One of the major problems with this manuscript is that it concerns a topic which has already been extensively studied by many soil scientists. Approaches to be used in this kind of studies on residual materials and analytical methods are well established. Crucial questions include:

- can the composition (both chemical and mineralogical) of the non-carbonate components of the 'residual' material be linked to the non-carbonate fraction of the limestone;
- if a residual origin must be assumed, how much limestone should have been dissolved and what implications does this have for the geomorphological development of the area.
- What may be the origin of the materials that do not originate from the original limestone, and that goes far beyond the ubiquitous loess cover, but today includes such materials as volcanic (micro)tephra, Sahalian dust, etc.
- To what extent are materials encountered the result of inheritance of early depositional characteristics or diagenetic processes (e.g. chert formation) or the result of much more recent subaerial weathering.
- In case of assumed recent neoformation: can the flux required for the production of the presumedly neoformed materials (stocks) be accounted for/ be explained. This requires a good understanding of the geochemistry of the system and fluxes of solutes that are possible under the specific conditions.

Crucial techniques include:

- Full chemical and mineralogical analyses of the soil material and the limestone and its residue, including a proper identification of the clay fraction. The latter has to include XR-diffraction data and not only EDS or other chemical analytical techniques.
- A proper description of the micromorphology of the material to have a good understanding of its fabric and provenance of components (e.g. clay, nodules, concretions, etc.).
- Eventually isotopic analyses to identify the origin of the various minerals encountered (e.g. Sr and Nd isotopes to establish the origin of tephra).
- If current soil formation and weathering are to be included in the research: information on the chemical composition of the soil solution and its link to geochemical processes.

The current manuscript basically consists of "static" chemical data at the nanometer scale (EDS) providing only information on element distribution in the soil matrix, and some general data on the distribution and habitus of Fe species (apart from standard very general soil data). That is all.

- there is no information on the chemical/mineralogical composition of the non-carbonate components in the residual soil nor in the limestone
- there is no full study of the potential provenance of the non-carbonate fraction
- there is no information on the presence of original or diagenetic features in the limestone (for example the presence of clay in fossils, which may well be of very early age and the presence of silica)
- there is no understanding at all of the geochemistry of these systems and behavior of the various species in this system.

As to techniques:

- no full chemical and mineralogical analyses, particularly no XR-diffraction data
- no full study of the potential provenance of the non-carbonate fraction.
- no micromorphology
- no isotopic analyses nor full study of trace elements to study the potential provenance of the various materials/components. Typical example is the Zr/Ti ratio which clearly indicates that the residual fill has very little to do with a dissolution residue from the limestone.
- no understanding of the geochemistry of these systems, e.g. the assumption that Al3+ plays a role in these systems and occurs as a solute, leading to isovolumetric substitution. Study of current composition of the soil solution and speciation of the solutes would easily have shown that.

Moreover, all kinds of terms are being used in connection with the apparently major phenomena: occurrence of clay size material in small voids: Isovolumetric replacement, pressure-driven metasomatic replacement, authigenic clay neoformation, exchange process characterized by substitution, pressure-driven isovolumetric replacement during authigenic clay neoformation, replacement processes, metasomatic processes.

There are very fundamental differences between the various processes basically coming to: a) precipitation from the solution and b) mass transport as suspended material in the solution. 'Replacement processes' is a meaningless term in this context. This holds the more, while 'replacement' cannot be observed as an active process, but is merely an interpretation of spatial structures and distribution of elements. What is dearly needed is a clear definition of the various terms and their strict application + arguments that exist for one or another interpretation. Now it is a mess and often completely obscure what is truly meant.

All in all, I am not very happy about this study, which in fact has only a few EDS results as 'new data' and rambles on from one assumption to another, and from quite poorly founded conclusions to bland nonsense. Moreover, the very extensive literature review is incomplete, missing major and highly relevant studies, highly unbalanced (a lot of completely irrelevant studies), and poorly structured, mixing results with assumptions and conclusions, and not to the point.

Typical example of the quality is the text in the lines 737-741: Extremely vague: can contribute – not yet possible – cannot yet be fully explained – further studies - should consider the possible role. In other words, one asks oneself what the contribution of this paper is if these are the conclusions. Not a very impressive contribution to science and that is also my general conclusion: *not a significant contribution to science at all. Just a few observations with EDS on some thin sections from residual limestone soils. Much too far reaching interpretations and too many unsubstantiated claims based on these limited data.*

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Isovolumetric replacement and aeolian deposition contributed to Terrae calcis genesis in Franconia (central Germany)

Bernhard Lucke[1], Helga Kemnitz[2], Stephan Vitzethum[1]

[1]Institute of Geography, Friedrich-Alexander University Erlangen-Nürnberg, Wetterkreuz 15, 91058 Erlangen, Germany

[2] Helga Kemnitz, Katharinenholzstr. 33 B, 14469 Potsdam, Germany

Correspondence to: bernhard.lucke@fau.de

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Abstract

We investigated Terrae calcis on limestone and dolomite in Franconia, as well as the red fill of deep cracks in the rock (*Karstschlotten*). SEM images of the rock-soil transition zones supported by EDS found amorphous clays along fissures that could be products of metasomatic, authigenic clay neoformation within microfossils, calcite, and dolomite grains, or of replacing deposition of amorphous clays inside the calcite, probably due to percolating waters (illuviation). In the SEM-images, the replacement appears as exchange process characterized by substitution of Ca and Mg against Si, Al, and Fe. There is no crystalline clay deposited within rock fissures, and the transition between calcareous minerals and amorphous clay is gradual. This and the presence of Fe let it seem possible that plant roots play a major role for the transport of elements and neoformation of clays, similar to clay pavements along eucalyptus roots in Western Australia. In this context, more or less uniform Fe(d/t) ratios contradicting other weathering indicators could be the result of neoformed phyllosilicates containing Fe^{3+}. Bulk soil and bedrock analyses indicate that the solum of the investigated Terrae calcis does mainly not represent insoluble bedrock residue. Dust deposition and bioturbation are evident due to sand grains coming from a loess surface cover, which buried pre-existing Terrae calcis and contributed to their substrate, apparently supplying quartz and clay-rich pseudosand aggregates.

1. Introduction

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Until today, there is no general agreement on the genesis of clay-rich red or brown soils on hard limestone in Mediterranean and temperate climates. It has even been suggested that they do not represent true soils but a type of claystone (Merino and Banerjee, 2008). The soil science community largely follows Kubiëna's (1945) model, which proposes that they represent true soils characterized by accumulation of clay. He termed mature profiles 'Terra fusca' (with brown color) and 'Terra rossa' (with red color). Despite the color difference, these soils are characterized by very similar properties. Their close relationship is expressed by the summarizing group name 'Terrae calcis' (Kubiëna, 1945), which has been adopted in the German soil classification guidelines (Ad-hoc AG Boden, 2005). Most other soil classification systems do not use such specific terms for clay-rich soils on limestone, but they are applied here as we consider them useful for referring to previous works and discussing the problems connected with the investigation of these soils. For an extensive summary of the literature and a discussion of classification issues, in particular the relation to similar soils in the tropics, see Skowronek (2016). [illegible]y a limited part of the literature on the subject can be summarized here; for more comprehensive information see also the reviews in Merino and Banerjee (2008), Trappe (2011), Fedoroff and Courty (2013), and Lucke et al. (2012, 2014).

