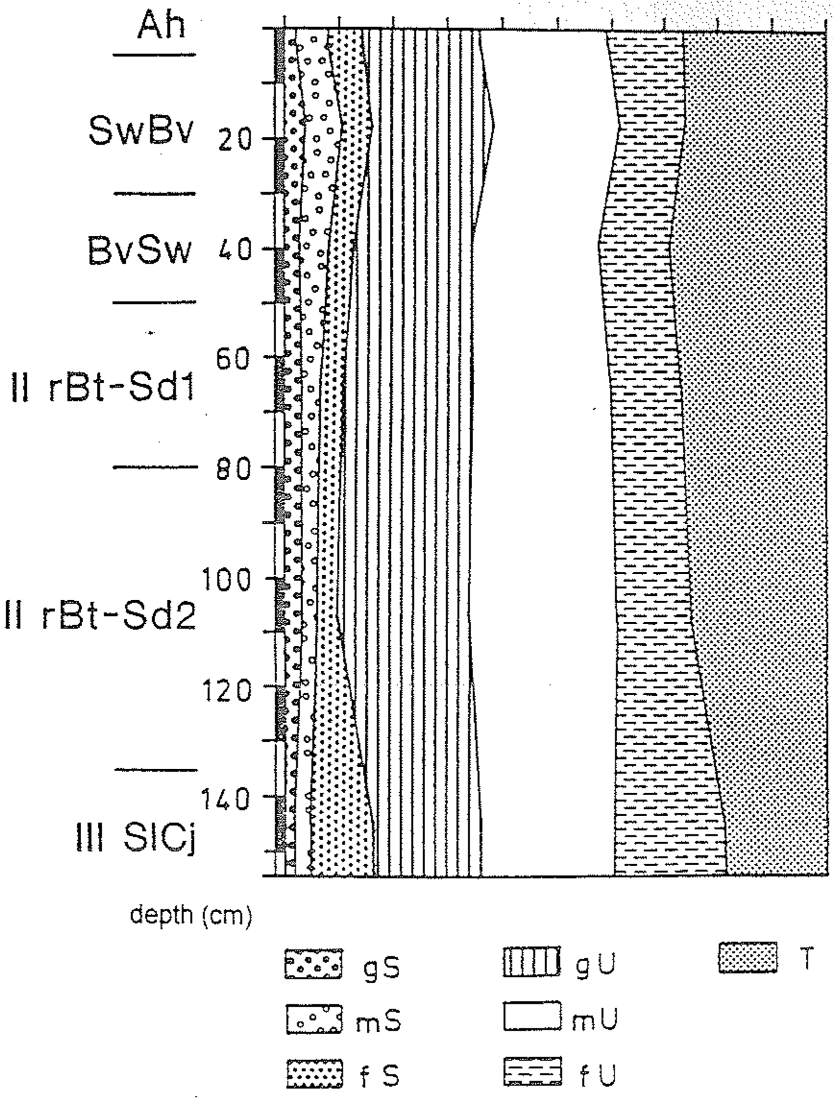


Figure 47: Soil profile Lingerhahn - particle size distribution (gS = 2.000 - 630 mm, mS = 630 - 200 mm, fS = 200 - 63 mm; gU = 63 - 20 mm; mU = 20 - 6,3 mm; fU = 6,3 - 2 mm, T = < 2 mm)

