



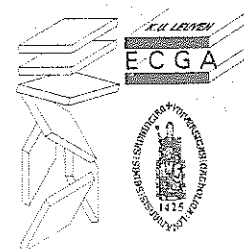
JUSTUS-LIEBIG-UNIVERSITÄT

GIESSENER BODENKUNDLICHE ABHANDLUNGEN

Institut für Bodenkunde und Bodenerhaltung

Band 13

EUROCLAY'95



under the auspices of the European Clay Groups Association

Soil formation and hydrothermal alteration
from the Mesozoic until the Holocene
in the Rhenish Massif

Mineralogy and genesis of saprolites, alteration zones, soils
and sediments

Excursion Guide

Peter Felix-Henningsen
and a contribution by Karl Stahr

Leuven and Giessen, August 26 - 27, 1995

ISBN 3-930600-35-8



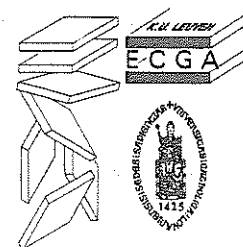
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Preface

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-scientific 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 kaolinitic weathering products of the Rhenish Massif.

The results, on which this excursion is based, were obtained from the research of the author undertaken between 1981 and 1987.

The suggestion, to prepare an excursion during the EUROCLAY conference in Leuven, Belgium, came from Karl Stahr, Hohenheim, who himself presents a contribution to the youngest section of the polygenetic profile.

The preparation of this excursion guide was undertaken by B. Eurich-Menden, T. Klein, 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, August 1995

P. Felix-Henningsen

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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 CO₂ 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 veins 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-hipidolite). 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.

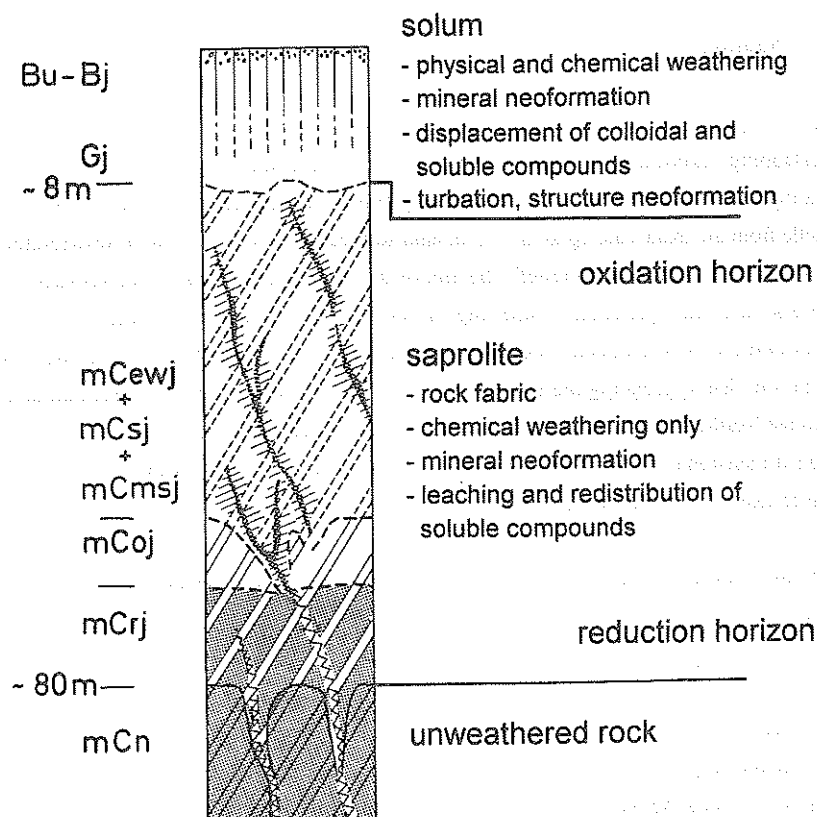


Figure 1: The Mesozoic-Tertiary weathering mantle of the Rhenish Massif - genetic units, morphological classification, and horizon symbols

- (mCrj): reduction zone, black-greyish colour of the fresh slate
 mCj: oxidation zone, brown-, to greyish olive colour, weak elution, no accumulation of oxides
 mCewj: bleached zone, white to light greyish colour
 mCs: accumulation zone of sesquioxides, yellow, brown, red and purple colours, relatively weak accumulation of oxides (<10% Fe₂O₃)
 mCmsj: massive, brown, red and purple-reddish iron stones ("Hunsrück iron stones") (>10% Fe₂O₃) 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.

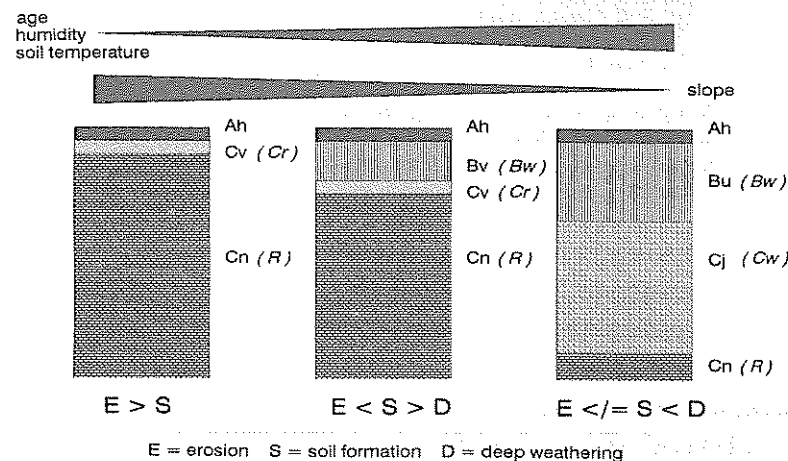


Figure 2: Factors and processes determining the formation of a weathering mantle (regolith), which consists of a solum and saprolite; horizationation according to German soil systematics (AK BODENSYSTEMATIK 1985) and FAO/UNESCO legend (1989) respectively

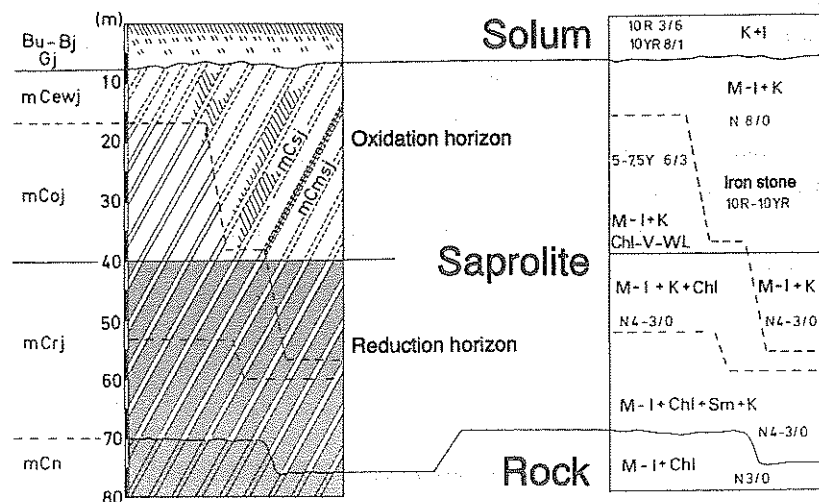


Figure 3: Morphological and mineralogical subdivision of the Mesozoic-Tertiary weathering mantle (Chl = primary Fe-Mg chlorite; Sm = smectite; M-I = muscovite-illite; Chl-V-WL = chlorite-vermiculite mixed layer minerals; K = kaolinite, explanation of horizon symbols see fig. 1)

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 occurred 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 ferrallitic 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 of thick bleached saprolite ("Weißerwitterung") 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 autochthonous 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. Therefore, 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 Plastisol" on the systematical level of soil type or subtype according to the German Soil Systematic does not seem to be justified.

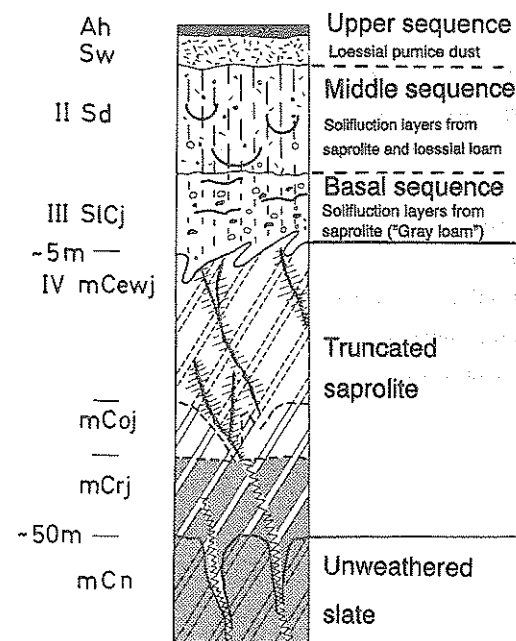


Figure 4: Vertical section of the partially eroded Mesozoic-Tertiary weathering mantle overlain by periglacial superficial layers (horizon symbols see fig. 1)

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 CO₂ 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 CO₂ 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 Hunsrück" (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.

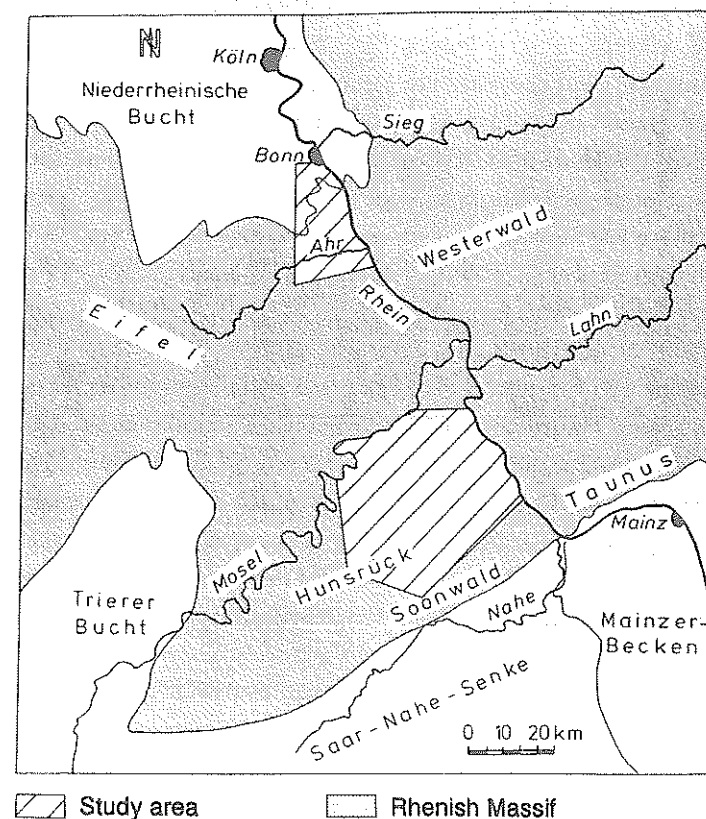


Figure 5: Excursion areas in the Rhenish Massif

2.1 Northeastern Eifel

Stratigraphically the Lower Devonian rocks of the Eifel and the Rhenish Embayment belong to the Middle and Upper Siegenian 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 acidic 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 fluvial incision of rivers during the Pliocene and the Pleistocene was not very intensive. The recent relief shows only a slightly changed relief formed by peneplanation at the end of the Miocene (QUITZOW 1978). According to the low erosion activities a denudation of the weathering mantle was only slightly given. 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

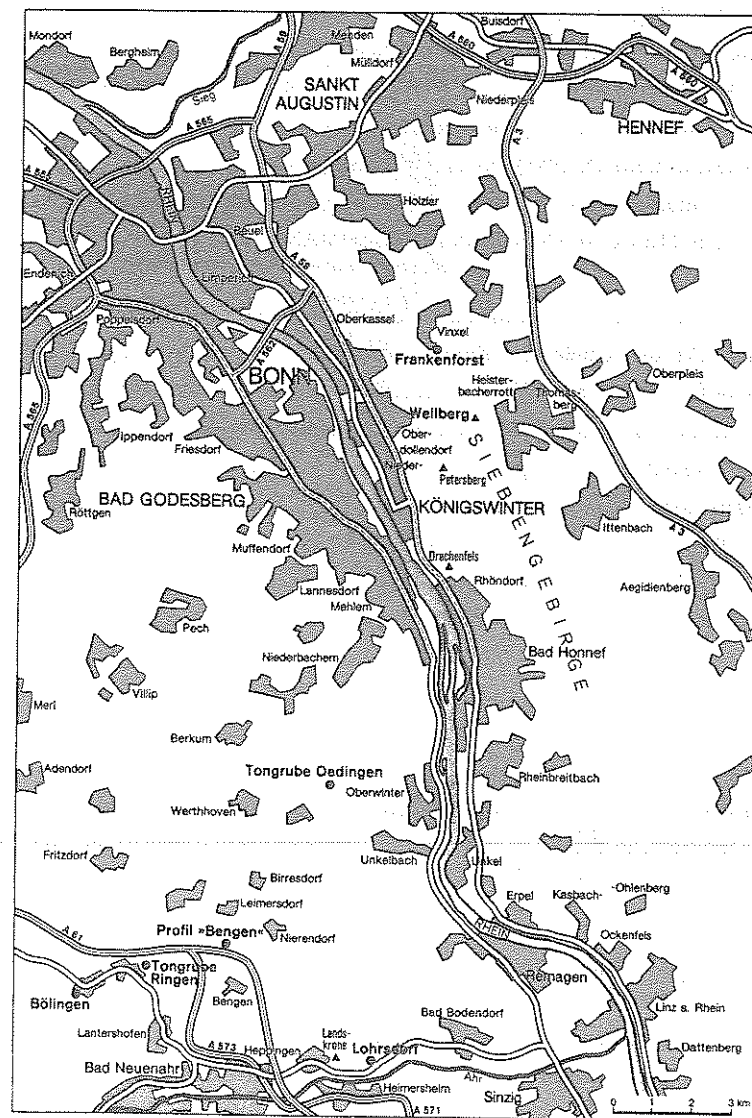


Figure 6: Excursion sites in the Northeastern Eifel

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 "Vallendarshotter" (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, soils 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,

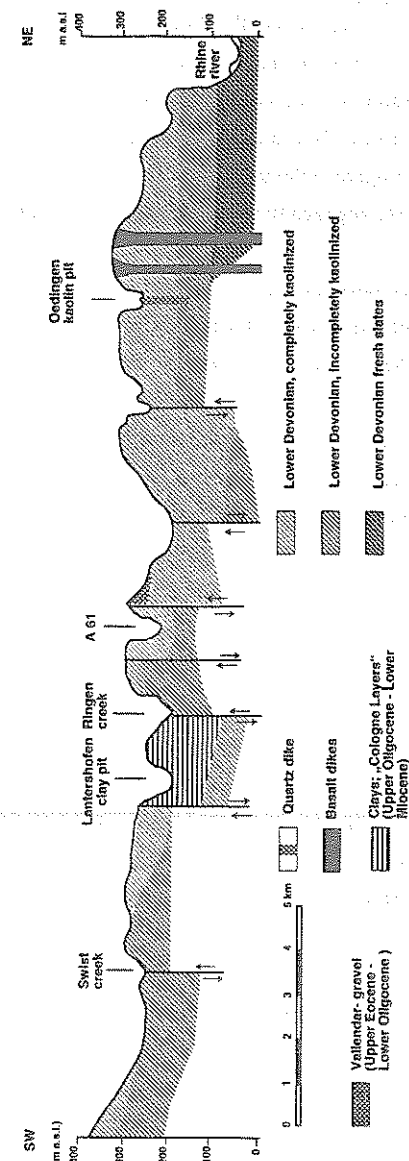


Figure 7: Landscape section of the Northeastern Eifel study area (after SPIES 1986)

sheet Altenahr and sheet Ahrweiler) and of AHRENS (1939, sheet Linz). In the West of the study 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 "Walpurgisque" 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 CO₂ springs exist in the Eastern Eifel area. The ascending water decomposes the rocks along the joints. Therefrom in 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. CO₂ 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 CO₂ 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 occurs 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 Å 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 Å) 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 $> 600^{\circ}\text{C}$. 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.

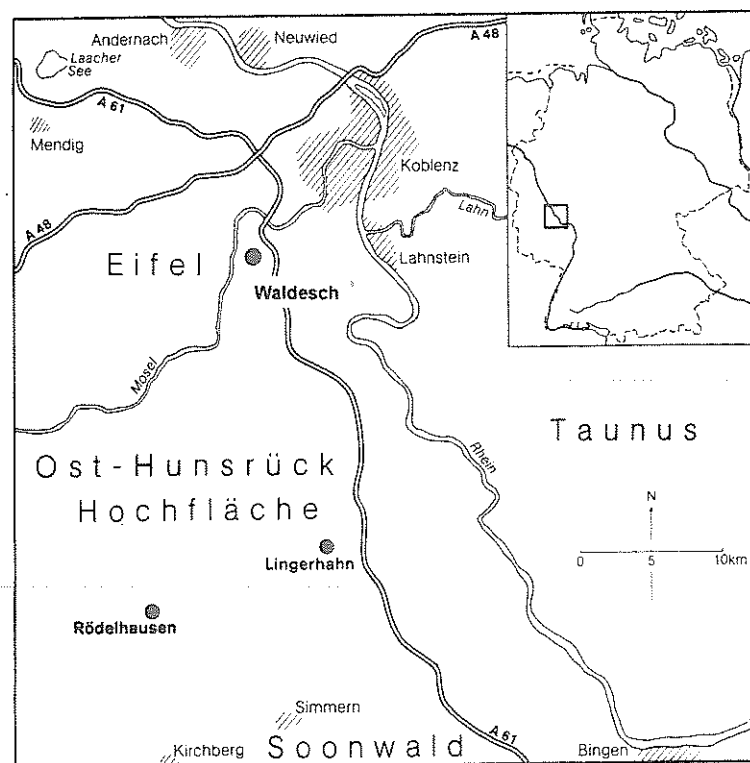


Figure 8: Excursion sites in the Eastern Hunsrück

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.