1.1 Parent materials

The debate on the genesis of Terrae calcis starts with the parent material. Leiningen (1930) and Kubiëna (1945) suggested that they resemble mainly the non-soluble residue of calcareous rocks after in-situ dissolution of limestone by meteoric water. However, already these authors contemplated that Terrae calcis may contain a major

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allochthonous component, possibly mainly from aeolian dust. As outlined by Schmidt et al. (2006), it seems well possible that the contributions of sources vary locally. Studies in Italy (Moresi and Mongelli 1988), China (Shijie et al. 1999; Ji et al. 2004a, 2004b), and Turkey (Temur et al. 2009) support the residual theory since the mineral assemblies and geochemistry of these soils are largely similar to the non-calcareous residue of the underlying limestones. However, at other locations substantial differences between soil and rock residue have been found (e.g. Leiningen 1915; Durn et al. 1999). As well, it seems questionable at some locations whether residual formation out of pure limestone could be possible, as this would require the dissolution of huge amounts of rock (Yaalon and Ganor 1973; Merino and Banerjee 2008). In this context, long-range transport of Saharan dust was found to play a significant role for soil formation on limestone in a large part of the northern hemisphere (e.g. Muhs, 2001; Muhs et al., 2007; Lucke et al., 2014).

1.2 Mechanisms of soil formation: aeolian deposition, bedrock dissolution, and illuviation

Closely connected with the question of parent materials is the mechanism of soil formation. Since a steady deposition of Saharan dust takes place in the Mediterranean (Martin et al. 1989), Yaalon and Ganor (1973) suggested that clay- and Fe-rich dust settling with precipitation is the main substrate of most Terrae calcis in that area. Saharan dust could even be traced in Terrae calcis of the West Indies (Muhs 2001; Muhs et al. 2007; Prognon et al. 2011). Danin et al. (1982) found fossil marks of lichen on limestone under a Terra rossa in Israel, suggesting that ~~that~~ the rock had once been exposed to sunlight before being covered by soil. In northern

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Jordan, Lucke et al. (2014) found a continuous dust signal in soils on different bedrocks and concluded that aeolian deposition must have provided a significant amount of the soil parent material, even though a specific and significant contribution of each different bedrock was clearly indicated as well. Therefore it seems possible that a mixture of aeolian deposition and bedrock weathering can contribute to the genesis of Terrae calcis.

Dissolution of limestone, in particular of clay-rich marls that are often interbedded in calcareous formations, could directly produce a clayey residue (Bronger et al., 1984). During assumed long periods of soil formation, such clay-rich interlayers could have disappeared due to weathering, which is why a divergent composition of the soil and the now underlying limestone does not necessarily prove an allochthonous origin of the solum. In this context, Frolking et al. (1983) and Fedoroff and Courty (2013, and references therein) suggested an illuvial origin of the phyllosilicates. Since smectites may maintain surface acidity even when dispersed in Ca-rich water (Mortland and Raman, 1968), clays might be transported by subsurface waters, trigger limestone dissolution, and accumulate, leading to an effective replacement of limestone by clay. As chert bands in the Galena dolomite in Wisconsin continued through the clays studied by Frolking et al. (1983), this replacement must have taken place isovolumetrically, i.e. not creating larger voids so the chert bands were not disturbed. That the clays had been transported was indicated by oriented coatings on slightly weathered dolomite in greater amounts than could result from in-situ rock dissolution (Frolking et al., 1983).

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1.3 Metasomatism in Terrae calcis genesis

An alternative way of Terrae calcis genesis was first suggested by Blanck (1915): the clay-rich substrate could not only be product of bedrock weathering, illuviation, or aeolian deposition, but consist of newly formed (authigenic) clay minerals that replaced the limestone in a pressure-driven metasomatic reaction. In this context, Stephenson (1939) and Ross and Stephenson (1939) discovered fossil mollusks that had apparently been replaced by beidellite and were preserved as clay structures in a limestone bed near Pontotoc, Mississippi. Monroe (1986) reviewed literature regarding the replacement of limestones by clay and conducted a replacement experiment based on circulation of mineralized groundwater through limestone: the experiment failed, but the reported evidence suggested that limestone could indeed be replaced by lime-free clay. These examples, however, do not only refer to the genesis of soils on limestone, but to clay layers within limestone beds and to clay fills of subterranean caves (see also Zippe, 1854; Weyl, 1959; and Fenelon, 1976).

Maliva and Siever (1988) simulated in the laboratory how chemically completely strange guest minerals can grow in host minerals if a superconcentration of ions precipitating as guest mineral is present: the guest mineral replaces the host mineral in a pressure-driven reaction while maintaining its bedding structures (by 'force of crystallization'). In this context, Zhu and Li (2002) described metasomatic relic bedding structures of the underlying limestone in Terra Rossa in southern China, which could be result of replacement processes as simulated by Maliva and Siever (1988). ino and Banerjee (2008) investigated thin sections of a 'bleached zone' in the rock-soil transition zone of a Terra rossa in Bloomington, Indiana, and described a 'reaction front' that was characterized by partial isovolumetric replacement of limestone by clay, as well as dissolution voids that were associated with the replacement. They calculated a thermodynamic model of the replacement reaction. According to this model, the reaction would on the one hand lead to a pressure-driven isovolumetric replacement of the limestone during authigenic clay neoformation, meaning that the mass balance of soil formation versus bedrock dissolution requires much less limestone for soil formation than the residue model. On the other hand, the reaction would produce acids which could explain the association of Terrae rossa with karst, and lead to additional chemical dissolution of limestone with a subsequent mixing of the non-soluble residue with the newly formed clay.

However, even the comprehensive model presented by Merino and Banerjee (2008) cannot fully explain (authigenic) clay neoformation: one major question is the supply of ions into the rock fissures. Merino and Banerjee (2008) suggested that dissolved aerosols would deliver the necessary elements (mainly Si, Al, and Fe). Banerjee and Merino (2011) further refined the replacement model by accounting for diffusion and infiltration processes. These were based on Amran and Ganor's (2005) dissolution half-lives of smectites in water – for pH 5. However, considering the often neutral to slightly alkaline pH-values as e.g. found by Lucke et al. (2012) for most Terrae calcis in northern Jordan, it seems still questionable how ions of Al that are hardly soluble under such conditions could be mobilized from the surface into the rock pores. Metasomatic features could be relic and have formed when soils were completely decalcified, which seems possible since there is evidence that Terrae calcis in Jordan

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were subject to re-calcification in the recent past (Lucke, 2008). However, organic matter might play a role too: Blanck (1915, 1926), Blanck et al. (1928) and Blanck and Oldershausen (1936) proposed that organic acids provide colloids that prevent ions from precipitating even when in contact with calcareous rocks (see also the comprehensive review in Blanck (1930). This idea could explain why red soils are largely absent on calcareous rocks of temperate zones: due to the much lower humus contents of soils in Mediterranean climates, ions must precipitate when reaching the calcareous rocks, but not if larger humus concentrations are present (Blanck, 1915). It could mean that Terra fusca might be less a product of replacement processes than Terra rossa due to the usually significantly higher contents of organic matter in Terra fusca.

However, other ion transport mechanisms seem possible too: Reifenberg (1927, 1947) argued that silicic acids, and not humus, provided the colloid that prevented flocculation of sesquioxides and growth of minerals before ions entered the rock pores. Reifenberg (1947) suggested further that the source of the ions in semi-arid areas might not be the soil surface, but ascending waters from the rocks. Lucke et al. (2012) suggested that plant roots might supply the necessary ions to the rock pores, based on the observation that plant roots can often be found in rock fissures, and on the reported neoformation of clays associated with root exudates of mallee eucalypts in geochemically completely different sand dunes that was observed by Verboom et al. (2009). This casts some doubts on a possible connection of organic matter and colors of Terrae calcis, although Terefe et al. (2008) suggested that repeated vegetation fires and thus organic matter could cause long-term red coloration.