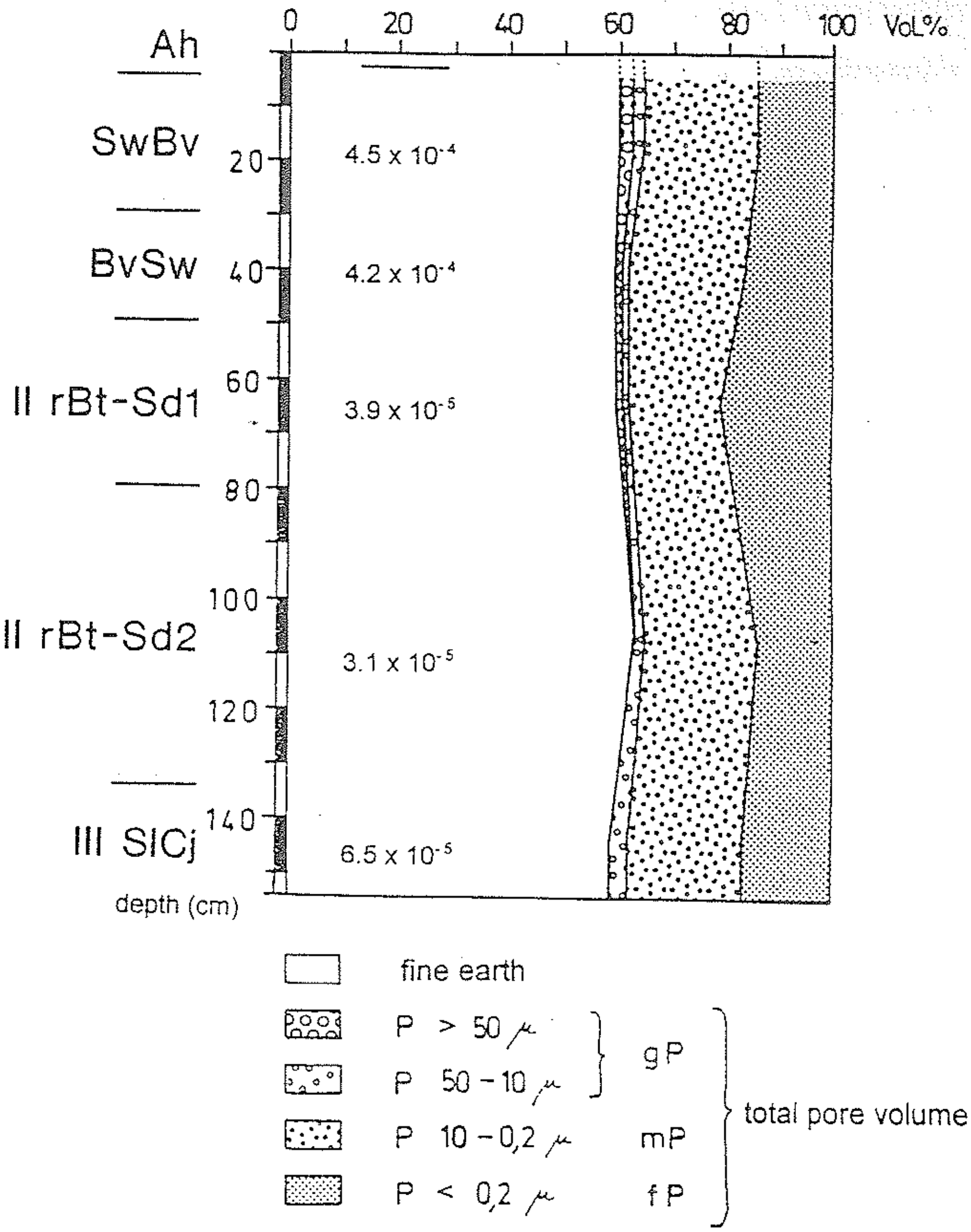


Figure 48: Soil profile Lingerhahn - pore volume, pore size distribution and saturated hydraulic conductivity (in cm/sec)

Clay minerals:

Table 10: Soil profile Lingerhahn - mineral composition and semiquantitative (reflex intensities) distribution of the Mg-saturated clay fraction (prim. chl. = primary Fe-Mg chlorite, sec. chl. = secondary (Al-) chlorite, ver. = vermiculite, ml = mixed layers, mu/ill = muscovite and illite, kaol. = kaolinite, qtz. = quartz, fsp. = felspars)

hor.	*prim. chl. (14)*	*sec. chl. (14)*	*ver. (14)*	*ml (12)*	*mu/ill (10)*	*kaol. (7,2)*	*qtz. (4,26)*	*fsp. (3,2)*
SwBv	4	11	-	-	35	50	+	+
BvSw	+	10	-	-	38	52	+	+
II(rBt)Sd	-	10	-	-	42	48	+	+
(rBt)-Sd2	8	-	-	chl/ver	48	42	+	+
IIISlCj	-	-	-	-	55	45	+	+