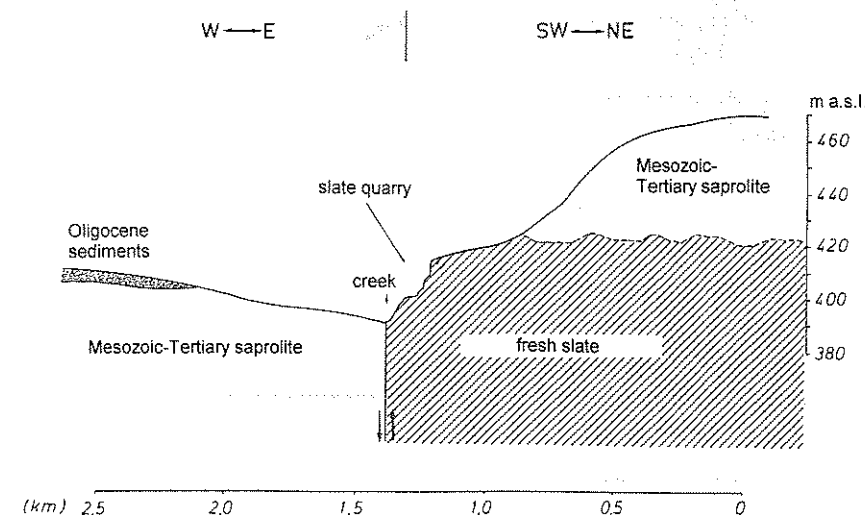


Figure 9: Eastern Hunsrück - cross section of the Alterkülz creek valley as an example for an asymmetric valley due to block faulting; at the uplifted block fresh slates are exposed which then are mined for production of roof shingles

At the end of 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 Würm 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.

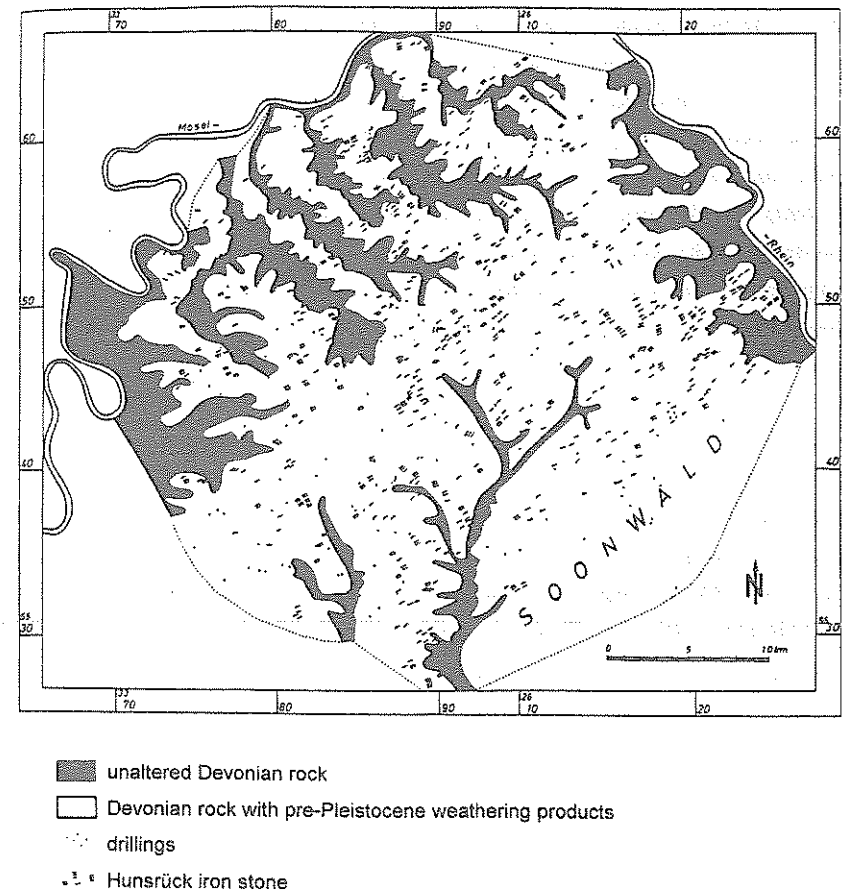


Figure 10: Range of pre-Pleistocene weathering products (without further differentiation) in the Eastern Hunsrück (SPIES 1986)

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 1 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 occurred 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 continuous primary organic substance resulted in an olive-gray brightening 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.

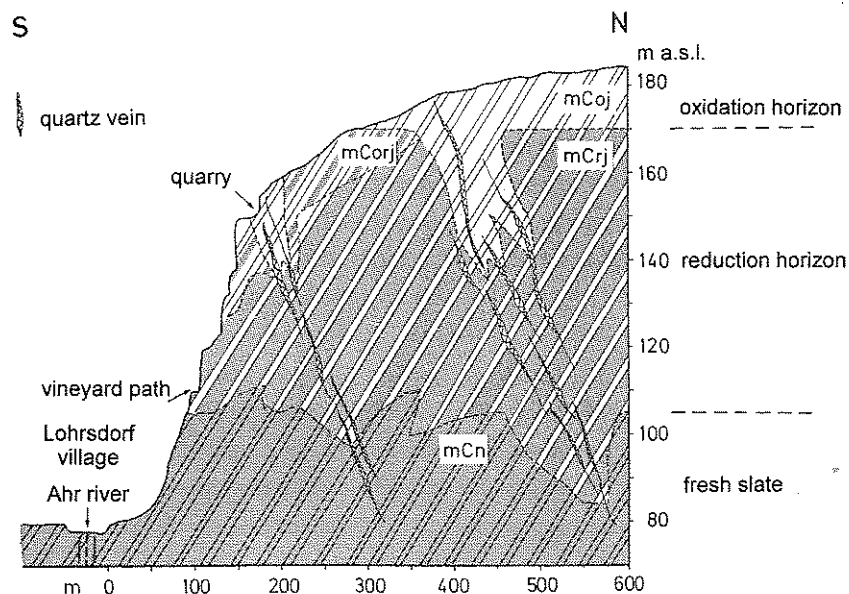


Figure 11: Ahr valley - cross section of the Northern slope near Lohrsdorf displaying the undermost saprolite zones (explanation of horizon symbols cf. fig. 1)

Description

Unweathered slates

Bulk density:

2,49 - 2,58 g/cm³ in clayey slates of the Hunsrück area (Hunsrück slates),

2,67 - 2,69 g/cm³ in slates of the Northeastern Eifel.

Spezific gravity:

2,70 - 2,72 g/cm³.

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 µm 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.-% K₂O 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).

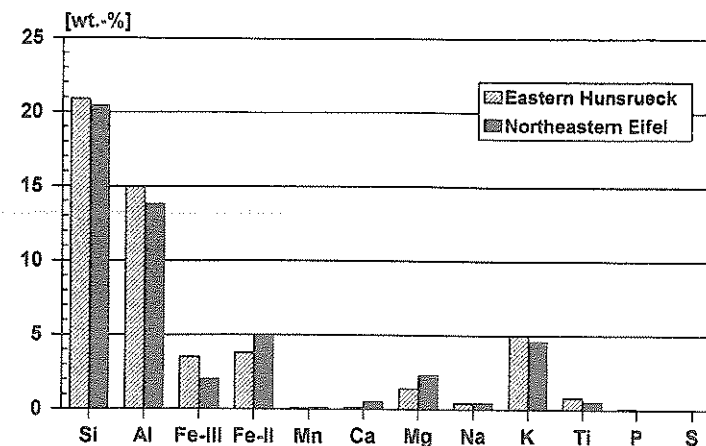


Figure 12: Fresh slates - amounts of elements of the clay fraction from fresh slates of the Northeastern Eifel and the Eastern Hunsrück (determined by XFA)

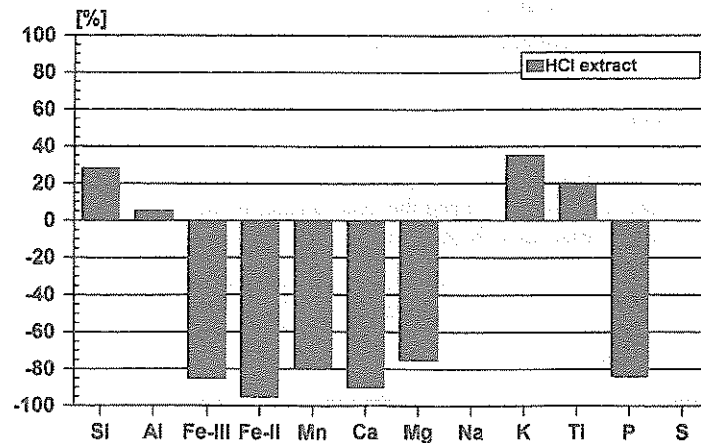


Figure 13: Fresh slates - relative differences between fresh slates and samples after HCl extraction; element losses due to extraction result from dissolution of primary Fe-Mg chlorite, element "gains" due to relative enrichment because of the mass loss of extracted chlorites

Base of weathering and reduction horizon

Morphological characteristics:

- mCn and: steep standing and slightly jointed black-gray (10 Y 4/1),
- mCrj 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 rust-brown 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:

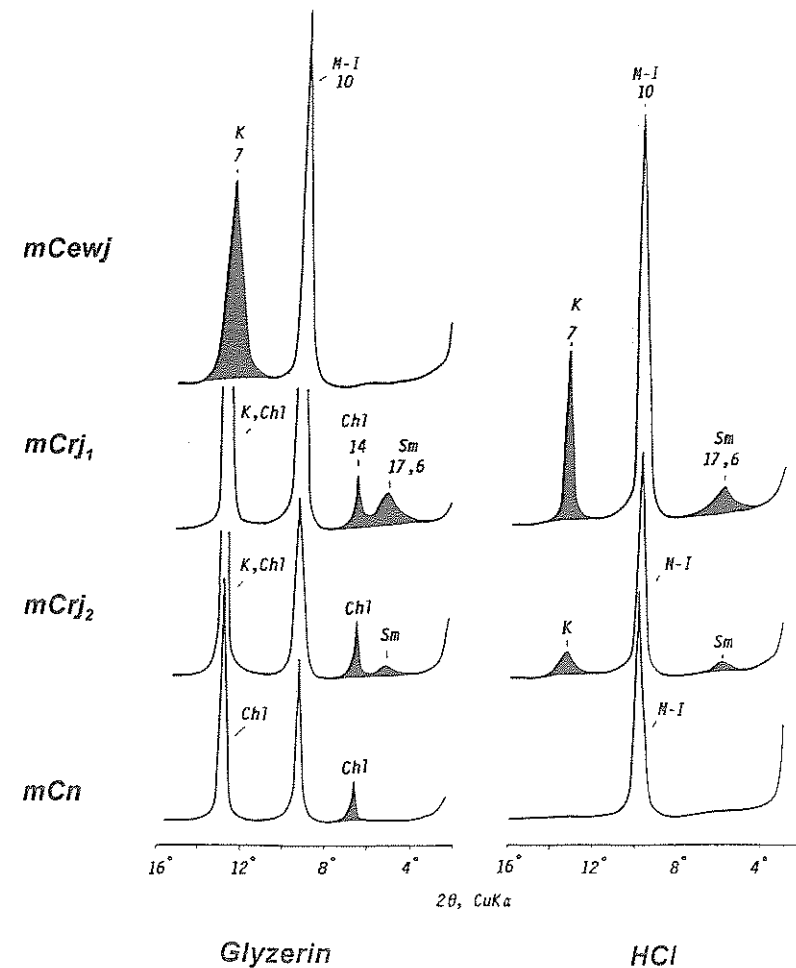


Figure 14: Mineralogical changes of the fresh slate (mCn) in the reduction zones (mCrj) and in the bleached saprolite (mCewj); example from the Eastern Hunsrück, site "Wahlbach" (K=kaolinite, M-I=muscovite-illite, Sm=smectite, Chl=chlorite)

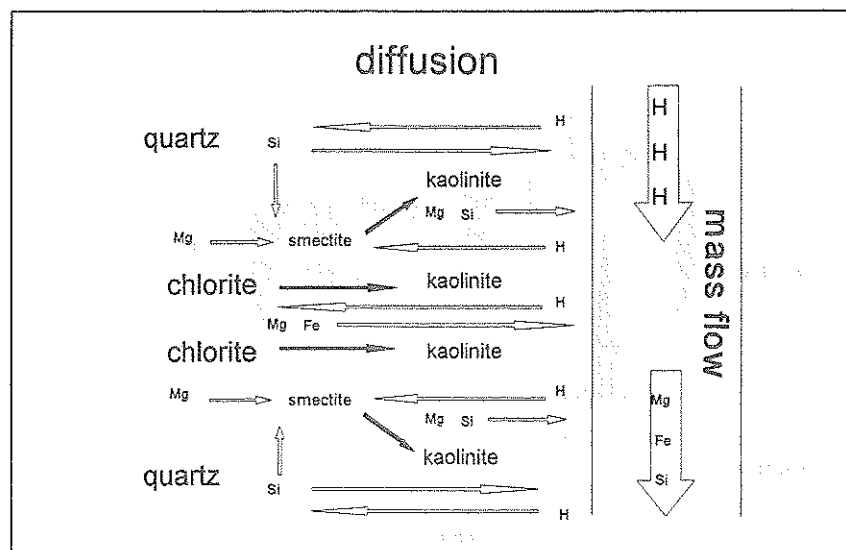


Figure 15: Scheme of the neo-formation of kaolinite and smectite in the reduction zone of the Mesozoic-Tertiary weathering mantle

Stop 2 Gimmingen quarry

Site: Forest next to the village Gimmingen North of the Ahr valley, 150 m a.s.l.
TK 5408 Bad Neuenahr r 25 82120 h 56 03480

Topics: Basal saprolite zone of the Mesozoic-Tertiary weathering mantle dissected by a basalt dike with smectite formation due to hydrothermal alteration

Summary

The outcrop is a basaltic stone quarry. The basaltic dike breaks through the Mesozoic-Tertiary weathering mantle in graywackes up to argillaceous slates of the "Siegenian layers". They are of light gray colour, strongly jointed and so friable that it is possible to crush the saprolite by hand. On individual joints white coatings of pure kaolinite were precipitated. It was formed by soluble ions in the Mesozoic-Tertiary ground water, which once filled the saprolite. The saprolite displays an incomplete kaolinitization of the primary Fe-Mg chlorite. The latter easily dissolves in HCl (3 x 2 h boiling with 2 N HCl, 80° C). Following this procedure kaolinite is easily detectable in XRD diagrams of the clay fraction as well as of the bulk sample.

The basaltic dike shows a strong texture, interstratified by columnar basalt and stronger disaggregated patches of nodular basalt. The latter are interstratified by green-olive lentils and fine veins with neo-formation of pure smectite, due to autohydrothermal alteration. Parts of the veins show characteristics of oxidation and goethite incrustation.

The kaolinitic saprolite displays the lower parts of the weathering mantle, the kaolinitization of the primary Fe-Mg chlorite is still incomplete. A higher kaolinite content of the clay fraction from graywacke in relation to clay slate is very typical, because muscovite and quartz as primary minerals are present in coarser fractions, while neo-formation of kaolinite from chlorite led to the development of smaller crystals. Smectite in the saprolite is not detectable in the bulk sample but only present in the clay fraction. It is possibly a mineral neo-formation due to weathering of the bottom zones of the saprolite. The saprolite directly neighbouring the basalt dike contains coarser smectite geodes and represents the influence of hydrothermal solutions.

The outer zones of the basalt dike were subject to very strong hydrothermal alteration of mafic minerals and plagioclase into smectite and partly Fe-oxides. Although the alteration of the basalt dike is complete, the intensity of alteration diminishes from the outer zone to the inner part of the basalt dike. In the inner parts, smectite was precipitated in joints. Together with smectite hydrothermal quartz was precipitated from solutions rich in silica. Bulk samples as well as the clay fraction of the smectite zone show rather high amount of quartz, while the altered inner parts of the basalt dike are free of quartz. With increasing intensity of alteration of basalt into smectite Fe, Ca, Mg, Ba and Sr were partly leached with migrating solutions. The altered basalt as well as the neo-formed smectite displays the same high amounts of the elements Ti, P, Ca, Mg, Cr, Cu, Ni, Zn; they are much lower in the neighbouring saprolite.

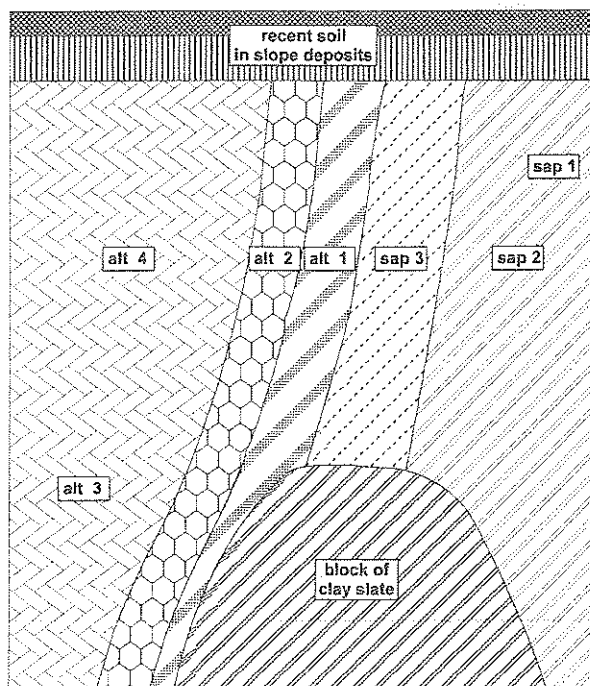


Figure 16: Gimmingen quarry - sketch (without scale) of profile and sample positions (sap1: graywacke saprolite; sap 2: silt slate saprolite; sap 3: silt and clay slate saprolite; alt 1: pure smectitic alteration zone of basalt dike; alt 2: nodular alteration zone; alt 3: veins filled with smectite and iron oxides; alt 4: blocky alteration zone of basalt)

Description

Saprolite:

- sap 1: saprolite of silt slate with olive-gray and dark gray mottles indicating the transition between reduction zone and oxidation zone of the saprolite; stronger oxidation of the graywacke banks due to better aeration
- sap 2: saprolite of graywackes, silty fine sand to fine sandy silt
- sap 3: 30 cm right of the autohydrothermal alteration zone, strongly decomposed saprolite from silty slate mixed with fragments of graywacke-saprolite; on clefts white clay coatings and precipitations of goethite.