1.4 Colors of Terrae calcis

Various ideas have been brought forward to explain the prevalence of brown and red colors of Terrae calcis. The red color of Terrae rossae could be inherited from the insoluble limestone residue (Bronger et al., 1984), could have formed during pedogenensis under warmer and more humid climates of the past (Klinge, 1958), or simply result from oxidized Fe^{2+} that was released during the weathering of carbonate rocks (Meyer, 1979). Schwertmann et al. (1982) suggested that rapid wetting-drying cycles as often prevailing in Mediterranean climates and on well-drained karst areas can lead to recrystallization of ferrihydrite as hematite, which gives red color even when present in only small concentrations. Although this process could not yet be modeled in the laboratory, Barrón and Torrent (2002) showed that ferrihydrite can transform into maghemite under presence of phosphate or other ligands capable of exchange of Fe-OH surface groups. Based on this, Torrent et al. (2006) suggested that maghemite formation is a precursor of hematite during ferrihydrite transformation in aerobic soils poor in organic matter, which matches evidence collected by Lucke and Sprafke (2015) along a climatic transect in northern Jordan. In contrast, the prevailing brown colors of temperate areas seem connected to less pronounced moisture differences, and it has been suggested that a change to moister and cooler conditions could have caused xanthization of formerly red soils, meaning that red-colored hematite would change to goethite (Boero and Schwertmann, 1987).

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2. Genesis of Terra calcis in Franconia (central Germany)

Franconia hosts widespread limestone plateaus which are partially covered by brownish and reddish Terra calcis (locally called *Alblehm*). These plateaus were mostly not glaciated, but situated in a periglacial environment during the Pleistocene. Terraes calcis are partly present at the surface, and partly buried by loess and sands, and can be found as fills of deep cracks and dolines in the limestones. While the plateau soils are mostly brown, the crack fills are often characterized by intense red colors. Their environmental significance is debated. According to Mückenhausen et al. (1975), red infillings in limestone cracks could be relics of a former soil cover, possibly of Terrae rossae or Ferralsols from the Cretaceous or Tertiary, which was eroded on the surface but preserved in the cracks. Zech et al. (1979) investigated red clayey fills in karst cracks of Franconia and concluded that their color testifies to formation during warmer and moister tropical climates of the past. This is supported by higher amounts of kaolinite in the clay infillings compared to the residue of the surrounding bedrock. However, in the light of theories of Terrae calcis formation discussed above, it seems also possible that the crack fills are products of illuviation, or clay neoformation – and the different color might be explained by divergent organic matter contents, since the cracks are not connected to the actual surface.

In this context, “powdery” layers of $CaCO_3$ of approximately 1 mm thickness have been described by Trappe (2011: 96) for the rock-soil transition zones of Terrae calcis in our studied area in Franconia, who interpreted them as potential evidence of insoluble limestone residue contributing to solum formation. However, the limestones are very pure: Häusler and Niederbudde (1992) estimated that about 3 mm of soil

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cover could have formed out of the respective limestone residue during the Holocene, meaning that Terrae calcis such as the ones investigated in this study would have experienced about 2.7 Ma of soil development under the current climate without erosion in order to reach the present depth. Trappe (2011) argued in this context that the Terrae calcis and crack fillings in Franconia represent mixed sediments, largely stemming from weathered chalk layers, since the limestones produce too little residue. However, no high-resolution study of the micromorphology of these soils and their transition zones to bedrock was yet accomplished.

Although a final explanation of the mechanisms of the metasomatic replacement process [illegible]not yet be offered, there is growing evidence that in-situ neoformation of clay can contribute to the formation of clay-rich soils on limestone (see e.g. Feng et al. (2009) and the review by Laverty (2012). Key evidence for isovolumetric replacement are 'shadows' of the original rock structures that are preserved in the soil-rock transition zone, in particular microfossils partially consisting of clay. If neoformation of clay minerals in limestone took or takes place, a spatially precise approach focusing on partially replaced microfossils can track it. And if partially replaced microfossiles can be confirmed for Terrae fuscae, it would suggest that metasomatic processes are less dependent on organic matter than suggested by Blanck (1915). [illegible]refore we studied the micromorphology of the rock-soil transition zones of two Terrae fuscae and a limestone crack filled with Terra rossa in Franconia with regard to the presence of partially replaced microfossils and minerals. In addition, bulk samples of the substrate and the microsurfaces of sand grains were investigated. These areas had been studied before by Blanck and Oldershausen

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(1936), and we attempted to re-visit some of their investigation sites in order to honor their prior efforts, applying now available more advanced methods of analysis.

3. The sampled profiles

From a total of five studied sites, two are presented here. The first profile 'Fricke' is located in a quarry approximately 4 km southeast of the town Weißenburg i. Bayern on top of a limestone plateau (N 49° 00' 36.6“, E 11° 01' 35.7“, see figs. 1, 2a and b). Here a thick hard limestone from the upper Jurassic/Malm δ containing *Ammonites pseudomutabilis* (locally called *Weißenburger Marmor*) is exposed, which is well-suited for construction and exported worldwide. The rock has vertical cracks that are filled with uniform red clay which was already observed and studied by Blanck and Oldershausen (1936). We named our profile according to the designation given by these authors, although the exact part of the limestone quarry which they studied has been removed by constant quarrying during the past 80 years. In the studied profile, the clay-filled cracks are not connected to the present surface, but interrupted by another layer of hard limestone. On this layer a zone of intense rock weathering (see fig. 2b) resembles the bedrock of soil formation on the current surface. It can however not be excluded that there was a connection of the crack to the surface in the front of the profile that was removed by quarrying.

The soil developed at the surface can be classified as Cambisol (Siltic) according to the World Reference Base of Soil Resources (WRB 2014). According to the German soil classification system (Ad-hoc AG Boden 2005), a Braunerde-Terra fusca is present: the lower part of the profile could be described as Terra fusca, which

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gradually changes into a Braunerde formed out of loess in the upper part. Soil horizons were classified according to the German system (Ad-hoc AG Boden 2005, see figs. 2a and b). There is a gradual transition from a dark-brown, clay-rich Terra fusca horizon (II TBv) to a bright yellowish, silty Bv horizon that apparently resembles loess which at some time buried a prior developed Terra fusca. Roots were present throughout the whole profile and even in the deepest crack fillings. Although we sampled the whole profile for bulk soil analysis, only the soil-rock transition zone of the red clay in the cracks was studied by micromorphology. Bulk samples of the crack infillings were taken in the upper and lower part of the crack (samples III Tu (1) and (2). The crack fillings are homogeneous and no horizons or indicators of fluvial deposition could be observed (fig. 2c). As well, the bedrock was sampled and analyzed for calcium carbonate, total element contents, residue particle sizes, and residue color.

Figure 1

Figure 2a

Figure 2b

Figure 2c

The second profile 'Schwaighauser Forst' is located at the eastern border of Franconia, locally called *Bruchschollenland*, an area characterised by strong faulting and dislocation of geological units. Therefore very different lithologies are exposed at the surface in small areas, and some volcanic activity about 50 km to the east was associated with the faulting. The studied soil represents an Epileptic Cambisol (clayic) according to the WRB (WRB 2014). According to the German soil classification system (Ad-hoc AG Boden, 2005) it can be classified as Terra fusca. It is located in an educational soil trail (N 49° 05' 10.7", E12° 00' 12.7") north-west of the city of Regensburg (TUM 2014), formed on dolomitic limestone from the Upper Jurassic/Malm ε-ζ. At this profile, a loess cover is not discernible, but may have eroded since the solum is much shallower than at the first profile (figs. 3a and 3b). Roots were present throughout the whole profile. Apart from each horizon, the bedrock was analyzed for calcium carbonate, total element contents, residue particle sizes, and residue color.