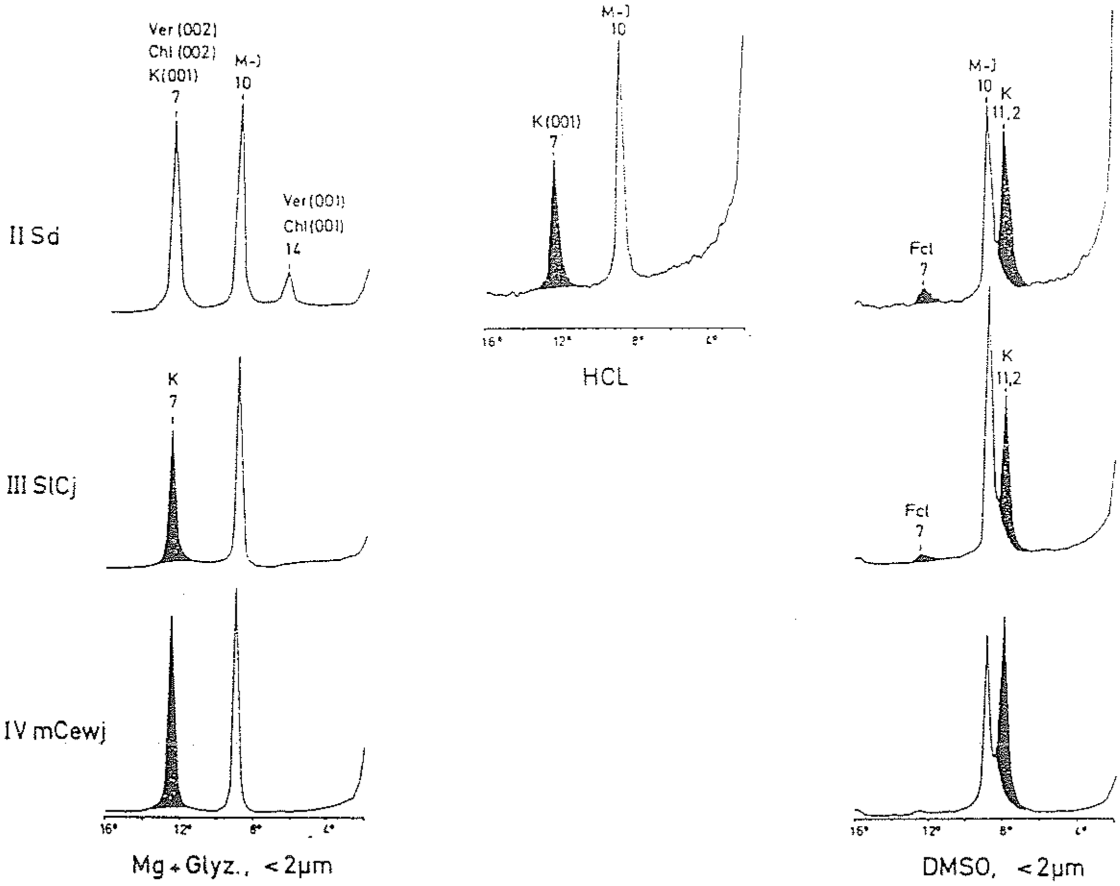


Figure 49: Soil profile Lingerhahn - XRD diagrams (glycerol, HCl and DMSO specimen) of the bleached saprolite (IV mCewj), the basal sequence (III SlCj) and the middle sequence (II rBt - Sd); (Fcl = intercalation disordered kaolinite, K = kaolinite, M-I = muscovite-illite, Ver = vermiculite, Chl = chlorite)

The saprolite of a profile about 80 m apart has not yet been completely kaolinized, whereas in this profile and the drilling, respectively, primary chlorite beside kaolinite occurs for the first time in 20 m depth. This shows that the degree of kaolinization of the saprolite may strongly change on short distance according to the properties of the rocks (quartz veins, clay content).