Alteration zone:

- alt 1: autohydrothermal altered basalt, soaked and interstratified by veins and geodes of pure olive-green smectite with a solid waxy consistency
- alt 2: nearly 50 cm to the left beside the autohydrothermal zone of alteration in the strongly jointed and nodularly structured and soaked basalt
- alt 3: joint within the blocky basalt, filled with hydrothermal clay and goethite
- alt 4: nearly 50 cm to the left of "alt 2" in weakly altered, coarse-blocky basalt. The stroke is blunt, greater mafic minerals are oxidated to yellow-brown goethite.

Table 2: Gimmingen quarry - XRD mineral composition (unweighted relative reflex intensities) of the bulk samples (18 Å: smectites; 14 Å: Fe-Mg-chlorite; 10 Å: biotite, muscovite, illite; 7 Å: kaolinite; 4,2 Å: quartz; 3,2 Å feldspars)

| samp. | 18 Å | 14 Å | 10 Å | 7 Å | 4,2 Å | 3,2 Å |
|-------|------|------|------|-----|-------|-------|
| sap 1 | 0 | 1 | 10 | 9 | 71 | 9 |
| sap2 | 0 | 10 | 7 | 3 | 70 | 10 |
| sap3 | 7 | 10 | 11 | 10 | 54 | 8 |
| alt 1 | 50 | 0 | 0 | 0 | 36 | 14 |
| alt 2 | 52 | 0 | 0 | 0 | 30 | 18 |
| alt 3 | 45 | 0 | 0 | 0 | 35 | 20 |
| alt 4 | 59 | 0 | 0 | 0 | 1,0 | 40 |

Table 3: Gimmingen quarry - XRD mineral composition (unweighted relative reflex intensities) of the clay fraction < 2 µm (18 Å: smectites; 14 Å: Fe-Mg-chlorite; 10 Å: biotite, muscovite, illite; 7 Å: kaolinite; 4,2 Å: quartz)

| samp. | 18 Å | 14 Å | 10 Å | 7 Å | 4,2 Å |
|-------|------|------|------|-----|-------|
| sap 1 | 27 | 16 | 33 | 18 | 6 |
| sap2 | 19 | 13 | 20 | 37 | 11 |
| sap3 | 25 | 17 | 31 | 21 | 6 |
| alt 1 | 62 | 0 | 14 | 12 | 12 |
| alt 2 | 67 | 0 | 12 | 7 | 14 |
| alt 3 | 77 | 0 | 15 | 8 | 0 |
| alt4 | 41 | 0 | 30 | 12 | 17 |

Table 4: Gimmingen quarry - total elements of the bulk samples (XFA), main elements in weight %, trace elements in mg/kg

| | sap 1 | sap 2 | sap 3 | alt 1 | alt 2 | alt 3 | alt 4 |
|--------------------------------|-------|-------|-------|--------|--------|--------|--------|
| SiO ₂ | 69,08 | 80,21 | 68,72 | 48,47 | 48,03 | 46,29 | 44,11 |
| Al ₂ O ₃ | 15,33 | 9,49 | 14,94 | 17,89 | 13,72 | 10,77 | 14,98 |
| Fe ₂ O ₃ | 3,91 | 2,62 | 4,18 | 6,45 | 12,92 | 22,94 | 15,13 |
| MnO | 0,03 | 0,02 | 0,01 | 0,03 | 0,37 | 0,13 | 0,12 |
| MgO | 1,26 | 0,81 | 0,96 | 1,7 | 1,85 | 1,96 | 2,02 |
| CaO | 0,23 | 0,27 | 0,28 | 1,88 | 1,32 | 1,63 | 2,72 |
| Na ₂ O | 0,15 | 0,35 | 0,04 | 0,02 | 0,25 | 0,6 | 1,06 |
| K ₂ O | 2,75 | 1,32 | 2,45 | 0,49 | 1,03 | 1,09 | 1,44 |
| TiO ₂ | 0,88 | 0,6 | 0,9 | 2,54 | 1,63 | 1,29 | 2,21 |
| P ₂ O ₅ | 0,2 | 0,23 | 0,21 | 1,08 | 0,5 | 0,47 | 0,60 |
| SO ₃ | 0,02 | 0,02 | 0,02 | 0,03 | 0,03 | 0,03 | 0,02 |
| H ₂ O ⁺ | 4,24 | 2,91 | 4,63 | 7,11 | 6,64 | 7,5 | 5,97 |
| H ₂ O ⁻ | 1,57 | 0,9 | 2,31 | 12,76 | 12,29 | 5,62 | 10,39 |
| Σ | 99,65 | 99,75 | 99,65 | 100,45 | 100,58 | 100,32 | 100,77 |
| Ba | 404 | 205 | 340 | 199 | 353 | 359 | 868 |
| Rb | 125 | 58 | 114 | 19 | 28 | 32 | 26 |
| Sr | 58 | 34 | 57 | 73 | 128 | 169 | 458 |
| Co | 20 | 27 | 30 | 48 | 23 | 38 | 36 |
| Cr | 237 | 229 | 270 | 360 | 265 | 277 | 333 |
| Cu | 24 | 20 | 38 | 58 | 119 | 75 | 76 |
| Ni | 96 | 88 | 87 | 145 | 153 | 147 | 164 |
| Pb | 19 | 9 | 16 | 16 | 4 | 9 | 6 |
| Zn | 61 | 33 | 34 | 51 | 72 | 92 | 132 |
| Zr | 312 | 624 | 389 | 506 | 250 | 360 | 312 |

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 Å-fraction (= illite + muscovite). Leaching of potassium proves a loss of about 30 % of the initial amount of 10 Å 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. Hinkley index varies with the texture of the saprolite. Kaolinites from sandstones display a higher index than those of clay or silt saprolite.

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.

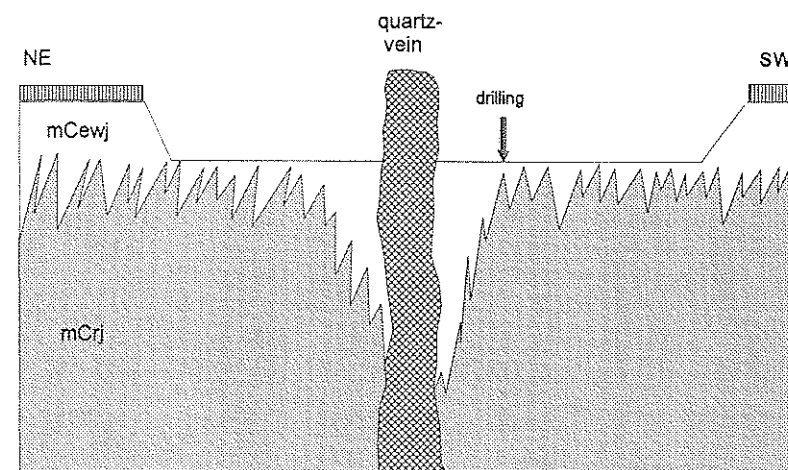


Figure 17: Schematic cross section through site Oedingen

DescriptionMorphological 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 (mCs_j, mCms_j) 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.

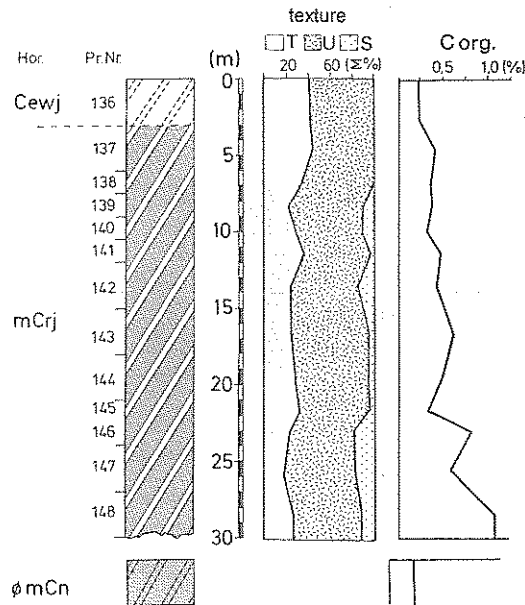
Petrographical characteristics:

Figure 18: Oedingen drill core - particle size distribution and content of organic carbon (Pr.Nr.=sample code)

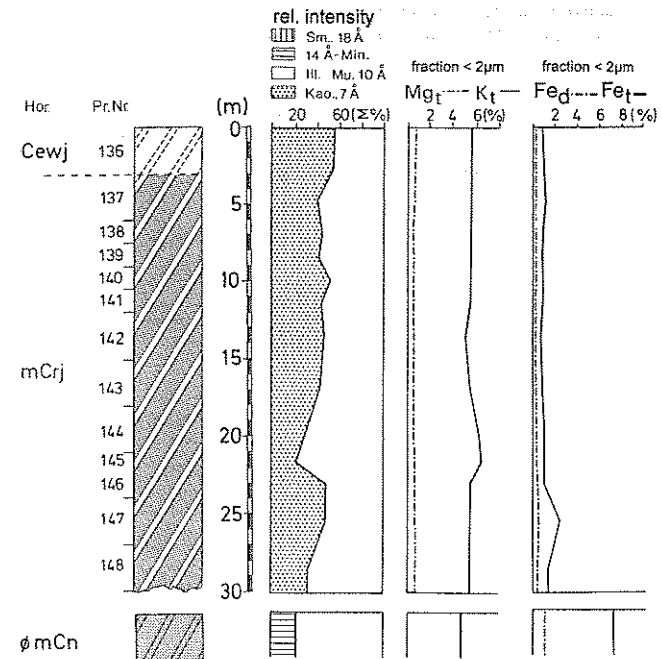
Mineralogical and geochemical characteristics:

Figure 19: 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 $g/100\text{ cm}^3$ 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 5: Isovolumetric balance of a saprolite profile (site "Wahlbach", Eastern Hunsrück).
I. Weight by volume ($\text{g}/100 \text{ cm}^3$) of element oxides of fresh slates (mCn) and differences of the weights by volume ($\text{g}/100 \text{ cm}^3$) 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 = $\text{MnO} + \text{CaO} + \text{Na}_2\text{O} + \text{P}_2\text{O}_5 + \text{SO}_3$, in $\text{g}/100 \text{ cm}^3$)

| zone minerals | mCn | mCrj (K), Sm | mCorj K, Sm | mCewj 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 6: 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 = $\text{MnO} + \text{CaO} + \text{Na}_2\text{O} + \text{P}_2\text{O}_5 + \text{SO}_3$, in $\text{g}/100 \text{ cm}^3$)

| zone minerals | mCn | mCrj (K), Sm | mCorj K, Sm | mCewj 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 |

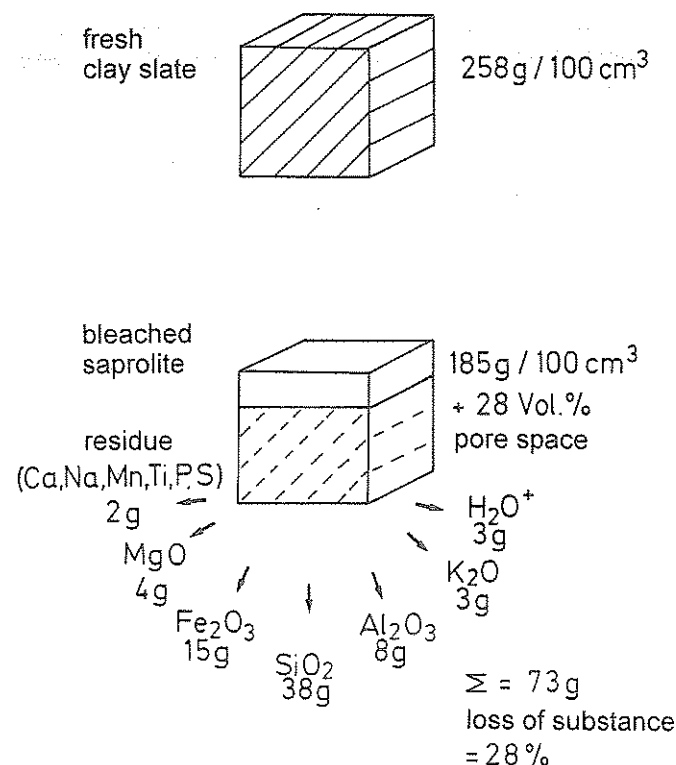


Figure 20: Element loss and gain of pore volume of the bleached saprolite compared with unweathered slate

Origin of the silica acid:

Table 7: $\text{SiO}_2 : \text{Al}_2\text{O}_3$ 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 8: 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 = 9 % |
| mCn | | 35 | 90 | 0 |

Kaolinite content and kaolinite crystallinity:

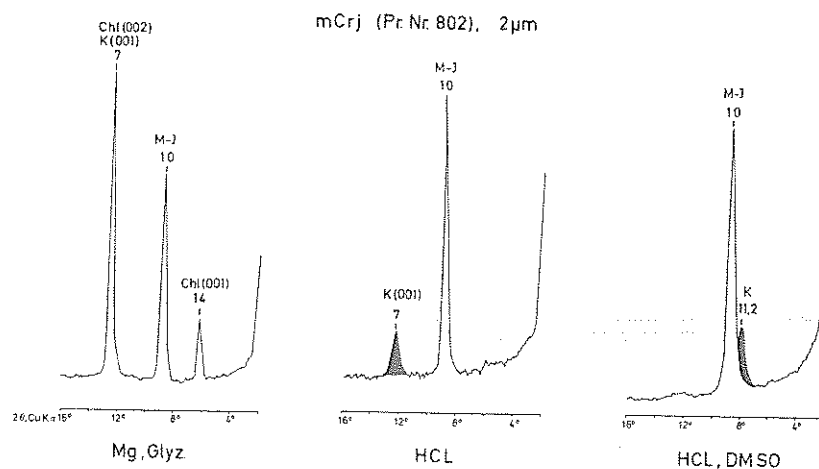


Figure 21: XDA plots of the clay fraction (orientated specimen) from the bottom zones of the saprolite with incomplete kaolinitization of primary Fe-Mg chlorite. The latter is easy soluble in HCl, so that the kaolinite is visible at 7 Å. The kaolinite is of b-axis disordered type and DMSO intercalation is possible, resulting in a shift of the kaolinite peak from 7,2 to 11,2 Å (K=kaolinite, M-I=muscovite-illite, Sm=smectite, Chl=chlorite, Pr.Nr.= sample code)

Hinckley-Indices

$$\begin{aligned} K\ 020 &= 4,47\ \text{\AA} \\ K\ 1\bar{1}0 &= 4,36\ \text{\AA} \\ K\ 11\bar{1} &= 4,18\ \text{\AA} \\ Q &= 4,26\ \text{\AA} \end{aligned}$$

< 0,45

saprolite from
clay and silt slate

0,65 - 0,8

saprolite from
sandstone

> 0,95

vein kaolinite

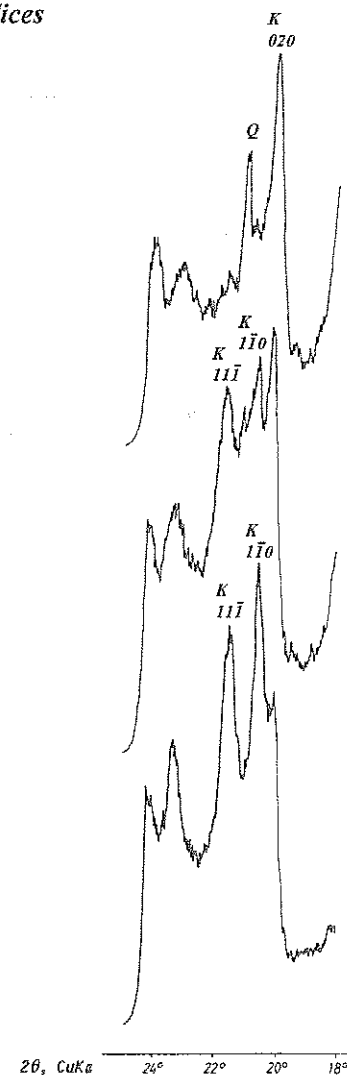


Figure 22: XDA plots of lower order peaks of kaolinites from the clay fraction (powder specimen) of saprolites with different texture (K=kaolinite, Q=quartz)

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:

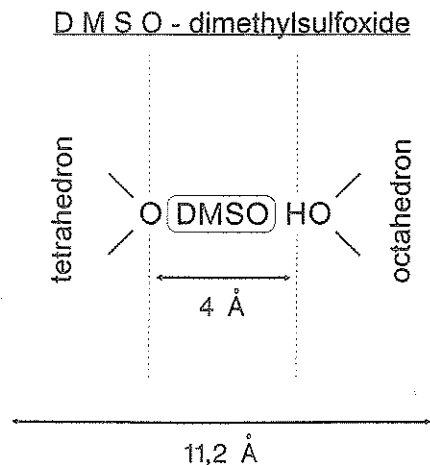


Figure 23: Principle of the expansion of kaolinite with dimethylsulfoxide (DMSO)

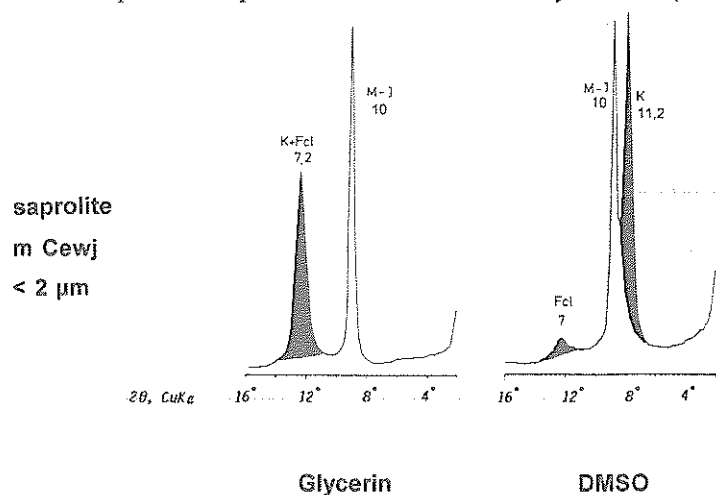


Figure 24: X-ray diagrams of the clay fraction from the bleached saprolite (mCewj). In all saprolite zones b-axis disordered kaolinite (expandable with DMSO) from 7 to 11,2 Å dominates, contents of fireclay (not expandable with DMSO) up to 10 % (K=kaolinite, M-I=muscovite-illite, Fcl=intercalation disordered kaolinite)

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-HENNINGSSEN & WIECHMANN (1985) and FELIX-HENNINGSSEN (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 Å, 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 ($< 0,2 \mu\text{m}$, 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, as well as the neo-formation of kaolinite from muscovite, occurred. 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 irregularly 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, simultaneously 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.