Figure 3a

Figure 3b

4. Methods

Our main aim was to check whether partially replaced microfossils can be found in the rock-soil transition zones of the sampled profiles, supported by some analyses of bulk soil and bedrock residue in order to describe soil development intensity. Micromorphological samples were taken from the transition of the unweathered bedrock to the clay of Terrae calcis, including several samples covering the whole distance from the apparently unweathered rock till clay aggregates of the solum. Thin but stable metal containers were placed on the transition of soil and rock and the samples slowly cut out with a knife. After freeze drying, samples were stabilized using Araldite A2020 epoxy resin. The thin sections received a diamond-polishing and were carbon coated. After optical analysis, microanalysis was done with a high resolution field-emission scanning electron microscope (FESEM; Carl Zeiss Ultra 55 Plus), equipped with an energy-dispersive system (EDS) by Thermo Fisher Scientific. In contrast to only optical analysis, scanning electron microscope analysis with EDS permits determining the geochemistry of the studied areas. This can allow detecting minerals that appear amorphous to X-ray diffraction and optical studies. In addition, large allochthonous clays such as biotite grains can be misinterpreted as in-situ formed minerals as shown by Lucke et al. (2012) if only optical analysis is applied, and the scanning electron microscope (SEM) allows investigating smaller features at scales of nanometers.

General soil analyses determined calcium carbonate and organic carbon contents with a Leco TrueSpec C-N analyser measuring samples before and after ignition of organic matter at 430 °C for two hours (Schlichting et al., 1995), based on the assumption that the remaining content of C represents carbon bound in calcium carbonate. The dolomite content of the dolomitic limestone was estimated from the residue mass after dissolution of the calcareous part of the rock with 10% HCl. Soil color of dry soil samples and the color of dried bedrock residue after dissolution with 10% HCl were determined using the Munsell color chart, and redness ratings calculated according to Hurst (1977). In order to control whether the treatment of the rock with 10% hydrochloric acid could lead to a loss of red color of the residue, samples of the Terra rossa limestone crack infillings were simultaneously treated with the same amount of acid during the same time of bedrock dissolution, but no color change could be observed. Analysis of clay minerals would require rock dissolution with weaker acids in order to exclude alteration of the minerals due to acid treatment (Ostrom, 1961; Rabenhorst and Wilding, 1984), but since only the texture and color of the residue were studied, faster treatment with stronger acid was chosen.

Pedogenic iron oxides were extracted with sodium dithionite at room temperature according to Holmgren (Schlichting et al. 1995), and the iron contents measured with an ICP Spectrometer (Thermo Scientific iCAP 6200 Duo). In case samples contained more than 4% $CaCO_3$, particle sizes were analyzed after removing $CaCO_3$ with 10% hydrochloric acid and washing the samples until conductivity dropped below 200 µS. These and the other samples containing less than 4% $CaCO_3$ were then dispersed with sodium hexametaphosphate ($Na_4P_2O_4$) and shaken overnight (Schlichting et al., 1995). Wet sieving determined the sand fraction according to DIN 19683 (1973), while the smaller particles were analysed with a Sedigraph (Micromeritics). For total element analysis by X-ray fluorescence, we determined the loss on ignition (LOI) by weighing the powdered samples before and after drying: 1) 12 hours at 105 °C in a cabinet dryer and 2) 12 hours at 1030°C in a muffle furnace. Major element oxides (SiO_2, TiO_2, Al_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5) and selected trace elements (Ba, Cr, Ga, Nb, Ni, Pb, Rb, Sr, Th, V, Y, Zn, Zr) were measured with a Spectro XEPOS at the GeoZentrum Nordbayern. Precision and accuracy are generally better than 0.9% and 5%, respectively.

5. Results

5.1 Micromorphology of the rock-soil transition zones

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Limestone beddings partially consisting of clay could be found in the rock-soil transition zones of both studied profiles. Figure 4 shows a calcite grain partially consisting of clay in the 'powdery' (see Trappe, 2011) transition zone of about 1 mm thickness, directly between the red clay and the limestone in the profile 'Fricke'. It appears that a prograding solution is encompassed simultaneously by the formation of clay. As shown by the serrated grain rim in fig. 4 (upper part), exchange seems to occur along zones of potential permeability such as fine fissures, at grain contacts, or through pores. That part of the calcite already consists of clay is shown by the spectral image in fig. 4 (lower part). Although secondary calcite needles were noted in some fissures, no clay could be observed in the pores: there are no clay films suggesting that allochthonous clay has been transported into the rock. As well, the original form of the calcite grain is so well preserved that the clay cannot be of allochthonous origin, but must represent the in-situ limestone, and there is no structure discernible that could be attributed to micro-clay beddings deposited during limestone formation. Conclusively, bedrock weathering may not simply proceed by chemical reaction processes which create voids in the rock due to chemical dissolution, but clay neoformation and rock dissolution could be part of the same process as suggested by Merino and Banerjee (2008).

Figure 4

About 1 cm deeper into the limestone, it appears rather unaltered to the naked eye and remains of biogenic shells can be observed macroscopically. But there are also some small reddish lines. Analysis with the SEM confirmed that some of these lines represent clay, which is partly present inside microfossils. Figure 5 shows a biogenic relict (probably alga or foram) partially consisting of clay which is surrounded by still largely unweathered limestone. Again, there is no evidence that the clay was transported into the microfossil, since the outer shell is still closed and consists of calcium carbonate. Though the outer shell seems preserved and closed, consisting of calcium carbonate, one has to account for the three-dimensionality of the organism and a high likelihood of pores. But the apparently amorphous structure of the clay inside the microfossil argues against allochthonous clay minerals. Furthermore, it still contains significant amounts of the former calcium carbonate filling (see spectral images in fig. 5).

Figure 5

The Terra fusca of the Schwaighauser Forst profile formed on a dolomitic limestone that is characterized by low density of microfossil remains in the rock. Yet, some microfossils partially consisting of clay could be observed in the direct soil-rock transition zone, inside the rock in about 10 µm distance to the border of the limestone as shown in figure 6. This microfossil is characterized by high contents of magnesium corresponding to bedrock chemistry. The minor Si peak that is detected in the inner section might either derive from naturally implemented traces of silica or indicates authigenic neoformation of clay, too.

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Figure 6

In a clay-filled fissure of the dolomite rock beneath the Terra fusca, we investigated serrated structures partly showing areas that appear darker in the SEM. Figure 7 shows a calcite grain directly bordering the clay-filled fissure. The EDS-analyses show how the calcite at the edge starting to disintegrate contains already some silica and magnesium (point 1). Since magnesium might also be a component of the carbonate, one might argue for an analytical effect because of the beam size. This, however, does not fall below under 1.5 µm in diametre in this case, such that the analyzed microvolume is restricted to the calcitic part of the grain. Comparison with the elemental composition of the clayey crack fill with the clay in the fissure (point 2), in particular regarding the Al:Si ratios, shows a clear clay mineral signal with a strongly reduced calcium content.

Figure 7

The replacement of calcium and magnesium by clay seems further indicated by an EDS cross-section (line scan) through a dolomite grain about 50 µm deeper into the bedrock (fig. 8). A darker domain of the dolomite proves as clay, characterized by a significant decline of Ca and Mg, while Si, Al, and Fe increase. However, this clay seems not yet fully de-calcified, and appears merely like an amorphous gel. We have not been able to identify crystallinity, and the area is too small to be determined by optical analysis, which would misinterpret it as calcite.