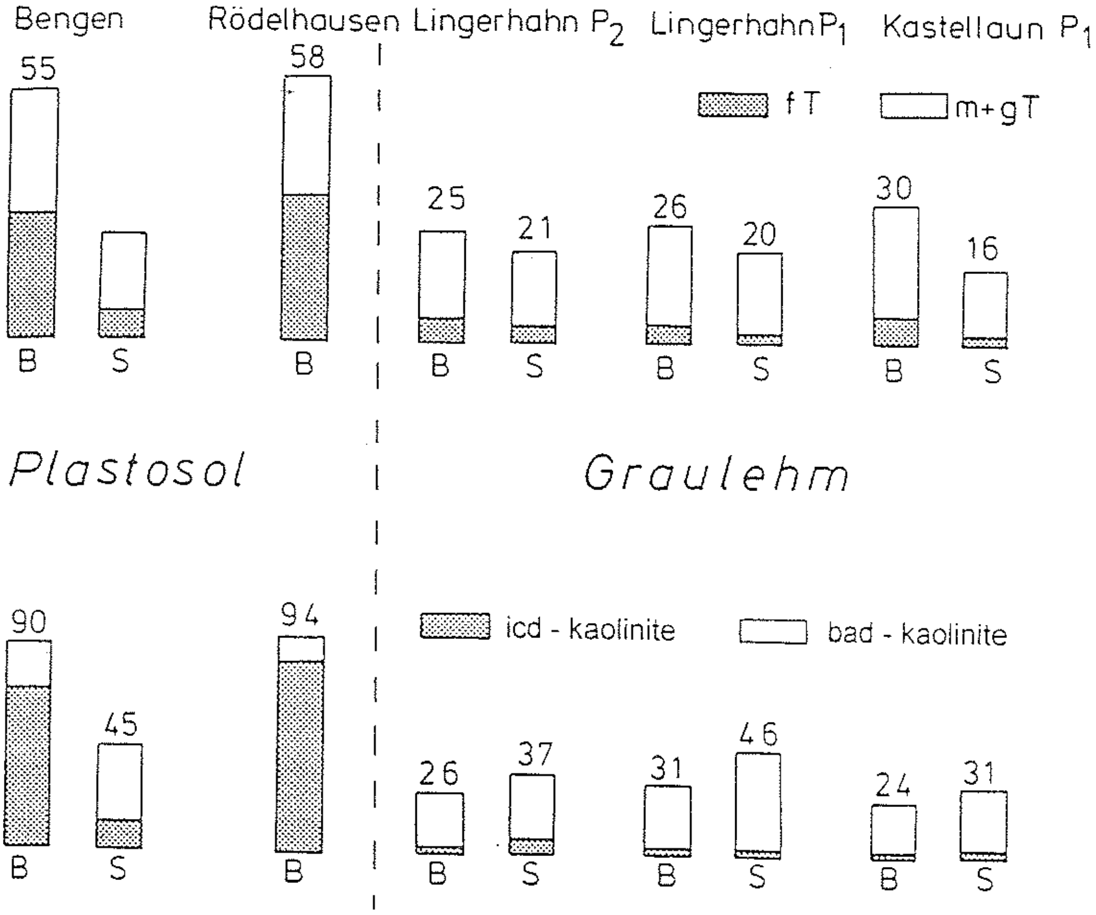


Figure 50: Mesozoic-Tertiary saprolite compared with paleosols (= Plastosol) and Gray Loam (= Graulehm, basal sequence) of soils of the Eastern Hunsrück upland area. 1. clay contents (weight %) with subdivision into fine clay (fT = < 0,2 mm) and middle + coarse clay (m+gT = 0,2 - 2 mm). 2. "content" of kaolinite (relative intensities of the clay fraction < 2 mm) with subdivision into intercalation disordered kaolinite (icd-kaolinite) and b-axis disordered kaolinite (bad-kaolinite). The amount of fine clay and of intercalation disordered kaolinite allow a discrimination between kaolinitic Mesozoic-Tertiary paleosols and solifluction layers from saprolite