Description

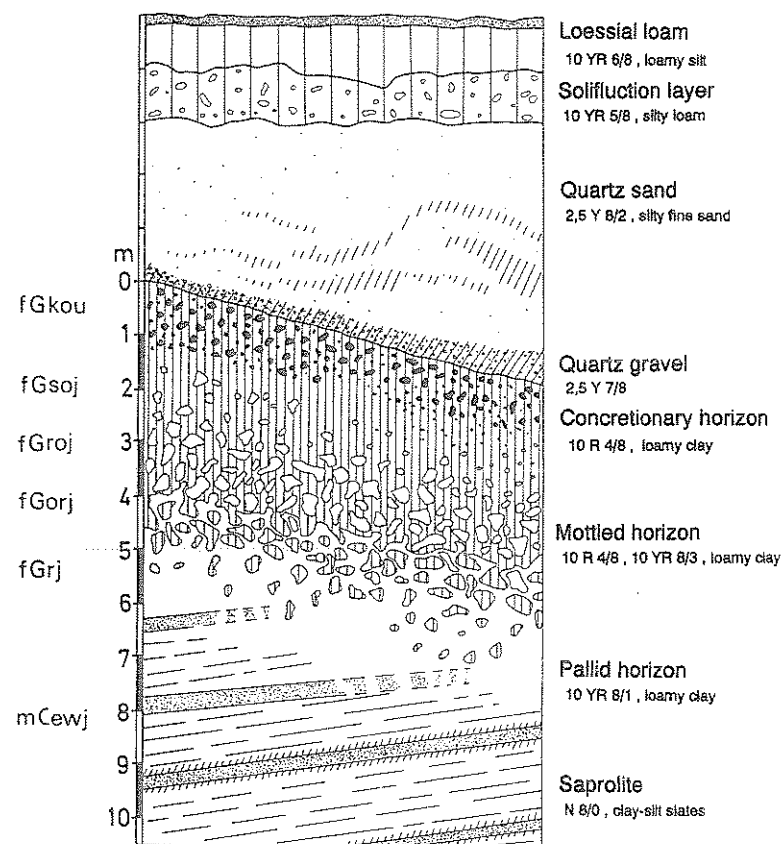


Figure 25: Profile Bengen - autochthonous fossil pre-Upper Oligocene Gleyic Acrisol exposed at a highway (A 61) cut exposure near Bengen village

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: red loamy clay (10 R 3/6 - 4/8) with small yellowish and white mottles, rounded red Fe oxide concretions with up to several cm 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 increasingly mottled with rounded white spots
- fGroj (10 YR 8/3), single Feoxide concretions and oxide incrustated sandstone fragments, gliding transition to
- fGorj

Pallid horizon:

- fGrj, 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

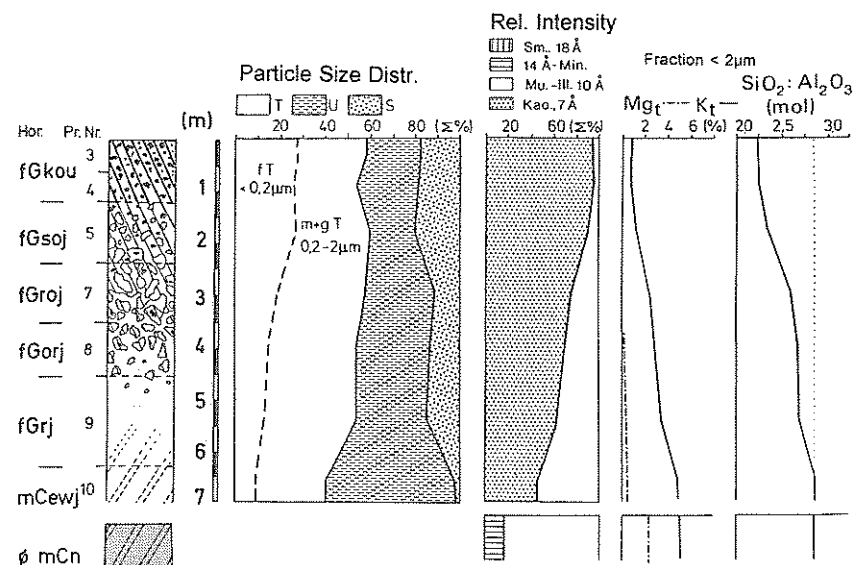


Figure 26: Profile Bengen - particle size distribution, clay mineral distribution (relative intensities), total amounts of Mg and K, and SiO₂:Al₂O₃ molecular relations of the clay fraction (Pr.Nr.=sample code)

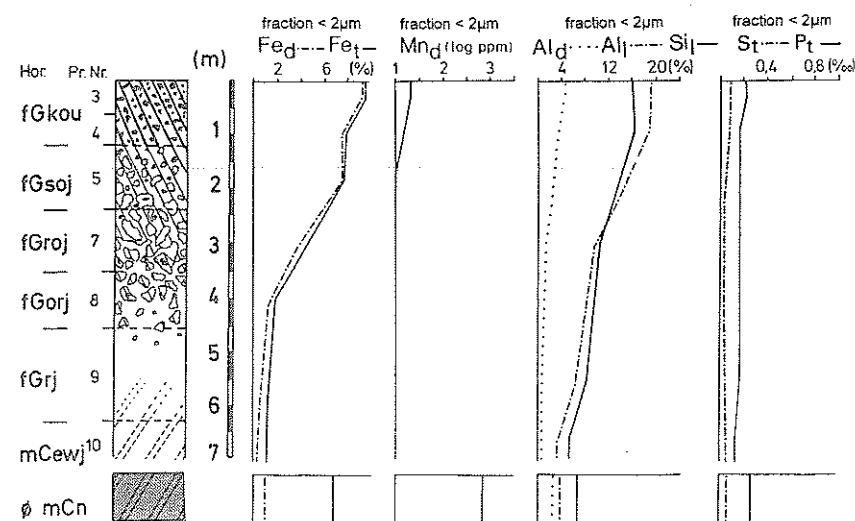


Figure 27: Profile Bengen - total amount of iron, silica and phosphate as well as pedogenic oxides (Fe_d, Mn_d, Al_d = Fe_{CBD}, Mn_{CBD}, Al_{CBD}, Pr.Nr.=sample code)

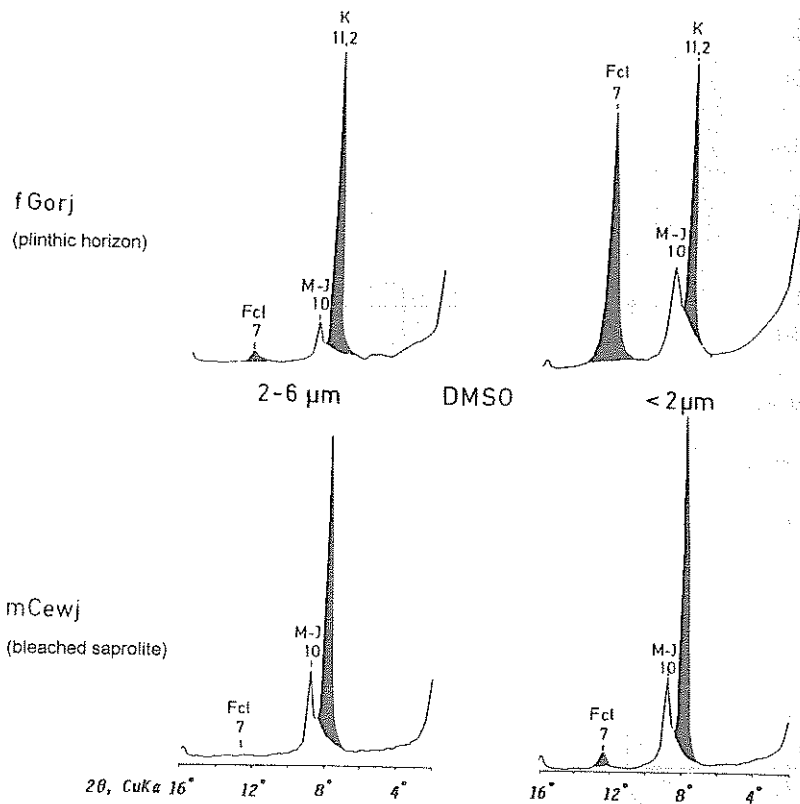


Figure 28: Profile Bengen - distribution of muscovite-illite (M-I), b-axis disordered kaolinite (K), and CBD (Fcl) in the fine silt ($6 - 2 \mu\text{m}$) and clay fraction ($< 2 \mu\text{m}$) of the plinthic horizon (fGorj) and the saprolite (mCewj). Neo-formation of intercalation disordered kaolinite 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

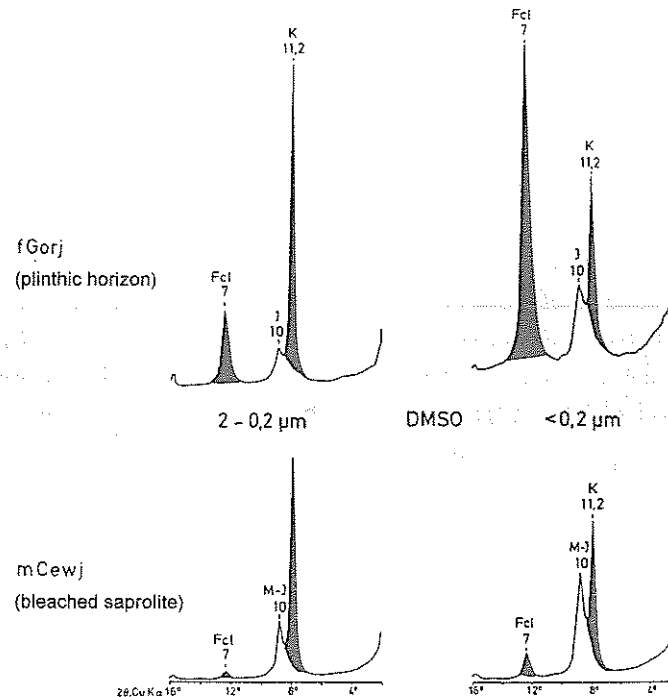


Figure 29: Profile Bengen - distribution of b-axis disordered kaolinite (K) and intercalation disordered kaolinite (Fcl) in the coarse ($2 - 0,2 \mu\text{m}$) and fine ($< 0,2 \mu\text{m}$) clay fractions of the plinthic horizon and the saprolite (M-I: muscovite-illite). Although in soil and saprolite 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" mountainous 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.

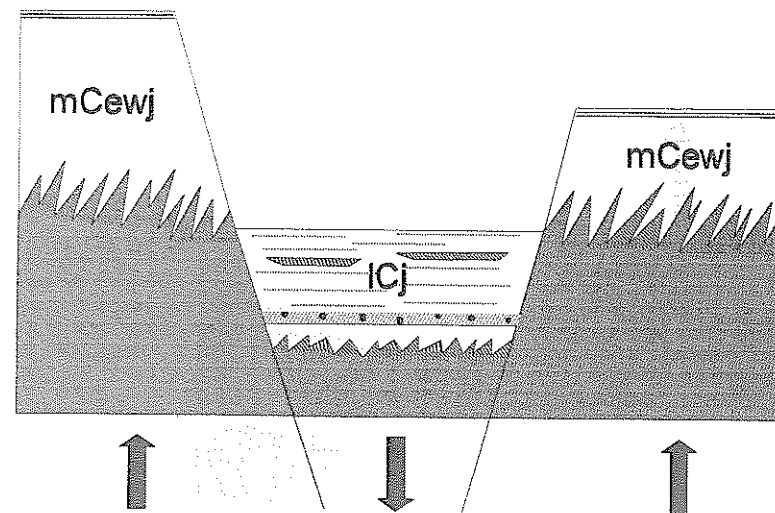


Figure 30: Kaolin clay deposit Ringen - sketch of a cross section (without scale), displaying uplifted blocks and fault troughs, which were sedimentary basins (mCewj=bleached saprolite)

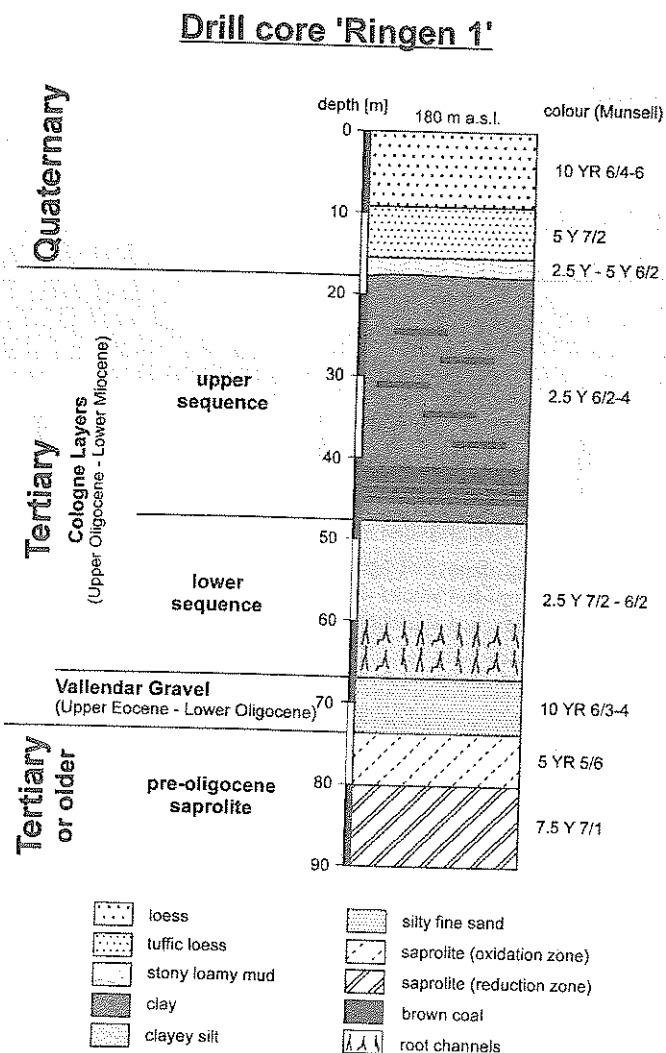


Figure 31: Kaolin clay deposit Ringen - horizationation and layers of a prospect drill core

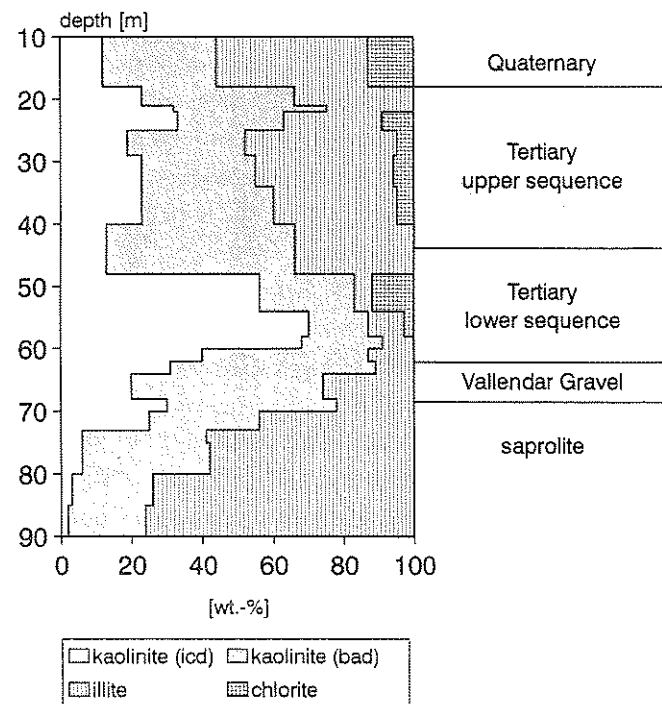


Figure 32: Kaolin clay deposit Ringen - distribution of clay minerals in samples of the prospect drill core (icd-kaolinite = intercalation, disordered kaolinite, "fireclay minerals"; bad-kaolinite = b-axis disordered kaolinite)

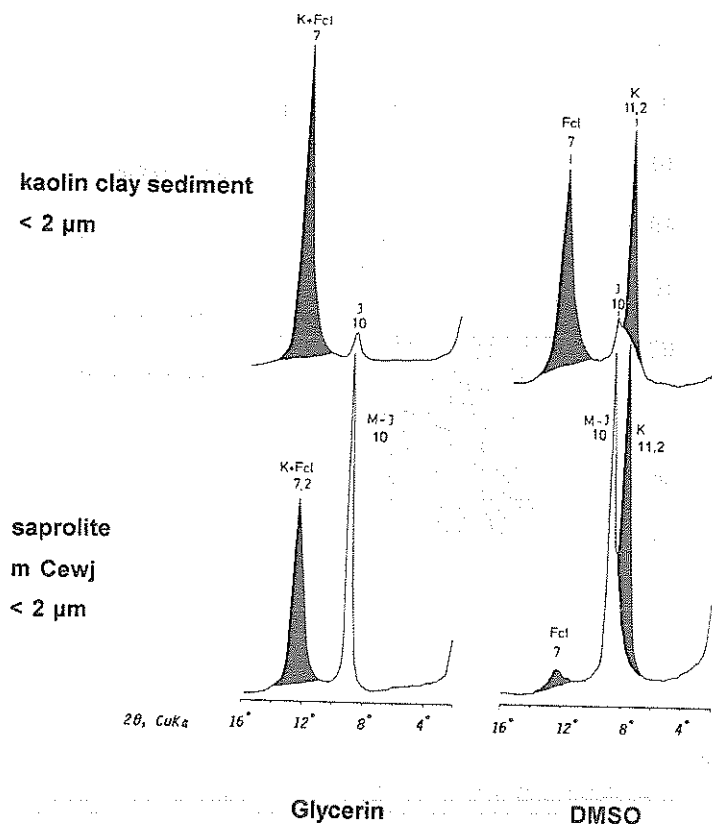


Figure 33: Kaolin clay deposit Ringen - XRD-diagrams of DMSO treated clay sediment and saprolite from the prospect drill core (K=kaolinite, M-I= muscovite-illite, I=illite, Fcl=intercalation disordered kaolinite)

Stop 6 Wehr caldera

Site: East of Wehr village, CO₂-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 CO₂ 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. CO₂ 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 CO₂ 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 Å mineral of hydrothermal alteration zones. It often occurs together with kaolinite of high crystallinity in white monomineralic (7 Å) 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. 37 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 CO₂ 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 CO₂ at the vegetated areas, while the root zones of the areas free of vegetation contain soil air enriched in CO₂, partly with more than 60 % vol. of CO₂ (see fig. 36).