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Figure 8

5.2 Bulk soil analysis

Results of both profiles are summarized in table 1. It can be observed that the Terra rossa red crack filling samples of the Fricke profile [samples Tu(1) and Tu(2)] are more or less identical, confirming the field impression that no horizons or deposition patterns are present in the cracks. However, the fills are distinct from the Terrae fuscae: apart from the red color, values of dithionite soluble iron are elevated. As well, values of oxalate-soluble silicium are elevated, pointing to a higher content of amorphous silica than in the Terrae fuscae.

The Terra rossa crack fillings are characterized by higher clay contents than the Terrae fuscae, but also by a higher sand content than the bedrock residue. The latter could to some degree be connected with the acid treatment to dissolve the rock. The crack infillings received no acid pre-treatment before grain size analysis due to low $CaCO_3$-contents, and since acid-pretreatment also removes calcite sand grains (Lucke and Schmidt, 2015), sand contents of crack infillings and bedrock residue are not directly comparable. Calcite sand grains in the Terra rossa-filled cracks might represent micro-"floaters" as suggested by Meert et al. (2009) regarding limestone blocks of larger scale "floating" in the Bloomington Terra Rossa in Indiana. However, the majority of sand grains in the crack fillings consist largely of rounded quartz grains of the finer sand fractions (6% coarse sand, 47% middle sand, 47% fine sand), with some equally rounded black grains that might reflect a primary detrital input. While some quartz grains of the coarse-sand fraction show densely set small V-shaped marks typical for aeolian transport during loess deposition (fig. 9), there are also grains being completely covered by clay minerals that are unsuitable for a grain surface characterization (fig. 10).

Figure 9

Figure 10

This suggests that allochthonous material, including grains transported with the overlying loess, was involved in the formation of the crack fills. The very similar sand contents in the two samples of crack fillings point to a very homogeneous distribution of sand within the cracks, which is in agreement with the field impression and other results of bulk soil analysis. The strongly elevated sand contents compared to the bedrock residue argue against inheritance from rock dissolution, and the absence of fluvial sorting and very homogeneous distribution of sand grains in the clay argue against fluvial deposition of the crack fills.

Although the crack fillings were affected by loess deposition on the surface, lab results support the field impression that two different soil formation processes took place. Very similar Ti/Zr values of the lower Terra fusca at the profile Fricke [sample II TCv] and the Terra rossa red clay crack fillings let a common parent material seem

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possible, which is different from the limestone residue. Although it cannot be ruled out that clay-rich beds - now removed due to weathering - provided residue contributing to soil formation, the analyzed rock sample suggests that neither the buried Terra fusca nor the Terra rossa crack fillings originated from the residue of the now adjacent limestone.

Table 1

The limestone and dolomitic limestone proved to be very pure with acid-soluble fractions of 98.1% and 99.99%. Their residue is extremely clay-rich compared to the crack fillings and the II TCv sample of the Terra fusca of the Schwaighauser Forst profile. As well, Ti/Zr ratios are different between rocks and soils, although there are gradients visible in the profiles. These supports the field impression that loess was deposited on the surface and mixed with pre-existing Terrae calcis, leading to a gradual lowering of the Ti/Zr ratio towards the tops of the profiles. Even though there was no loess addition apparent in the Schwaighauser Forst profile, particle sizes clearly support that silty material was mixed into the soil. This is further stressed by the absolute content of dithionite-soluble iron, indicating that less weathered material was deposited on top of the profiles. However, in contrast to the other parameters, Fe(d/t) ratios suggest that weathering intensity remained nearly constant through the profiles. This is not an uncommon phenomenon: Günster (1999) and Lucke (2008) encountered similar Fe(d/t) values in Terrae calcis of southern Spain and northern Jordan, which did not match other indicators of pedogenesis intensity. It could be

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explained assuming that some of the dithionite-extractable iron in well-developed Terrae calcis might not result from oxidation of Fe^{2+} during weathering, but represents pre-weathered Fe^{3+}-rich phyllosilicates released from the rock residue – or enters the system from outside as Fe^{3+}. The latter might be happening when mineral neoformation due to isovolumetric replacement, illuviation of amorphous clay, or dust deposition contribute to soil formation.

The contents of organic matter and calcium carbonate are mostly low throughout the profiles. The Terrae fuscae seem to contain more organic material than the Terra rossa of the crack fillings, which matches expectations. However, in the profile Fricke only the Ah-horizon contains a relatively high amount of organic matter, while the lower horizons have only little more than the crack fillings. On the one hand, it is surprising that the crack fillings do contain organic matter at all, since they seemed disconnected from the present surface. On the other hand, roots occur in limestone fissures even in great depth, so that the organic matter present in the limestone cracks most likely represents roots.

pH values are mostly neutral – only in the upper part of the Fricke profile values between 4.5 – 5.5 can be observed, but this matches the high amount of organic matter and the field impression that the parent material of this part of the profile is mainly decalcified loess. There is no difference of the pH values of the red clay infillings of the limestone cracks and the Terra fusca of Schwaighauser Forst. In this context, the bedrock residue of both profiles is not red, but brown and greyish brown. Therefore it seems unlikely that the color was inherited from the bedrock residue.

Last but not least, calcium carbonate values are low throughout all profiles, except in the TCv horizon of the Terra fusca developed on dolomitic limestone in the Schwaighauser Forst profile. Apparently the dolomite has not completely been weathered, and thin sections showed that calcium carbonate re-precipitated in the soil matrix.

6. Discussion

6.1 Parent materials

It is evident that the investigated Terrae fuscae and Terra rossa crack fillings cannot represent only bedrock residue. This is indicated by the differences of color and particle size between the soils and bedrock residues. In addition, grains of the sand fraction of the crack fills confirm that there has been a deposition of material from the covering loess into the fills. Moreover, at the microscale it seems possible that metasomatic processes took or take place in the direct rock-soil transition zones of all investigated profiles, leading to replacement of bedrock with clay in the approximately outer 50 µm of the bedrock. In this context, clay neoformation seems a gradual replacement process: the SEM observations point to a gradual exchange of Ca and Mg against Si, Al, and Fe. Newly formed (authigenic) clay appears as gel-like material, distributed along calcite as well as dolomite grain boundaries, or in patches and small domains within and around decaying carbonate rock and its incorporated

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microfossils. No crystallinity can be identified. Often, the contact between calcite/dolomite and clay is present as an irregularly prograding, indenting front, which is important to note as it constrains a simultaneous transformation from one mineral to the other.

6.2 Amorphous (metasomatic?) clays

All clays occurring in microfossils and minerals are connected to grain boundaries, fissures, and pores occurring within the soil-rock transition zone, while the unaltered rock in areas remote from fissures lacks those observations. Thus underlines a correlation between the replacement process and the movement of solutions in the rock. There are no deposition structures such as oriented crystalline clay layers that could be connected with illuviation. However, it cannot be ruled out that amorphous clay is transported into the transition zones. If amorphous phyllosilicates are transported by percolating waters as proposed by Frolking et al. (1983), they are apparently not accumulating in voids, but adhere to calcite and dolomite grain surfaces. Most of the observed phyllosilicates contain iron, implying that it has either been transported as coating of amorphous clay minerals, or as ions. At few locations secondary $CaCO_3$ needles precipitated near fissures, suggesting at least temporary presence of solutes in the pore water. There is no discernible microstructural difference between Terra fusca and Terra rossa in the scanning electron microscope images.