Stop 9 Rödelhausen

Site: *Rödelhausen village, gravel pit , 455 m a.s.l.*

TK 6009 Sohren, r 25 95425, h 55 40500

Topics: *Middle to Upper Oligocene marine sediments deriving from Mesozoic-Tertiary paleosols*

Summary

Already KUTSCHER (1954) mapped a number of areas in the Eastern Hunsrück upland region, which display Tertiary sediment deposits on top of eroded remnants of the autochthonous weathering mantle. They were interpreted as fluvial or fluvial-limnic formations. Such, at least 25 m thick deposits, are the gravels of Rödelhausen village, which display less rounded quartz gravels, imbedded in a clayey and silty ground mass.

The deposits are directly situated on top of the recent water divide between the Mosel valley in the North and the Nahe valley in the South. The question, which river and from where had sedimented such deposits was open until now. From sedimentpetrographical point of view, the pure quartz gravels and the clay fraction with >90 % kaolinite, mainly of intercalation disordered type, indicate a lokal source from the soils of the Mesozoic-Tertiary weathering mantle. Recent geomorphological investigations of ZÖLLER (1983, 1985) led to the conclusion that a Middle Oligocene marine transgression, Rupelian stage, came through transverse valleys of the Soonwald hill chain (Southern edge of the Eastern Hunsrück) from the Mainz basin. The transgression led to abrasion of the upper parts of the weathering mantle and a deposition of sediments as a beach ridge, which is exposed in Rödelhausen. This evidence is supported by the finding of marine foraminifers in clay lenses within the deposit of Rödelhausen.

Description

Morphology and petrography:

The sediments are 20 - 25 m thick, but only the upper 10 m are exposed. Poorly rounded middle and fine gravels are embedded in a predominantely white (N 8/0), loamy-clayey fine substance. The skeletal portion > 2 mm amounts up to 55 wt.-%. Stratification is hardly to identify, isolated, irregular shaped, more clayey layers and streaks are inserted. In the upper meters spots of red colour (10 R 4/8) appear, which are sharply marked off against the white matrix. Petrographic differences between these colour zones do not exist. Micromorphologically in the red zones Fe-oxides can be identified as undisturbed precipitation borders on the edge of cavities. They point to a ground-water dynamics after the deposition of the sediments. This postsedimentary pedogene superimposition happened in a warm climate (haematite) before the tectonical uplift of the Eastern Hunsrück during the Upper Oligocene, which was followed by a lowering of the ground-water table (deep oxidation of the saprolite).

The fine substance < 2 mm, in which the gravels are embedded, consists of 58 % clay < 2 mm, in which the fine clay < 0.2 mm dominates with 32 wt.-% (see fig. 51). The sample contains only 12 % silt, while the portion of the sand fraction amounts to 30 %. The particle size distribution of the white and red zones is almost identical. The high portion of fine clay, which is characteristic for Lower Tertiary soils of the peneplain and which is almost absent in the saprolite zones, indicates a large participation of soil material in the sediments.

Minerals of the clay fraction:

In the clay fraction kaolinite dominates with 90 % related to the relative intensities. Illite participates with less than 10 % and shows a broad asymmetric 10 Å-reflex. The clay mineral distribution is almost equivalent to that of the uppermost Tertiary soil horizons of the autochthonous solum from Ringen (see stop 4). Beside the phyllosilicates very low quantities of quartz and feldspar appear in the clay fraction.

The cristallinity of the kaolinite minerals in the sediment also shows a large similarity to the mineralogical features of the soil horizons in the profile "Ringen" (see stop 4). In both cases 90 % of the 7 Å-minerals consist of fireclay-minerals. They indicate that the sediment material derived from the solum of the weathering mantle.

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