Drill core 'Wehr 1'

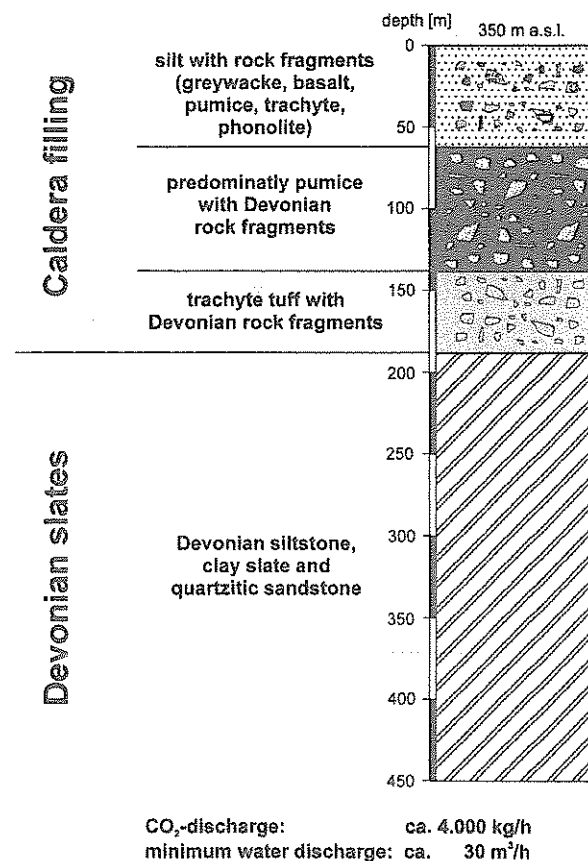


Figure 34: Wehr caldera - sketch of the lithological sequence in a deep drilling

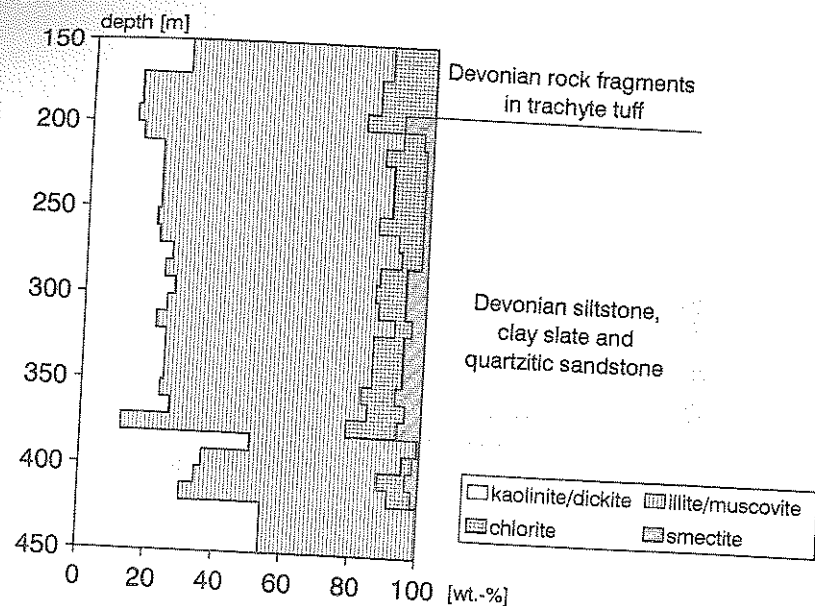


Figure 35: Wehr caldera - distribution of clay minerals (18\AA = smectite, 14\AA = Fe-Mg chlorite, 10\AA = illite/muscovite, 7\AA = kaolinite and dickite)

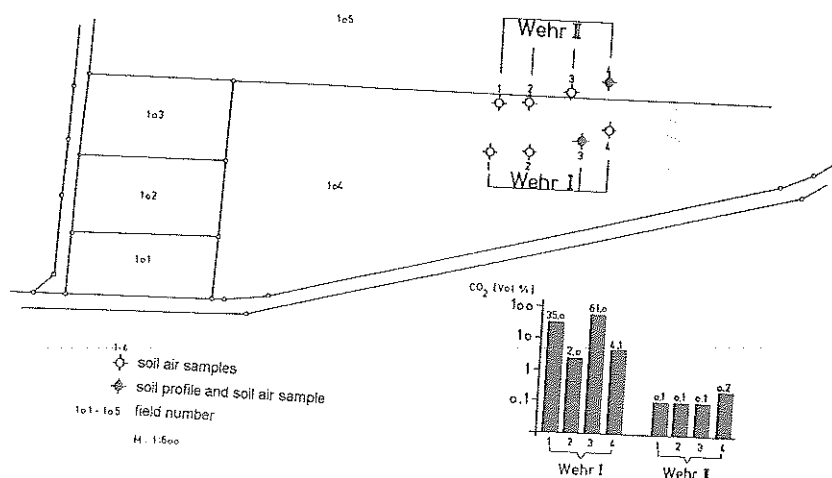


Figure 36: Wehr caldera - amounts of CO_2 in the soil air in 1 m depth at the basis of the rooted soil (BERNS 1988; Wehr I=non-vegetated areas, Wehr II=neighbouring vegetated areas, M=scale)

Table 9: Wehr caldera - total elements of iron ochre from the CO_2 spring, compared with the mean element contents of saprolitic "unsrück" 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 |
| Σ | 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, neo-formation 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 hydrogen 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.

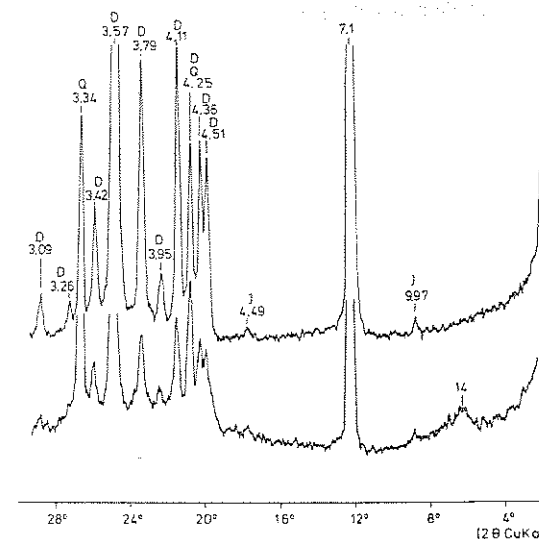
Beside the neo-formation of dickite, fibrous goethite and quartz, the occurrence of sericite, which covers all joint planes of the sandy and quartzitic saprolite layers may be an indicator of hydrothermal alteration. Compared to bleached saprolite from Hunsrück slates the Waldesch saprolite is enriched 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 CO₂ 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 ¹⁸O/¹⁶O 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)

dickite

Mg²⁺, Glyz.

600 °C



kaolinite

Mg²⁺, Glyz.

600 °C

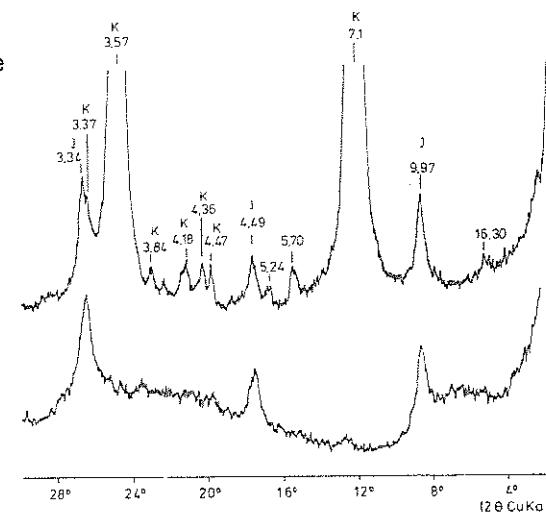


Figure 37: XRD-diagrams (glycerol-air dry and 600 °C heated specimen) of dickite (veins of Waldesch quarry) and kaolinite (veins of Oedingen kaolin pit) (D=dickite, K=kaolinite, I=illite, Q=quartz)

Table 10: 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 ₂ O ₃ | 19,40 | 17,11 | 8,79 | 11,26 | 21,84 |
| Fe ₂ O 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 ₂ O | 0,15 | 0,01 | 0,12 | 0,26 | 0,35 |
| K ₂ O | 3,77 | 4,54 | 1,50 | 3,47 | 4,27 |
| TiO ₂ | 0,99 | 1,04 | 0,48 | 0,89 | 1,28 |
| P ₂ O ₅ | 0,05 | 0,05 | 0,5 | 0,13 | 0,13 |
| SO ₃ | 0,02 | 0,03 | 0,02 | 0,02 | 0,02 |
| H ₂ O ⁺ | 4,82 | 2,98 | 6,38 | 2,84 | - |
| H ₂ O ⁻ | 0,36 | 0,48 | 0,70 | 3,40 | - |
| Σ | 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-HENNINGSSEN & 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 contaminated by talus deposits and eolian sediments in different amounts (v. ZEJSCHWITZ 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.

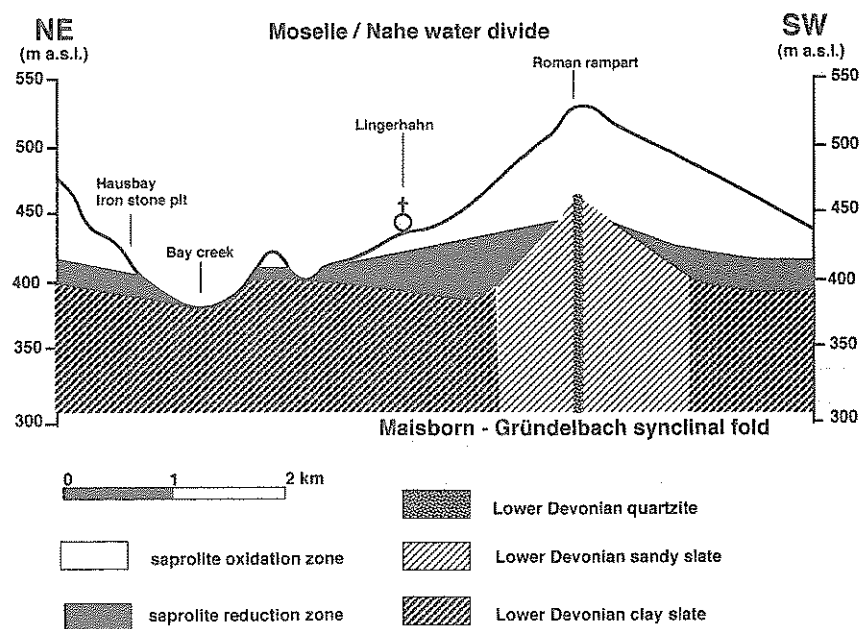


Figure 38: Cross section of the landscape around Lingerhahn village

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.

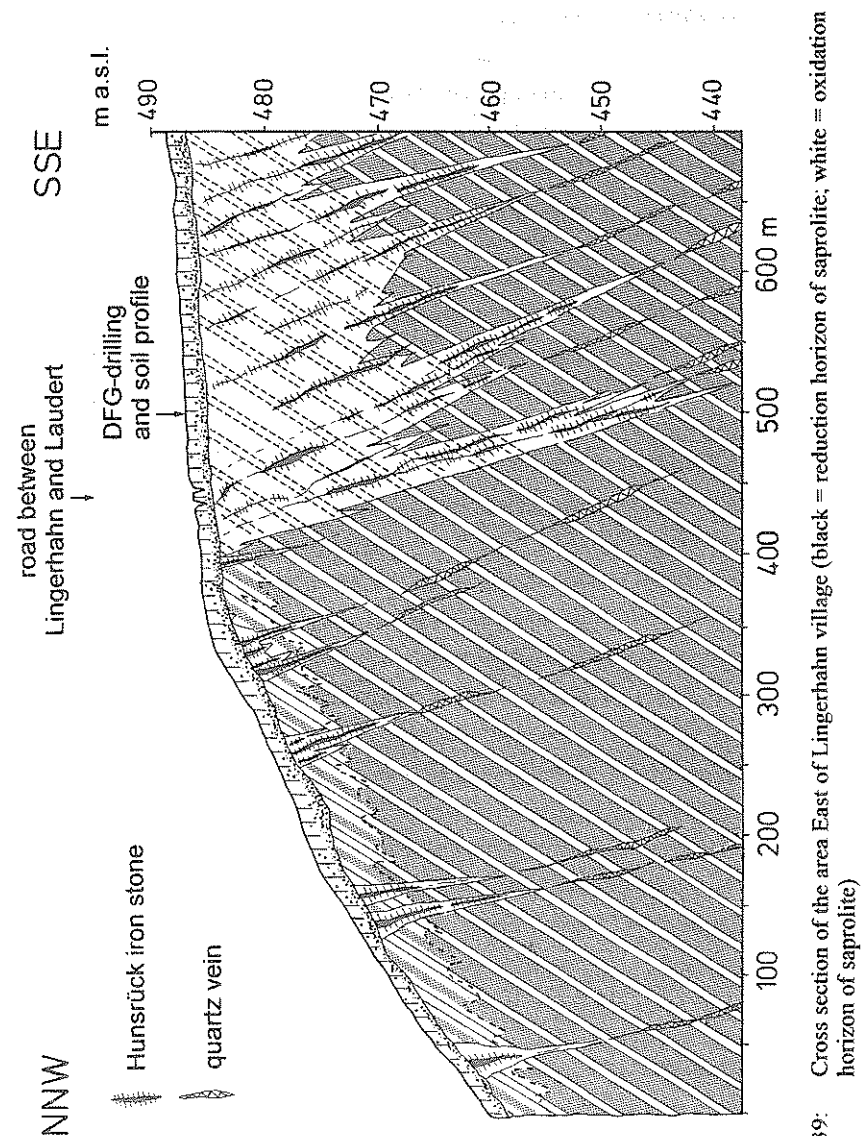


Figure 39: Cross section of the area East of Lingerhahn village (black = reduction horizon of saprolite; white = oxidation horizon of saprolite)

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. 39). 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, bordering the quartz veins (see fig 39).

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 bordering 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.

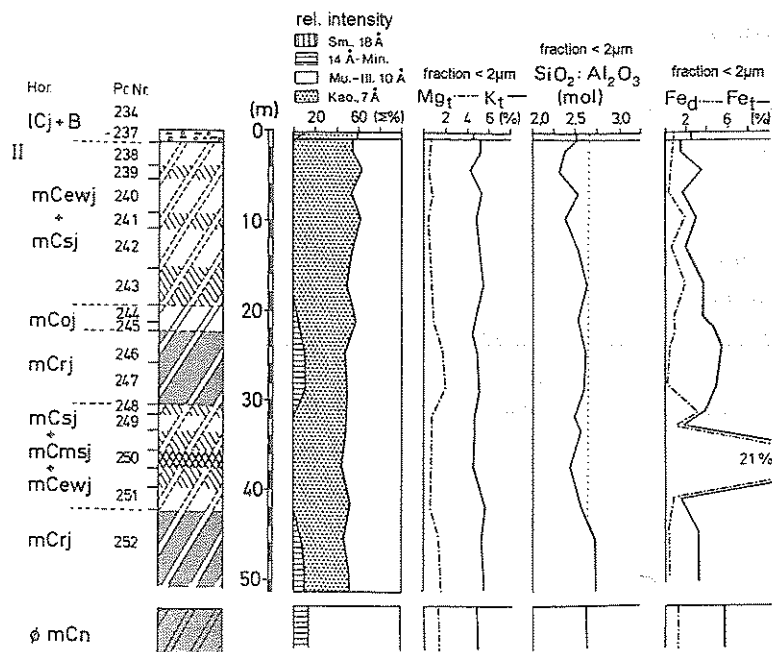


Figure 40: Drill core Lingerhahn - mineralogical and geochemical composition of the clay fraction < 2 μm (legend of clay mineral distribution: relative intensities of sm = smectites, 14 Å Min = chlorites, Mu-III = muscovite/illite, Kao = kaolinite; total amounts of Mg, K and Fe, $\text{SiO}_2:\text{Al}_2\text{O}_3$ molecular relations as well as free iron oxides, $\text{Fe}_d = \text{Fe}_{\text{CBD}}$, 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 dissolved 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 dissolved 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, which still had been 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, 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.