6.3 Bulk soil analysis

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Bulk soil analyses let it seem possible that replacement and/or transport of amorphous clays contributed more to the genesis of Terra rossa in the crack fillings since the contents of oxalate-soluble silica are higher in the Terra rossa. However, there is no reason to assume that higher contents of organic matter in Terrae fuscae prevent or strongly limit processes of metasomatism and/or transport of amorphous clays. This argues against Blanck's (1915) suggestion that topsoil organic matter contents play a role in Terrae calcis genesis. In this context, the very similar pH values of the Terra rossa crack infillings and the Terrae fuscae suggests that the pH value does not play a major role for the development of red or brown color – at least if assuming that the actual pH is relevant for amorphous clays and the formation of replacement features. Similarly, it does not seem probable that organic matter contents affect the color of Terrae calcis since the differences between Terra rossa and Terra fusca are not very pronounced, at least in the Fricke profile.

The Terra rossa and Terrae fuscae are characterized by similar particle sizes. At both sites the particle sizes indicate deposition of loess in the upper part of the profiles. Since the bedrock residue is at both profiles characterized by much finer particle sizes, it seems unlikely that the residue of bedrock dissolution contributed a major part of the solum. This is further supported by the Ti/Zr ratios, which are different between the rock and overlying soil. They indicate that loess did not provide the main parent material of Terrae calcis genesis, but altered soil properties during deposition on pre-existing soils. There is a strong similarity between the Terra rossa crack fillings and lower part of the Terra fusca in the Fricke profile, which lets it seem possible that similar parent material was involved in formation of these soils. Whether this was

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aeolian dust cannot be deducted from the available data: the Ti/Zr ratios support the impression of loess deposition and mixing only into the upper part of the profiles, but do not deliver insights into possible aeolian parent materials of earlier pedogenesis. Here the dominant finer sand fractions in the Terra rossa crack fillings, as well as the absence of horizons or depositional structures connected with fluvial sediments, support that an early phase of aeolian sedimentation might have been connected with formation of the red fills. These aerosols could have delivered elements driving replacement reactions as well. The very homogeneous distribution of sand grains in the clay of the crack fill speaks against fluvial sorting patterns. The most likely explanation how sand grains entered the cracks seem root channels and shrink-swell cracks in the clay, while the dominance of the finer sand fractions indicates an aeolian source of the grains – possibly largely from loess deposition.

Similar to the sand, small aggregates consisting of silt and clay could have been transported into the limestone cracks by wind and bioturbation. Fedoroff and Courty (2013) suggested that wind-blown transport of clayey pseudosands from pre-existing red soils contributed to the genesis of many Terrae calcis, possibly following events of sudden and considerable pressure such as airbursts during cosmic impacts. Apart from the presented sand grains, we could not observe pseudosand structures in the clay matrix of the studied profile, but they could have been lost during shrink-swell processes. Such processes could also have blurred clay illuviation cutans in the solum (Fedoroff and Courty, 2013).

One major question is the iron dynamics of the studied soils. The absolute amounts of dithionite-soluble iron suggest that the Terra rossa crack infillings contain more pedogenic iron than the Terrae fuscae. This could indicate that iron dynamics are connected with organic matter contents as suggested by Blanck (1915), since higher contents of dithionite-soluble iron seem to correspond to lower values of organic matter. However, there is no correlation to the pH-value, and more important, no correspondence to the Fe(d/t) ratio. According to Cornell and Schwertmann (2003), this ratio can be interpreted as indicator of Fe^{2+} oxidation to Fe^{3+}, which is usually a marker of mineral weathering and pedogenesis. Since it remains more or less constant in nearly all investigated samples, this essentially contradicts the impression of stronger weathering given by the particle sizes in the lower part of the profiles. The Fe(d/t) ratio has been problematic in other studies of Terra calcis soil development. For example, Günster (1999) suggested that it should be modified by the clay content in order to achieve reasonable results not contradicting other indicators of soil development intensity, since he observed a strong correlation of Fe_d-contents with clay in southern Spain. In contrast, Lucke (2008) found that the contents of Fe_d in Terrae rossae of northern Jordan showed some correlation to contents of calcium carbonate, and suggested modifying the index with the calcium carbonate content.

At the studied profiles in Franconia, however, those two modifications are inapplicable since there is no apparent connection between the contents of iron, calcium carbonate, and particle sizes. Since limestone might contain threevalent iron from sediments, the problematic Fe(d/t) values could be explained by pre-weathered bedrock residue. However, in light of our microstructural and analytical results regarding clay neoformation, a different hypothesis is formulated here: that not only 'classical' pedogenesis is connected with the Fe(d/t) ratios in Terrae calcis. Instead, we regard it possible that the iron content is affected by neoformation of phyllosilicates involving the transport of external Fe^{3+} ions. If we assume that aluminium, which is hardly soluble at neutral pH values, can be transported into the rock-soil transition zone, it seems possible that iron can be transported too, possibly involving the same transport mechanism. In this context, iron transport by thermal waters due to volcanism seems possible in the geological context of the Schwaighauser Forst profile, although there is no direct evidence for that. However, the Fricke profile seems located rather far from zones of volcanic activity, and there are so far no clear indications of volcanic ash deposition.

It seems certain that metasomatism and/or illuviation of amorphous clays can contribute to Terra calcis genesis regardless of the climate or temperature. Further, it seems likely that the development of red color is connected with strong wetting and drying cycles as suggested by Cornell and Schwertmann (2003). Related to this, we think it possible that the Terra rossa of the limestone crack infillings of the Fricke profile was subject to stronger climatic switches than the upper part of the profile - or only the upper part was subject to xanthization.

6.4 Evidence from related studies

Küfmann (2008) observed that the thickness of Terrae calcis in the northern calcareous Alps was linearly correlated to the proportion of insoluble residue of

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limestone bedrock. However, her calculation of the possible contribution of bedrock residue (about 20%) and aeolian deposits (about 50%) during the Holocene could explain only about 70% of the present soil thickness. Longer time periods of soil formation do not seem probable since the Alps were glaciated during the Pleistocene. The missing part might be the contribution by isovolumetric replacement and/or illuviation of amorphous clays, which could also explain the positive correlation of soil depth with bedrock residue. Since the metasomatic model of Merino and Banerjee (2008) predicts that acids are produced during the replacement process, the non-soluble residue of the limestone rocks also contributes to soil development: more residue will be released in less pure limestones, leading to quicker build-up of the profile.

For now it has to be left open how the transport mechanism leading to superconcentration of ions in the rock pores can be explained, but we think that roots which are present in larger rock fissures and even in the deepest part of the studied clay-filled cracks seem the most probable transport agents. Verboom et al. (2009) found that roots of eucalypts colonizing sand dunes in Western Australia were capable of transporting Al, Fe, and Si, leading to the construction of clay pavements along the roots in a geochemically alien surrounding. The same elements were found in the amorphous clays of our studies, which indicates that these probably represent largely authigenic, newly formed clay minerals that stem from reactions triggered by plant roots.

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Our study suggests that bulk soil and rock analyses alone can deliver only limited insight into Terrae calcis development, at least at sites where clay neoformation contributes significantly to the genesis of these soils. It appears that bedrock weathering does not only proceed by chemical reaction processes which create voids in the rock due to dissolution, but that neoformation of new minerals and rock dissolution can be part of the same process. Unfortunately it was not yet possible to study the mineralogy of the crystalline clays. In the future, a better understanding of mineral crystallization out of the observed apparently amorphous clays could help to better explain the factors controlling Terrae calcis formation.