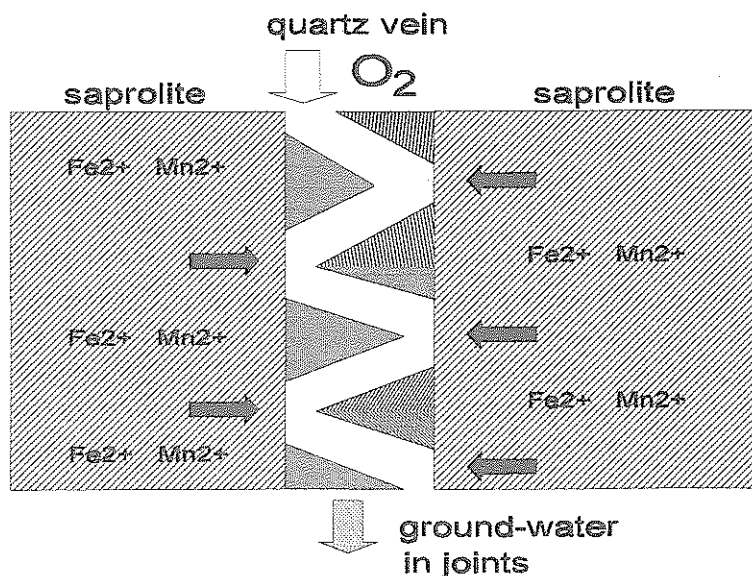


Figure 41: Formation of Hunsrück iron stones along a dissolved quartz vein due to descending ground water table with consequence of aeration of the saprolite and migration of reduced elements from the water saturated saprolite matrix along a redox gradient by diffusion

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. 44). 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. 42). 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. 43), which reflects the gradient of increasing Al availability and acidity respectively, from deeper to upper zones of the saprolite.

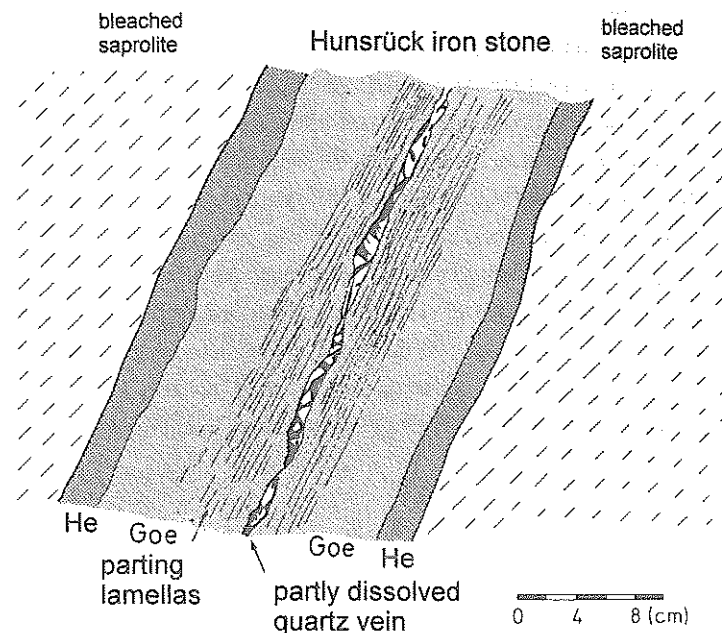


Figure 42: Hunsrück iron stone from accumulation of goethite (Goe) around a dissolved quartz vein and with an outer margin of hematitic goethite (He)

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. 11) 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 $1,5 \text{ cm}^3$ of kaolinite. The dissolution of kaolinite may have been one source for the Al substitution in Fe oxides.

Table 11: 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_2 | 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 |
| 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 12: Hunsrück iron stones - significant interelement correlations (Pearson) of Fe_{CBD} and Mn_{CBD} 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 ⁺⁺⁺ | |

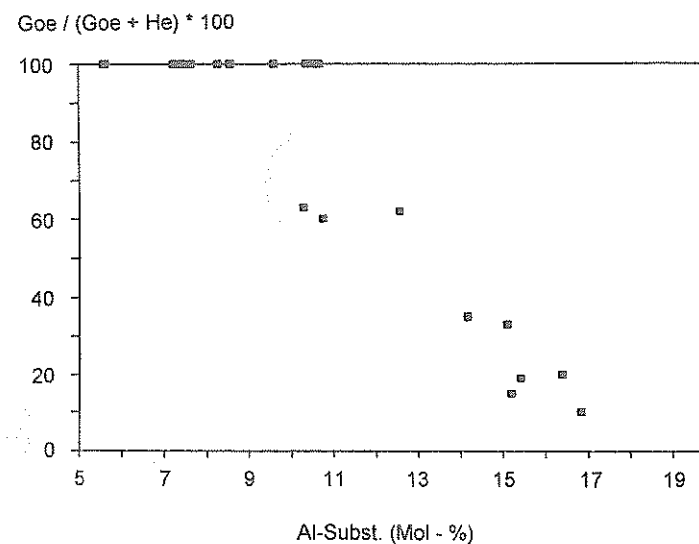


Figure 43: Hunsrück iron stones - Al substitution in goethite in relation to the amount of goethite (Goe=goethite, He=hematite)

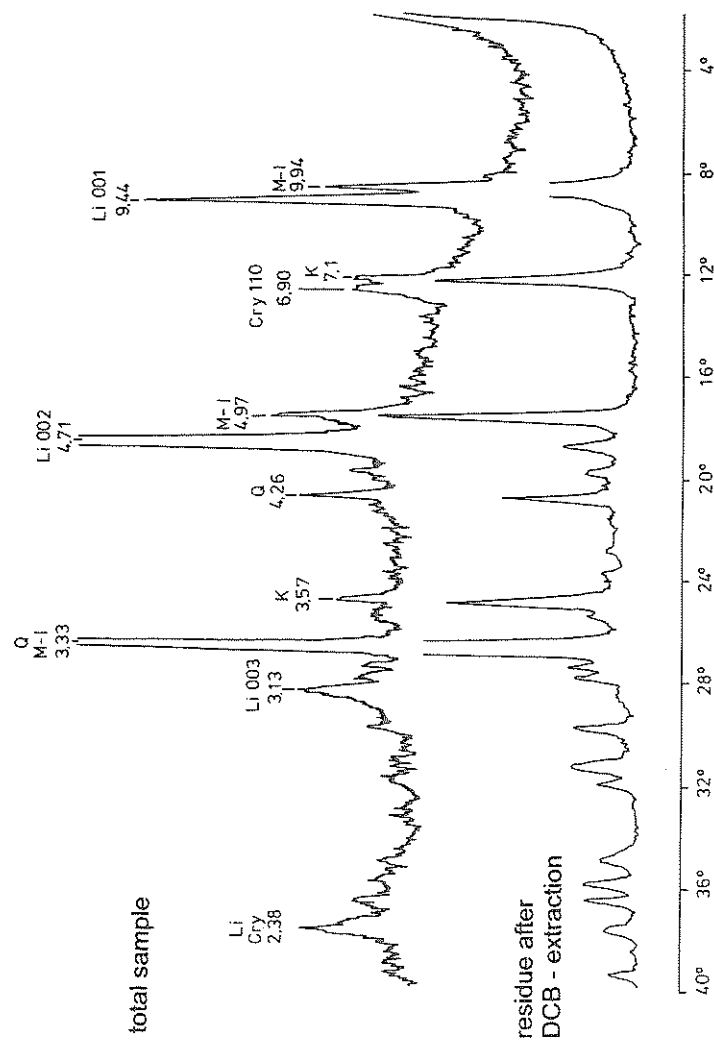


Figure 44: Hunsrück iron stones - XRD diagrams of Mn concretions consisting of lithiophorite (Li) and cryptomelane (Cry) impregnating the silicatic matrix of the saprolite (M-I = muscovite - illite, K = kaolinite, Q = quartz) and of the silicatic matrix after CBD extraction

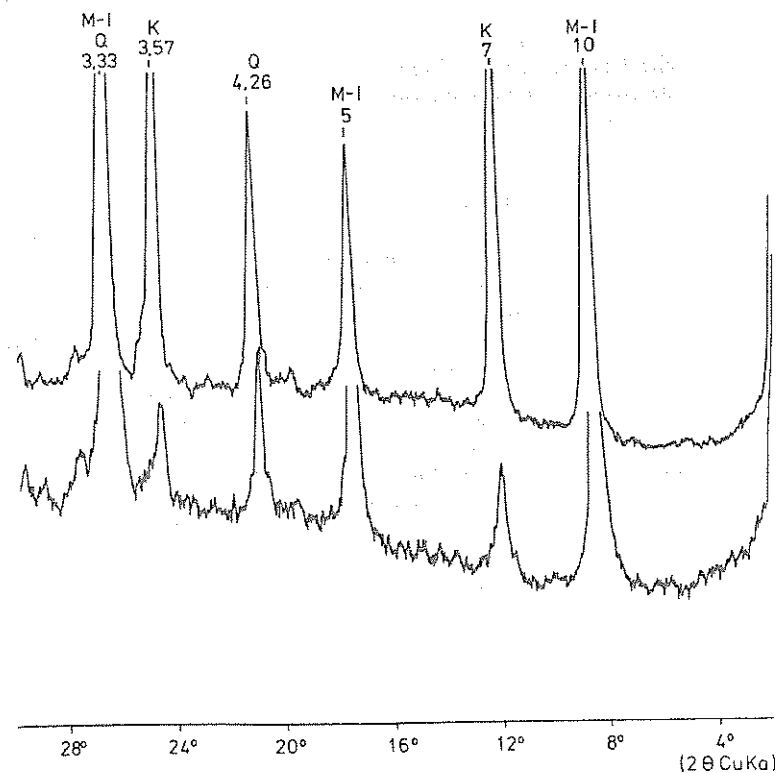


Figure 45: Hunsrück iron stones - XRD diagrams of the silicatic matrix of a hematitic goethite iron stone after CBD extraction compared to the silicatic matrix of the directly neighbouring saprolite (M-I = muscovite - illite, K = kaolinite, Q = quartz)

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 Ochraqult

| | | |
|-----------|---------------|---|
| Oi | 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, polyhedral-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 SICj | 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, stony 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 the Upper Pleistocene.

Mottles and concretions:

Down to a depth of 50 cm the horizons contain well rounded, sharply bordered 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 bordered, light gray bleached zones.

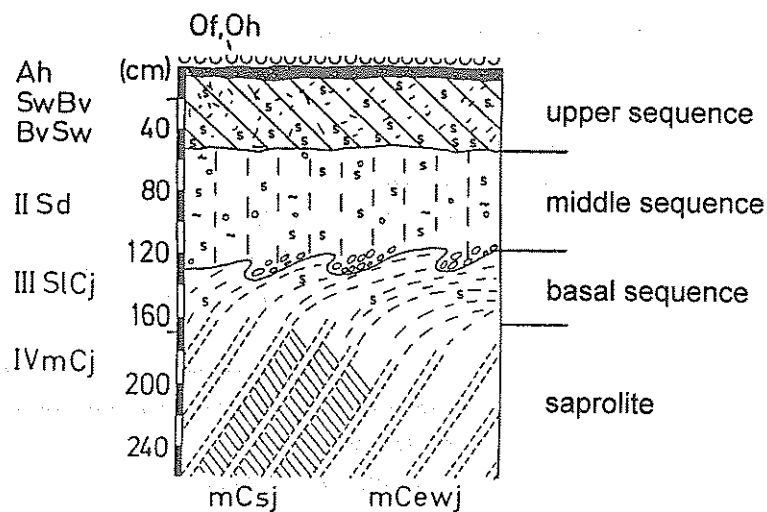


Figure 46: Soil profile Lingerhahn - superficial layers and horizonation (mCsj=accumulation zone of sesquioxides, mCewj=bleached saprolite)

Distribution of heavy minerals:

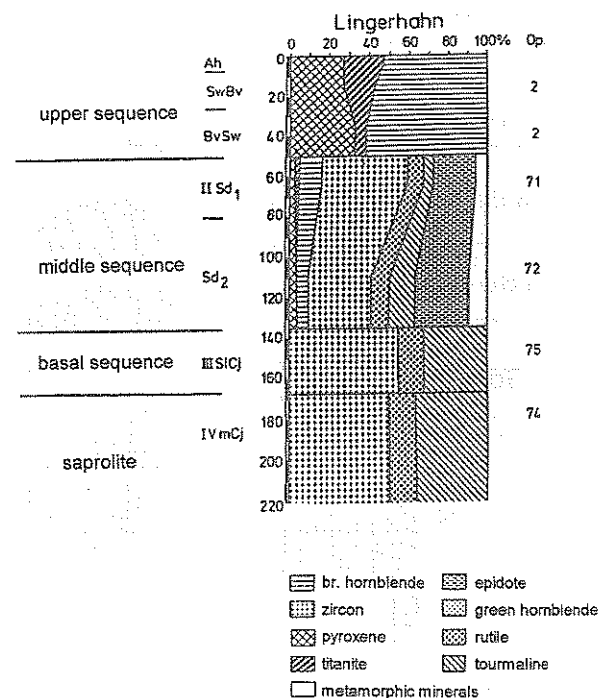


Figure 47: Soil profile Lingerhahn - distribution of heavy minerals of saprolite and superficial layers (in weight % of the summarized transparent heavy minerals of the fraction 30-400 µm; Op.= % opaque minerals)

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 spectrum 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:

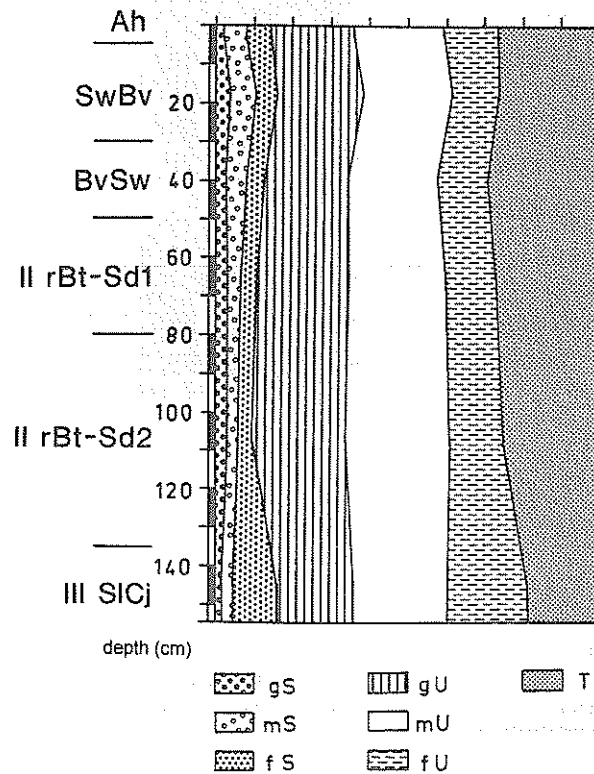


Figure 48: Soil profile Lingerhahn - particle size distribution (gS = 2.000 - 630 μm , mS = 630 - 200 μm , fS = 200 - 63 μm ; gU = 63 - 20 μm ; mU = 20 - 6,3 μm ; fU = 6,3 - 2 μm , T = < 2 μm)

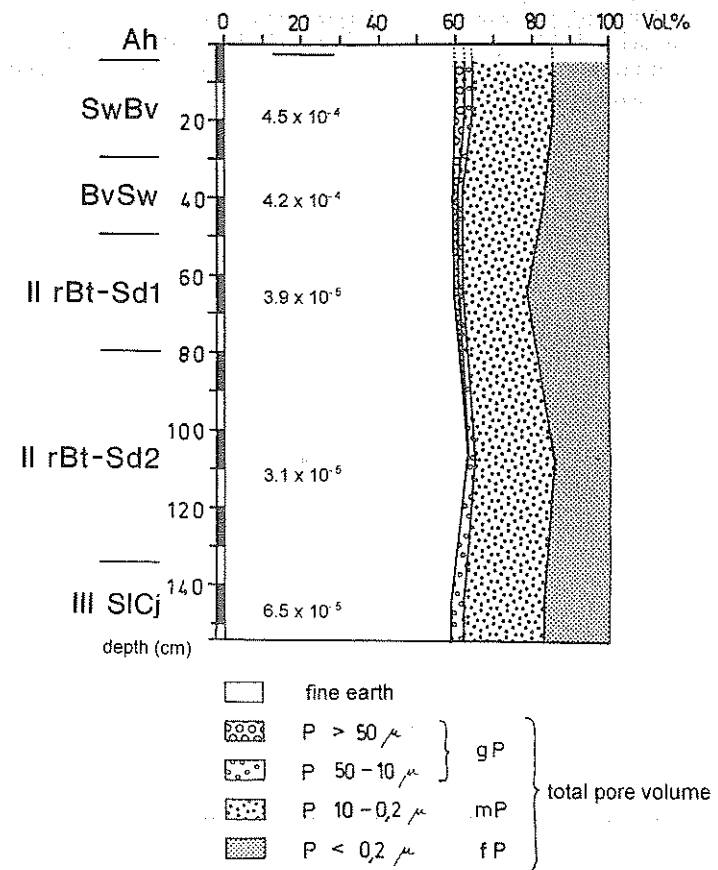


Figure 49: Soil profile Lingerhahn - pore volume, pore size distribution and saturated hydraulic conductivity (in cm/sec)

Clay minerals:

Table 13: 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. = feldspars)

| 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 | + | + |
| IIISICj | - | - | - | - | 55 | 45 | + | + |

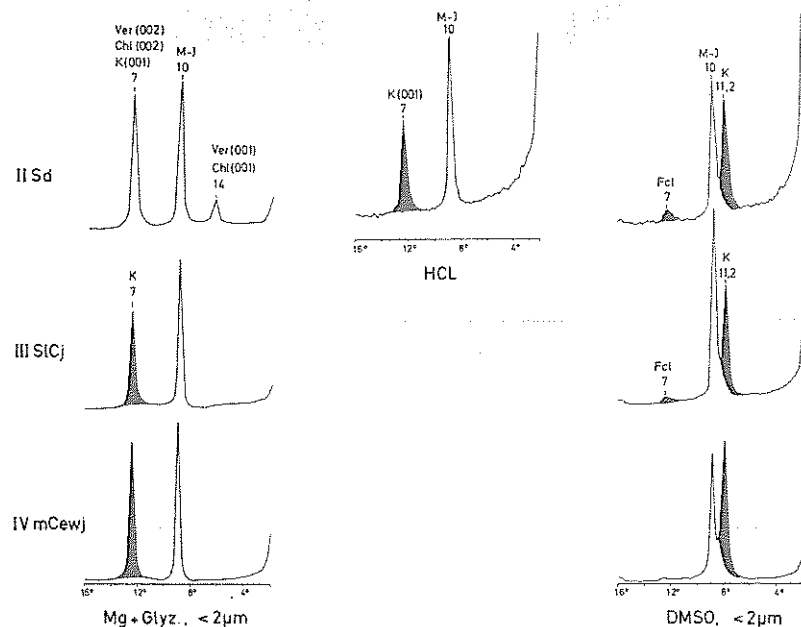


Figure 50: Soil profile Lingerhahn - XRD diagrams (glycerol, HCl and DMSO specimen) of the bleached saprolite (IV mCewj), the basal sequence (III SICj) and the middle sequence (II rBt - Sd); (Fcl = intercalation disordered kaolinite, K = kaolinite, M-I = muscovite-illite, Ver = vermiculite, Chl =

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).

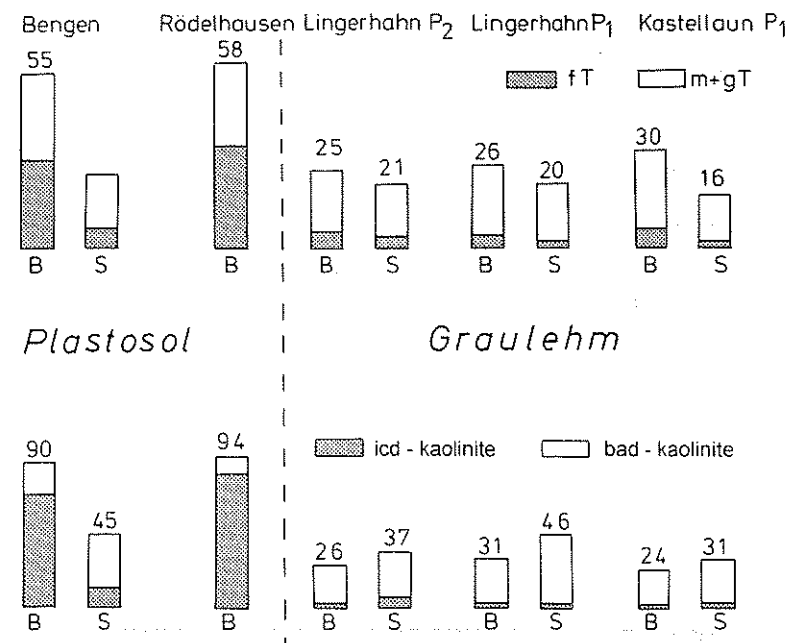


Figure 51: Mesozoic-Tertiary saprolite compared with paleosols (= Plastosol) and Gray Loam (= Graulehm, basal sequence) of soils of the Eastern Hunsrück upland area. 1. clay contents (weight %) with subdivision into fine clay (fT = < 0,2 µm) and middle + coarse clay (m+gT = 0,2 - 2 µm). 2. "content" of kaolinite (relative intensities of the clay fraction < 2 µm) 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.

DescriptionMorphology 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 predominantly 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 µm, in which the fine clay < 0.2 µm 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.

Stop 10 Buchholz soil site

Site: Old soil pit in the Buchholz forest, section 63, Forest Department Boppard, situated between the Autobahn Mainz - Köln and the Hunsrück-Höhenstraße

TK 5711 Boppard, r 33 94 720, h 55 66 390, 375 m a.s.l.

Topics: Holocene soil formation from Laacher See Pumice, velocity and amount of weathering, Andosols in Central Europe

Description of the soil profile

Morphology: almost flat, inclination: West to Southwest. Flat depression on the Hunsrück plateau, source area of the Lehenscheider Bach, draining into the Moselle and Rhine system

Annual precipitation: 660 mm

Mean annual temperature: 7,9 °C

Land use: Forest, oak plantation, 20 years, after spruce. Natural vegetation is Melampyro-Fagetum

Parent materials: Pumice of the Laacher See eruption 5 with volcanic ash, possibly with loess addition, overlaying paleosol materials from clay shists (Hunsrückschiefer)

Dating: Holocene soil formation from late Pleistocene volcanic and periglacial sediments above fossil soil formation from Lower Devonian (Oberems) metamorphic rock

Soil type: Typische Lockerbraunerde

FAO: Haplic Andosol

USDA: Alic Hapludant

| | | |
|---------|-------------|---|
| L | 7 - 5 cm: | oak litter |
| Of | 5 - 0 cm: | black (10 YR 2/2-3/2), completely altered organic layer, possibly from former spruce humus |
| Ah | 0 - 5 cm: | darkbrown to black (10 YR 4/4-3/4), crumbs, very loose, permeable, intense roots, sandy loam, few fragments of shists, high humus content |
| AhBv | 5-15 cm: | darkbrown (10 YR 4/4-3/4), flocculated crumbs, very loose, intense roots, sandy loam, some shists fragments, high humus content, irregular transition |
| Bv1 | 15 - 35 cm: | darkbrown (10 YR 4/4-3/4), flocculated crumbs to subangular structure, very loose, permeable, intense roots, sandy loam, few shists fragments, medium humus content |
| Bv2 | 35 - 45 cm: | darkbrown (10 YR 4/4), subangular structure, very soft, loose, frequent roots, humus containing spots, some pumice and shist fragments, gradual to sharp boundary |
| Bv3 | 45 - 68 cm: | yellowish to greyish brown (10 YR 5/8 and 4/4), subangular to crumb, rather loose, some fine roots, loamy sand with weathered pumice admixed, sharp boundary |
| Cn | 68 - 80 cm: | varying in depth and properties, unweathered or slightly weathered pumice and grey volcanic ash, former stratification destroyed probably by cryoturbation |
| II SdCv | 80 - 86 cm: | withish grey, yellow and brown mottles (5 Y 7/3 and 2,5 Y 6/2), clay loam with shist fragments of different size, impermeable paleosol relic, varying in thickness, few root channels |
| III Cn | > 86 cm: | weathered and broken Hunsrückschiefer, withish clay coatings along sheer plains, gradual transition into unweathered rock. |

Comments

1. The Laach Lake Tuffs

The Laach Lake event was until now the last volcanic eruption in the volcanic history of the Eifel mountains and the Rheinisch massif. The vulcanism lasted for a period of about 7 million years. The location of the last eruption named LST 5 took place where we now find the crater lake of Maria Laach. The lake occupies 331 ha and has depth of 53 m and lies in an altitude of 276 m a.s.l. Nearby there has been founded the famous Benedictine abbey in 1093 with the well-known romanian church of 1156. The volcanic rock blown out was of trachytic nature. The eruption was rich in gas therefore we do find today this material in the area surrounding the crater as pumice layers of the several decameters thickness. The volcanic tuffs consists of three main components which are glassy pumice particles (German Bims) together with lithofragments of sedimentary and volcanic rocks and finally single crystals as early crystallisation within the magma. In the tuffs we find the crystals often surrounded with a volcanic glass cover or as crystalfragment, which have been produced during the eruption. The most typical minerals are sanidine feldspars, brown hornblende crystals and yellow titanite. Other minerals present are pyroxene, olivine, zircon and others (POETSCH, 1975, FRECHEN, 1953, EMMERMANN, 1967) Tab. 14. The material erupted during the late pleistocene alleröd period, when the basin of Neuwied was already inhabited by stoneage people. Therefore we do find remnants of this population, covered by the bims sediments. Furthermore the time of eruption is well documented in lake sediments and bogs where the dating can be done by pollen analysis (FIRBAS, 1963).

2. The influence of the Laach Lake Tuffs on soilscape

The Laach Lake event offers an unique possibility for soil genetic studies. This is because the time of eruption is well known, also the mineralogy of the volcanic component is sufficiently well defined. In addition the volcanic glass within the material is easy weatherable. Therefore the progress of weathering can be documented without analytical problems. The Laach Lake event took place after the main loess sedimentation period in Central Europe. In addition it covers the main solifluction deposits in Central German mountain areas. But after

the Laach Lake event there was still a short period of periglacial climate with active cryoturbation and cryoclastics and also a local transport of loess sediments was described for the period after the event (SCHÖNHALS 1957). Especially the last fact has brought some misunderstanding into the interpretation of late pleistocene and holocene soil formation.

The erupted material in their influence on soil development can be divided into 3 zones. All this zones are elongated in a south-west-north-east direction (Fig. 57). In a central zone the cover of trachytic tuff is thick enough to be the parent material for entire new soils. The formation was mainly, that of an Andosol, but through its treatment as agricultural soil and erosion only few places have been preserved under the natural conditions. In places where the thickness of the trachytic tuffs was about two meters there was observed a soil formation through the tuffs into the underlying loess layers (HUGENROTH, 1971, GEBHARDT et al., 1969, STÖHR, 1966).

In the 2nd zone there was a continuous cover of more than 5 cm. In this part there have been spots, where the tuffs formed thicker layers, but have been generally mixed at least in the top layer with local material during the late periglacial Younger Dryas Period (SCHÖNHALS, 1960 und POETSCH, 1975). In this area we have several sites documented, which have been almost continuously under forest. Therefore we can here quantify the soil formation best.

The 3rd zone is also an area which has been affected by the tuff sedimentation but only with layers of a few cm or mm. In this area the volcanic tuff has been mixed into upper soil and can hardly be detected today in terrestrial soils. But in lake sediments colluvial and bog sites, we often find the remnants of the tuff as a time marker in the profiles. Furthermore we can compare soil formation from zone 3 or even from the zone 4, which was unaffected, with information from the zones 1 and 2. The compared profiles in the tables and figures are 30, 70 and 250 km from the eruption center.

3. Properties of the Buchholz site

The Buchholz soil is an extremely loose soil with the very intense root system. It has a high humus content, contains no lime and is in top soil extremely acid in subsoil moderately acid. Over remnants of a paleosol, we do find still some rather fresh volcanic material.

From the soil classification point of view the major question is, if this soil falls into the category of Andosols (FAO) and Andisols (US)? This is locally important because the German soil classification does not key out Andosols. There are three requirements for andic soil properties (LEAMY, 1988). First is, that aluminum plus 1/2 iron extractable by ammonium oxalate must be more than 2,0 %. This is met throughout the profiles (Fig. 57). Using the method, which is a laboratory routine in Germany, we would not meet the requirement. This is obviously only a problem of methodology. The 2nd requirement is the bulk density to be less than $0,9 \text{ g/cm}^3$. This is also met to a depth of more than 50 cm. An typical observation is, that the other "Lockerbraunerden" with less volcanic addition have even a lower bulk density (Fig. 58). The last requirement is a phosphate retention by the Blackmore et al. method of more than 85 %. This is only met in the Bv₂ horizon. While the other compared profiles do have it. But still the profile has to be called an Andosol, because the requirement of phosphate retention is waved, if there is still volcanic glass in the silt and fine sand fraction and the requirement of the oxalate soluble aluminium is met. Because this is the case, we do call the profile an Andosol/Andisol anyway. An interesting byproduct of the study is, that we do have mountain soils, which can be called Andosols without having significant volcanic ash addition.

4. Soil development quantification

Also the organic matter content in the top soil is high, the total amount of organic matter, due to the low bulk density, is only 100 t/ha^{-1} . This is about the average for forest soils while the compared profiles have 200 (K) and 260 (W) t/ha^{-1} .

The next important process is the clay formation. If one counts only the clay dispersed in regular grain size analysis (ammonium dispersion) there is a yield of 176 kg/m^2 of clay throughout the profile. After subtracting the so called primary clay (POETSCH, 1975, JAHN, 1988) we end with $145 \text{ kg clay} \cdot \text{m}^{-2}$. Divided this figure by 11.000 years of soil formation we reach an annual increment of $13 \text{ g} \cdot \text{m}^{-2}$. This is not high above the values which have been found in other studies in Southwest Germany (loess $10 \text{ g} \cdot \text{m}^{-2}$, granite debris $12 \text{ g} \cdot \text{m}^{-2}$). The problem here is, if we really get all the clay into dispersion. Earlier analyses of the same profile only came out with about $6 \text{ g} \cdot \text{m}^{-2}$ and year (HUGENROTH, 1971).

The second important soil formation process is the oxide formation. Only calculating the dithionite soluble iron as Fe_2O_3 reaches $7,6 \text{ kg} \cdot \text{m}^{-2}$, which would be only one third of the oxide formation in loess and granite areas. But if we add the oxalate soluble aluminum and silicate, which is probably correct, because this fraction does not disperse during routine analyses. We end up with additional 83 kg, which is the allophane and imogulite fraction. Calculating this, we have now $8 \text{ g} \cdot \text{m}^{-2}$ and year of oxide formation, which is four times more than observed in intense weathered loess profiles and five times more than in granitic rocks. This underlines the important role of oxide formation in the early Andosol stages (compare JAHN, 1988).

If we add oxide formation and clay formation then we can conclude that until now 42 % of the primary soil material has weathered in 11.000 years, that means we do have a time of approximately 15.000 to reach a 50 % breakdown of the primary rock material. In comparison soils from other materials this is about the minimum time. Loess has a half degrading period of 50.000 years and granite of 100.000 years in soil profiles of comparable depth.

Comparing the total element content of the soil with contents of unweathered Laach Lake Tuffs, we have the loss of 50 - 65 % of Ca, Mg and Na, but a loss of 35 - 40 % of potassium only. This is a sign that the breakdown of primary minerals has reached a higher degree than is calculated from the clay and oxide analyses. All these calculations are under the expectation that in the fine earth only the weathering of the trachytic tuffs are of importance.

5. Site properties

The soil of Buchholz is a soil with the moderate to deep root system and of excellent rootability. The aeration in the upper 60 cm is excellent. The water capacity is high to very high and in subsoil there is slope water observed especially in spring. The profile is a relatively warm one, and has a good nitrogen and potassium availability. Problems may be the low phosphate mobility and the high activity of aluminum.

Table 14: Mineralogy of Laacher Bimstuff (70 km from eruption center), 20 - 200 μ m fraction, % of grains counted

| | TOTAL | | HEAVY MINERALS | |
|----------------|-------|--|----------------|----|
| HEAVY MINERALS | 5 | | PYROXENE | 48 |
| FELDSPARS | 25 | | HORNBLende | 33 |
| GLASS | 33 | | TITANITE | 6 |
| LITHOFRAGMENTS | 35 | | MAGNETITE | + |
| UNDETERMINED | 2 | | APATITE | + |
| | | | ZIRCON | + |
| | | | OLIVINE | 7 |
| | | | BIOTITE | 1 |

Table 15: Mineralogy of the soil profiles, 20 - 200 μ m fraction, % of grain counted

| | BUCHHOLZ | | KÖHLERWALD | | WAGENSTEIG | |
|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | B _{v2} | B _{v3} | B _{v1} | B _{v2} | B _{v1} | BC ₂ |
| HEAVY MINERALS | 9 | 9 | 12 | 12 | 3 | 2 |
| FELDSPARS | ++ | ++ | 14 | 14 | + | + |
| GLASS AND BIMS | + | + | - | - | - | - |
| LITHOFRAGMENTS | - | - | - | - | + | + |
| MICA | - | - | 4 | 6 | 8 | 12 |
| QUARTZ | + | + | 50 | 40 | 35 | 25 |
| UNDETERMINED | + | + | 20 | 28 | + | + |

Table 16: Heavy minerals of the compared soil profile, 20 - 200 μ m fraction, % of grain counted

| PROFILE, HORIZON | BUCHHOLZ | | KÖHLERWALD | | WAGENSTEIG | |
|------------------|-----------------|-----------------|-----------------|--------------------|-----------------|-----------------|
| | B _{v2} | B _{v3} | B _{v1} | II B _{v1} | B _{v1} | BC ₂ |
| PYROXENE | 62 | 67 | 46 | 30 | - | - |
| HORNBLende | 12 | 12 | 3 | 3 | - | 13 |
| TITANITE | 18 | 16 | 1 | 1 | - | - |
| MAGNETITE | nd | nd | nd | nd | nd | nd |
| APATITE | nd | nd | - | - | - | - |
| ZIRCON | nd | nd | 2 | 1 | 45 | 69 |
| OLIVINE | nd | nd | - | - | - | - |
| BIOTITE | nd | nd | 3 | 4 | - | - |
| GRANATE | nd | nd | - | - | 51 | 14 |
| OTHERS | 8 | 5 | 45 | 60 | 4 | 4 |

Table 17: Crystalline clay minerals of the compared profiles

| PROFILE, HORIZON | BUCHHOLZ | | | KÖHLERWALD | | | WAGENSTEIG | | |
|------------------|----------|-----------------|-----------------|-----------------|-----------------|--------------------|-----------------|-----------------|----------------|
| | AB | B _{v2} | B _{v3} | B _{v1} | B _{v2} | II B _{v1} | B _{v1} | BC ₂ | C _v |
| KAOLINITE | - | - | - | + | + | ++ | + | + | + |
| HALLOYSITE | ++ | ++ | ++ | (+) | (+) | + | - | - | - |
| ILLITE | + | - | - | + | + | ++ | - | + | + |
| SMECTITE | - | - | - | - | - | - | - | + | + |
| VERMICULITE | + | + | - | - | - | - | - | - | - |
| Mg CHLORITE | - | - | - | + | + | ++ | + | + | + |
| Al CHLORITE | - | - | - | ++ | ++ | + | ++ | + | + |
| MIXED LAYER | + | + | - | - | + | + | - | + | + |
| OTHERS | - | - | - | GIBBSITE | | | - | - | - |