7. Conclusions

Our study found amorphous clays in the direct rock-soil transition zones of all studied profiles. Although it cannot be stated whether these are ongoing or relic features, it can be concluded that:

- Isovolumetric replacement of limestone due o metasomatism and/or illuviation of amorphous clays took or takes place in Terrae fuscae as well as Terrae rossae in Franconia.

- Current topsoil organic matter contents and soil color apparently do not matter for the occurrence of these features.

- Amorphous clays are observed only close to micropassages in the rock-soil transition zone, suggesting that rock pore solutions play a role for their occurrence. These clays do not fill voids, but are present only in contact with calcite structures.

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- There is a gradual transition between calcareous minerals and amorphous clay, and no sharp boundary as would be expected from dissolution and deposition processes.

- The presence of Fe suggests that replacing amorphous clays are either iron-coated during illuviation, or Fe-ions are transported in a similar way as Al and Si. Since the same elements can be found in clay pavements around Eucalyptus roots in Western Australia, this suggests that root activity might play a major role for the formation of amorphous clays.

- No crystalline illuvial clay could be observed in pores, but allochthonous sand was deposited into the limestone cracks during loess deposition by wind and bioturbation. It seems well possible that pseudosand clay aggregates contributed to the solum. These might explain a part of the substrate, but not the amorphous clays observed in the rock-soil transition zones.

- The investigated Terrae calcis represent true soils and not claystones, since they contain a significant share of allochthonous material and are subject to processes induced by plants – which, by definition, means that pedogenesis takes place.

We conclude that replacement processes can contribute to the genesis of Terrae calcis in Franconia. It is not yet possible to quantify their contribution, and the mechanisms of the process cannot yet fully be explained. However, further studies should consider the possible role of plants for authigenic clay neoformation in Terrae calcis genesis.

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Figure and table captions

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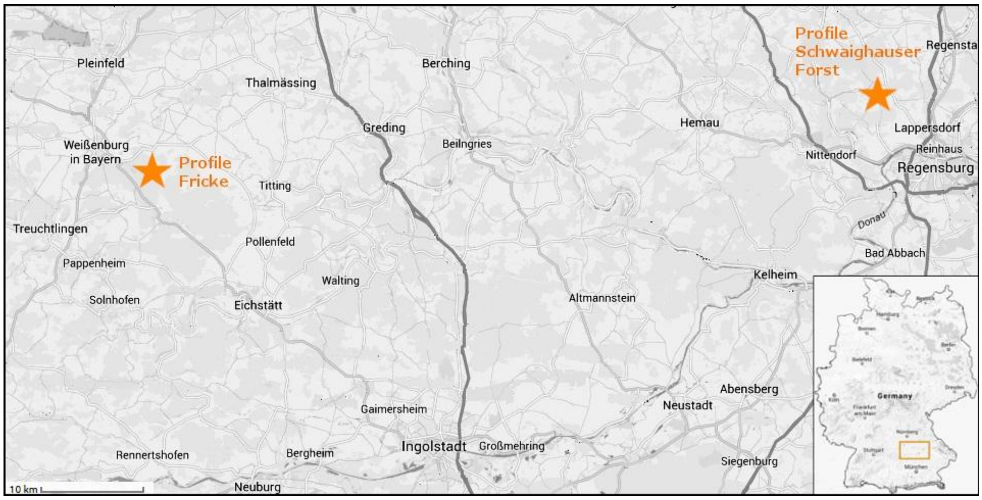

Figure 1: Map showing the location of the investigated profiles in Franconia, and the region inside Germany. Map based on www.openstreemaps.org (Open Database License, ©OpenStreetMap contributors).

Figure 2a: The profile "Fricke" sampled near Weißenburg i. Bayern. The left side shows the upper part of the profile, which connects to the lower part shown on the right side as indicated by the rectangle. Due to a step-wise exposition of rock cuts in

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the quarry, it was not possible to obtain a picture showing the whole profile. Sampling locations are marked by the horizon labels. Each mark on the meter tape represents 10 cm.

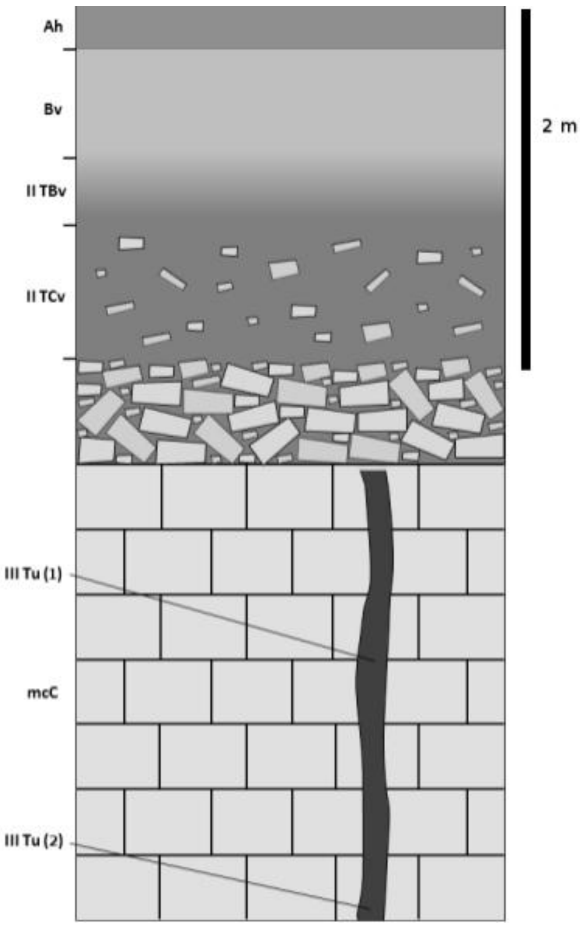

Figure 2b: Schematic drawing of the profile "Fricke" for a better illustration of soil horizons.

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Figure 2c: Close-up of crack infillings. The red clay is homogeneous throughout, there are no horizons, and no indicators of fluvial deposition could be observed. Transition to bedrock occurs in a zone of 'powdery' limestone of about 1 mm thickness as described earlier for other crack fills by Trappe (2011).

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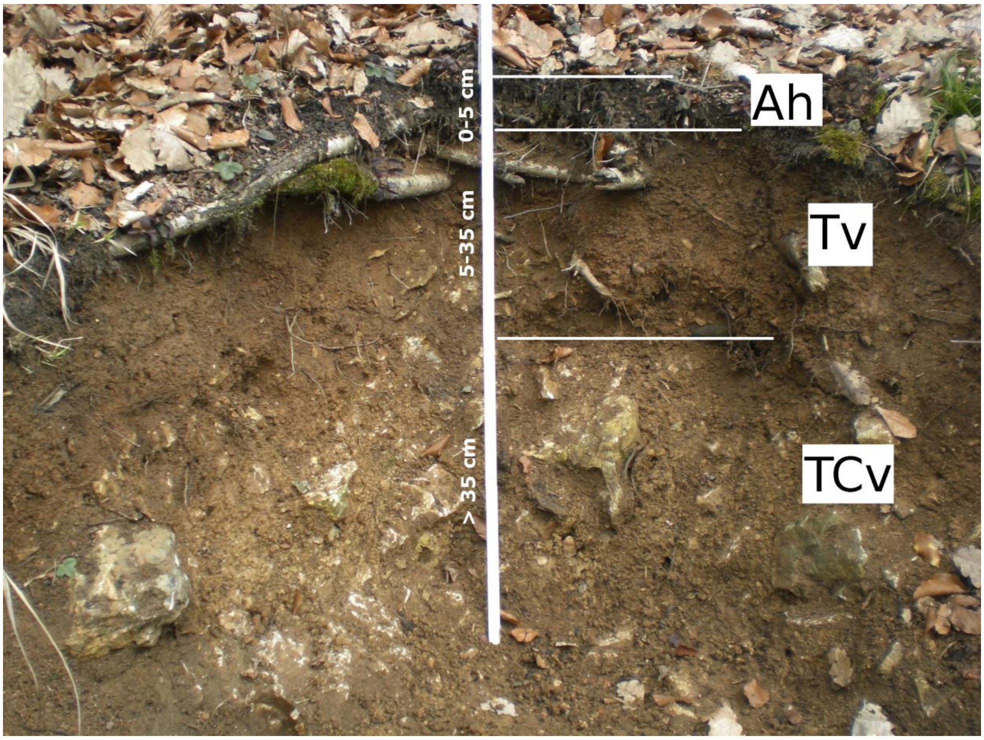

Figure 3a: The profile "Schwaighauser Forst" near Regensburg. Sampling locations are indicated by the horizon labels, and soil depths are marked along the white bar.