Table 18: X-Ray amorphous materials in clay fraction

| PROFILE, HORIZON | % OF FINE EARTH | | | | REMARKS ⁺⁺ |
|--------------------|---|--------------------------------|--------------------------------|-------------------------------------|-----------------------|
| | NH ₄ -OXALATE (4 ^h MOIST) | | | | |
| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | ALLOPHANE ⁺ + Im + Fh | |
| BUCHHOLZ | | | | | |
| AB | 0,77 | 6,80 | 0,98 | 12,4 | - |
| B _v | 4,93 | 17,7 | 1,05 | 34,3 | - |
| Cn | 3,64 | 14,0 | 0,60 | 26,4 | - |
| KÜHLERWALD | | | | | |
| B _{v1} | 0,53 | 8,4 | 0,24 | 13,3 | 9,9 (9,0) |
| B _{v2} | 0,55 | 7,7 | 0,22 | 12,3 | 8,7 (7,0) |
| II B _{v1} | 0,79 | 8,0 | 0,23 | 13,0 | 6,7 |
| WAGENSTEIG | | | | | |
| B _{v1} | 0,34 | 5,22 | 1,42 | 10,1 | ~1 (1,0) |
| BC ₁ | 0,73 | 4,88 | 1,03 | 9,6 | (3,0) |

+ CALCULATED ACCORDING TO WADA

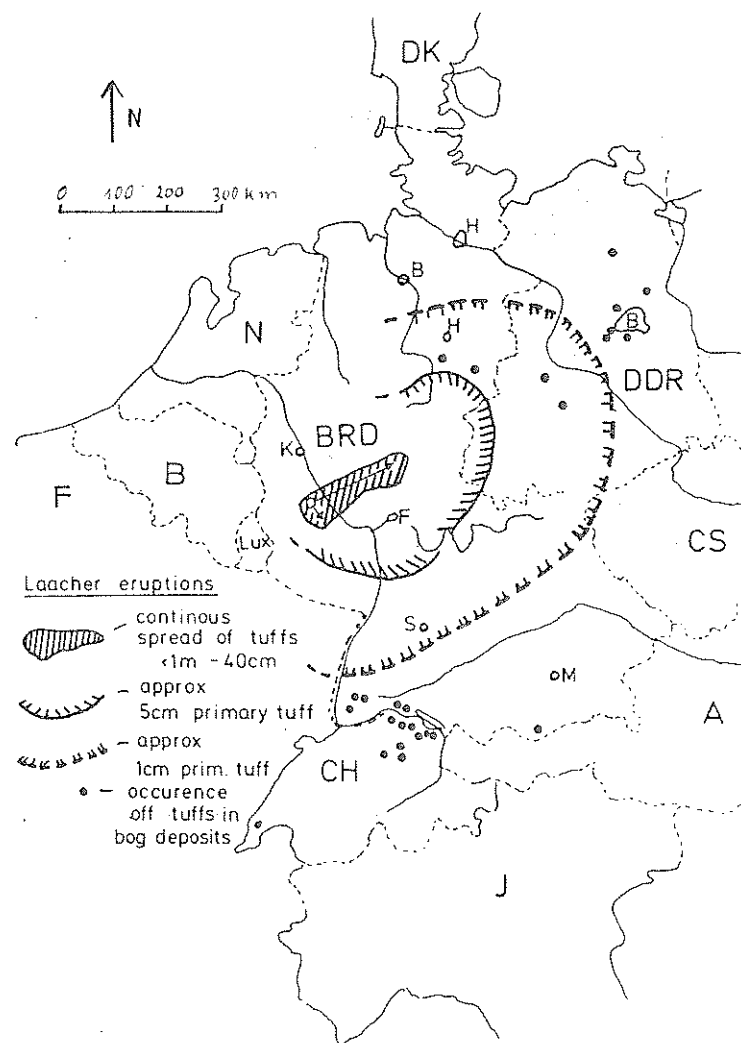
++ ESTIMATED ALLOPHANE + IMOGULITE ACC. TO DTA, HASHIMOTO + JACKSON AND
(ELECTRONE MICROSCOPE)

Figure S2: Distribution of Laacher See trachytic tuffs from the eruption LST 5 in the alleröd period (10 000 a.Chr.)

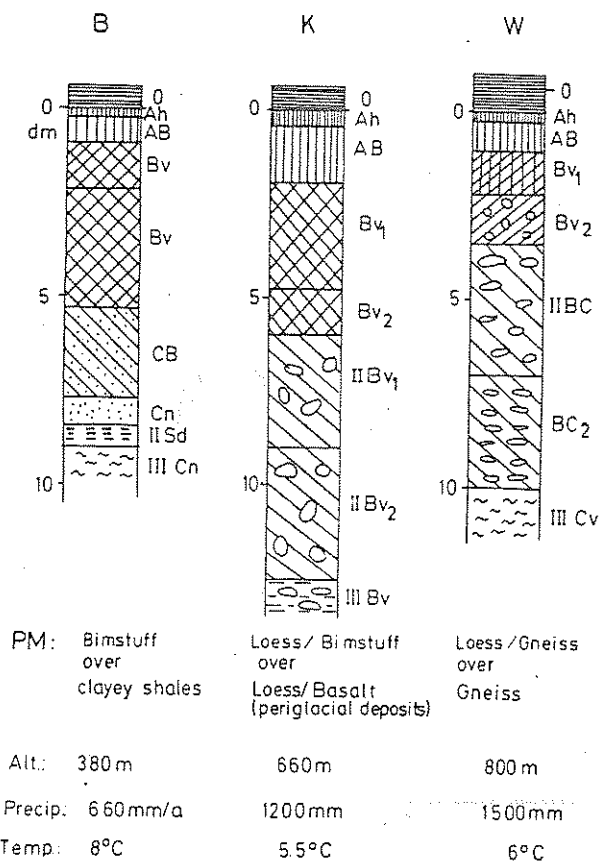


Figure 53: Generalised drawing of Lockerbraunerde "Buchholz" and "Köhlerwald" as well as Sauerbraunerde "Wagensteig"

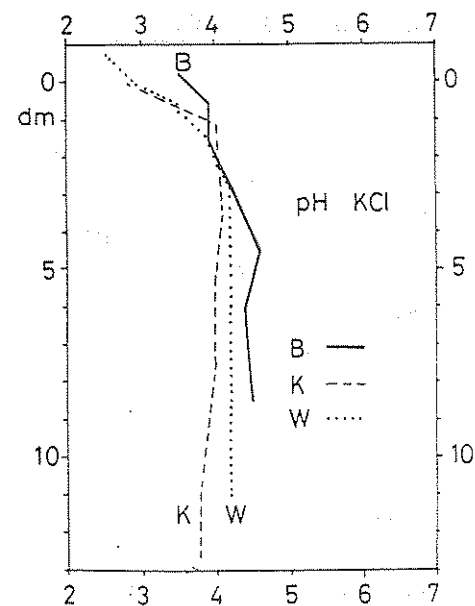


Figure 54: Depth function of pH for the profiles Buchholz, Köhlerwald and Wagensteig

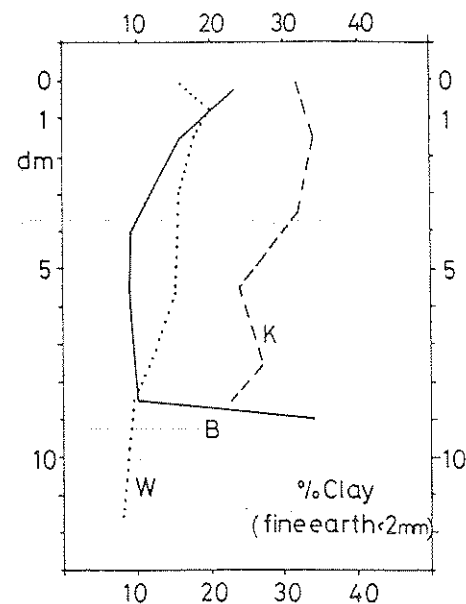


Figure 55: Depth function of clay fraction for the tree profiles Buchholz, Köhlerwald and Wagensteig

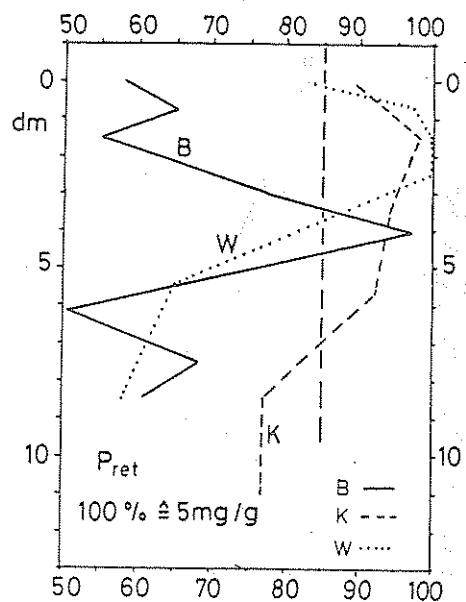


Figure 56: Depth function of P-retention in the profiles Buchholz, Köhlerwald and Wagensteig

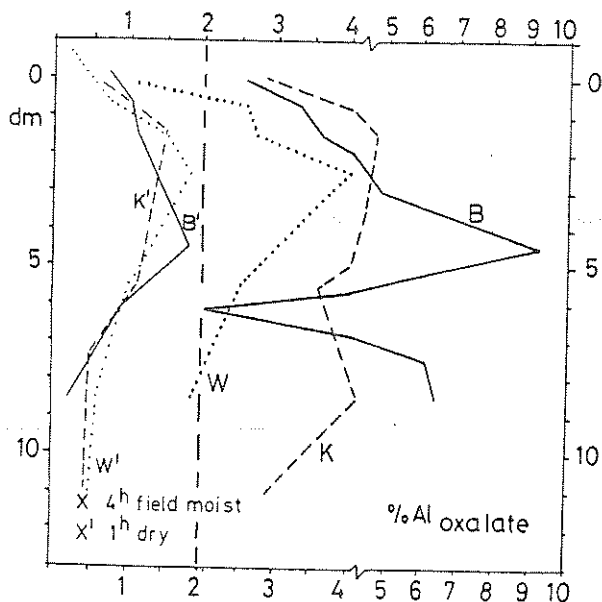


Figure 57: Depth functions of Aluminium soluble in NH_4 -oxalate of field moist samples compared with dried samples

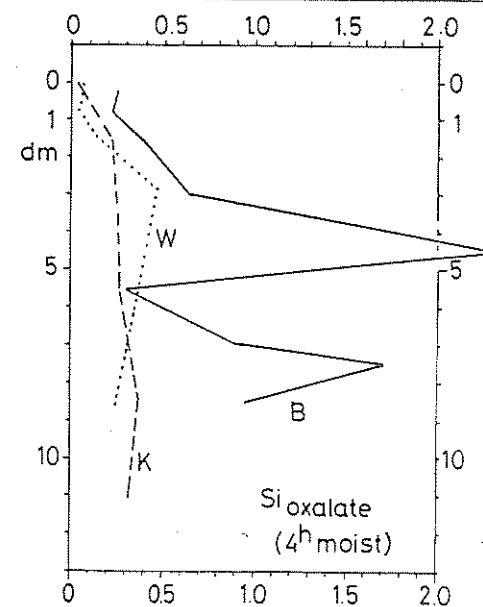


Figure 58: Depth function of NH_4 -oxalate soluble Silica in field moist samples of the profiles Buchholz, Köhlerwald and Wagensteig

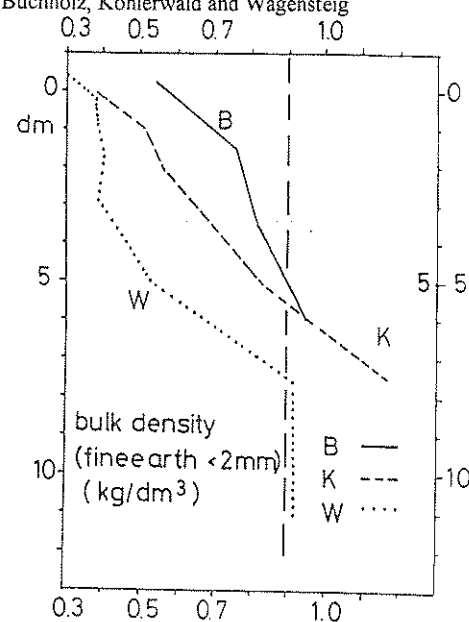


Figure 59: Depth functions of bulk density (fine earth) for the profiles Buchholz, Köhlerwald and Wagensteig

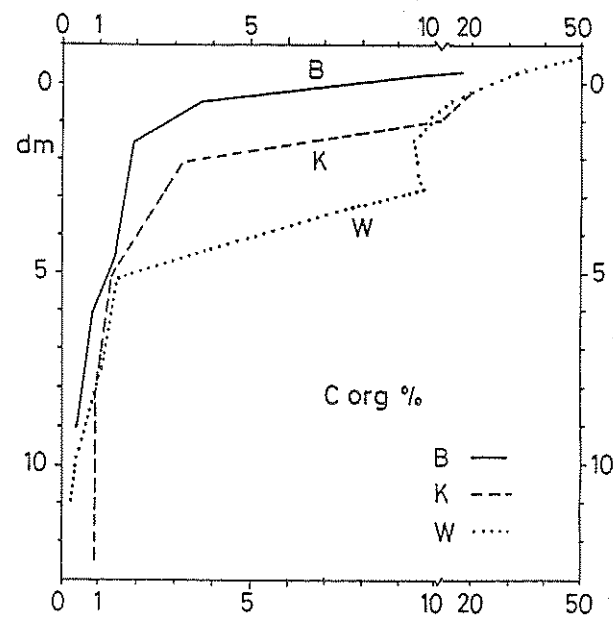


Figure 60: Depth functions of organic carbon for the profiles Buchholz, Köhlerwald and Wagensteig

Analytical data of Profile Buchholz

Table 1:

| sample | horizon | depth | pH H ₂ O | pH KCl | pH CaCl ₂ | pH NaF | C _{org} [%] | N _t [g/kg] | LOI [%] | water pF _{4.2} [%] |
|--------|---------|-------|---------------------|--------|----------------------|--------|----------------------|-----------------------|---------|-----------------------------|
| 1 | Oh | 5-0 | 3.9 | 3.5 | 3.8 | 8.4 | 13.1 | 5.4 | 27.3 | 19 |
| 2 | Ah | 0-5 | 4.3 | 3.9 | 4.0 | 8.8 | 3.7 | 2.3 | 17.6 | 18 |
| 3 | AhBv | 5-15 | 4.3 | 3.9 | 4.1 | 9.4 | 1.9 | 1.4 | 9.1 | 17 |
| 4 | Bv1 | 15-35 | - | - | - | 9.3 | - | - | 7.3 | 18 |
| 5 | Bv2 | 35-45 | 5.4 | 4.6 | 4.8 | 9.9 | 1.4 | 0.9 | 5.1 | 20 |
| 6 | Bv3 | 45-68 | - | - | - | 9.4 | - | - | 2.6 | 10 |
| 7 | Cn | 68-80 | 5.5 | 4.4 | 4.7 | 9.6 | 0.8 | 0.6 | 4.0 | 14 |
| 8 | Cn | 74-80 | - | - | - | 9.6 | 0.4 | 0.7 | 4.3 | 14 |

Table 2:

| sample | hor. | KOH-extr. [g/kg] | | P-retent NZ [%] | oxalate-extr. [g/kg] | | grainsize distribution (µm) [%] | | | | | |
|--------|------|------------------|------|--------------------|----------------------|------|---------------------------------|-----------|----------|---------|--------|------|
| | | Al | Si | | 4h-moist-dark | | 2000 - 630 | 630 - 200 | 200 - 63 | 63 - 20 | 20 - 6 | <2 |
| 1 | Oh | 0.57 | 0.16 | 60 | Si | Al | - | - | - | - | - | - |
| 2 | Ah | 0.65 | 0.1 | 65 | 2.5 | 27.6 | - | - | - | - | - | - |
| 3 | AhBv | 0.59 | 0.08 | 55 | 2.3 | 31.4 | - | - | - | - | - | - |
| 4 | Bv1 | 0.61 | 0.08 | 77 | 3.6 | 36.0 | 8.3 | 23.2 | 10.1 | 7.7 | 8.1 | 33.3 |
| 5 | Bv2 | 1.32 | 0.04 | 95 | 6.2 | 52.0 | 9.6 | 24.5 | 11.1 | 7.0 | 9.0 | 30.0 |
| 6 | Bv3 | 0.32 | 0.06 | 40 | 23.0 | 93.5 | 12.4 | 31.9 | 11.8 | 6.6 | 4.8 | 8.0 |
| 7 | Cn | 0.49 | 0.11 | 48 | 3.0 | 20.2 | 15.4 | 25.0 | 15.4 | 9.5 | 9.4 | 26.7 |
| 8 | Cn | 0.72 | 0.13 | 68 | 8.9 | 31.7 | 11.6 | 24.4 | 10.4 | 7.2 | 6.8 | 31.2 |
| | | | | | 16.0 | 74.1 | 10.1 | 34.1 | 13.0 | 6.4 | 8.3 | 23.6 |

Analytical data of Profile Buchholz - continued-

Table 3: Total Element analysis [g/kg]

| sample | hor. | Ca | Mg | K | Na | Al | Fe | Mn | Ti | P |
|--------|------|------|-----|------|------|-------|------|------|-----|------|
| 1 | Oh | 7.6 | 3.3 | 23.5 | 10.0 | 83.8 | 30.6 | 1.25 | 4.7 | 0.83 |
| 2 | Ah | 7.5 | 3.7 | 24.6 | 11.2 | 94.0 | 33.6 | 1.05 | 6.0 | 1.20 |
| 3 | AbBv | 8 | 3.9 | 29.2 | 12.7 | 101.3 | 36.0 | 1.38 | 6.0 | 0.57 |
| 4 | Bv1 | 8.6 | 3.4 | 29.6 | 13.4 | 113.5 | 37.2 | 1.76 | 6.4 | 0.65 |
| 5 | Bv2 | 11.2 | 3.7 | 31.8 | 15.2 | 114.0 | 37.3 | 1.66 | 6.5 | 0.68 |
| 6 | Bv3 | 11.7 | 5.0 | 38.3 | 17.1 | 106.1 | 38.9 | 1.28 | 8.0 | 0.37 |
| 7 | Cn | 11.3 | 3.7 | 31.6 | 15.0 | 115.6 | 35.0 | 1.53 | 6.5 | 0.54 |
| 8 | Cn | 4.2 | 2.7 | 25.0 | 17.5 | 121.4 | 30.6 | 2.30 | 4.0 | 0.59 |

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