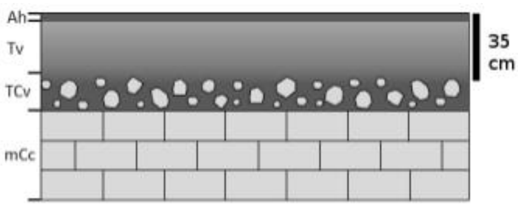

Figure 3b: Schematic drawing of the profile "Fricke" for a better illustration of soil horizons.

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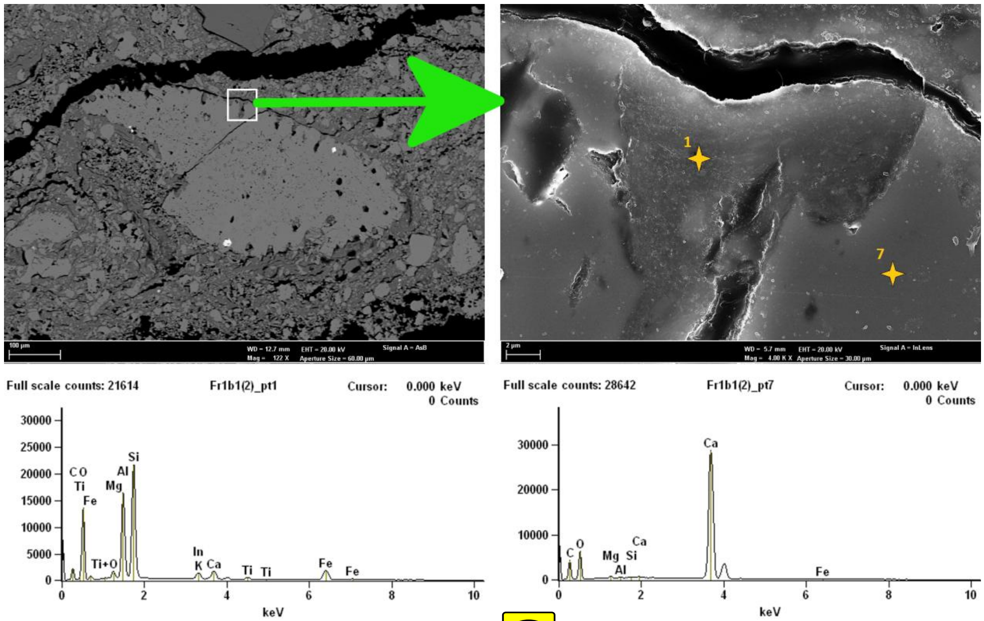

Figure 4: Calcite grain starting to be replaced by clay in the rock-soil transition zone of the Terra Rossa limestone crack fillings in the profile "Fricke". Right is an enlargement of the square marked on the left. The geochemical composition determined by EDS is shown at the bottom for point 1 (left) and point 7 (right), indicating that clay formation maintaining the original bedding structure took place in the darker area of the calcite grain.

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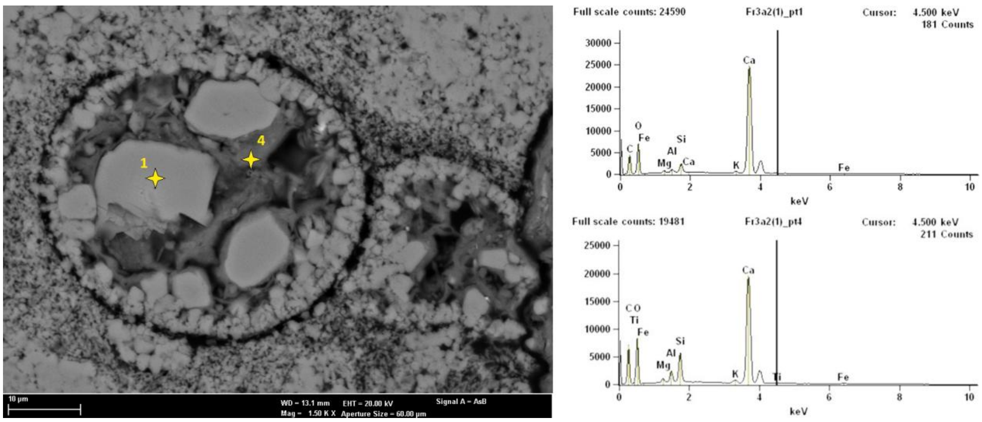

Figure 5: Round microfossil partially filled with amorphous clay in the rock-soil transition zone of the Terra Rossa limestone crack fillings in the profile "Fricke". The geochemical composition determined by EDS is shown to the right for point 1 (above) and point 4 (below), indicating that part of the inner microfossil consists of clay although there are no traces of crystalline allochthonous clay or cracks in the fossil's shell.

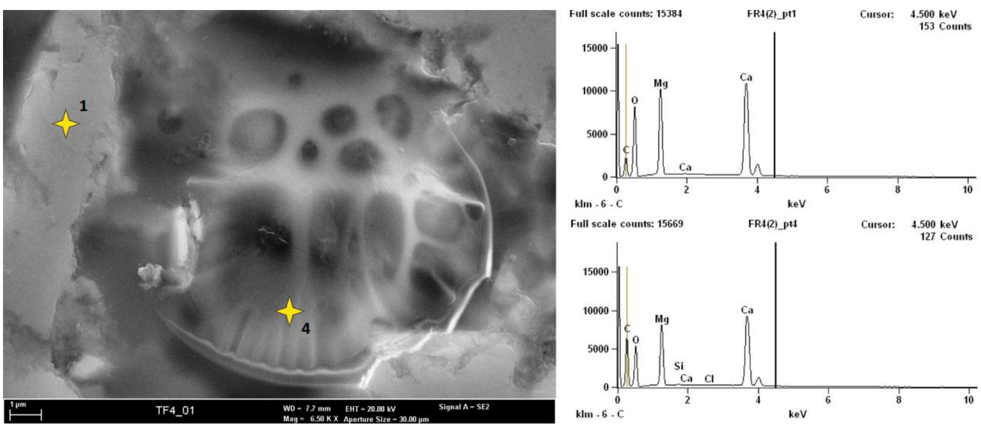

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Figure 6: Remains of a microfossil in the rock-soil transition zone of the dolomitic limestone of the "Schwaighauser Forst" profile. EDS-analyses demonstrate the high magnesium context of the rock (point 1, top right), but also show a slight increase of Si and decrease of Ca and Mg in the darker areas inside the microfossil, indicating a beginning of clay formation (point 4, bottom right).

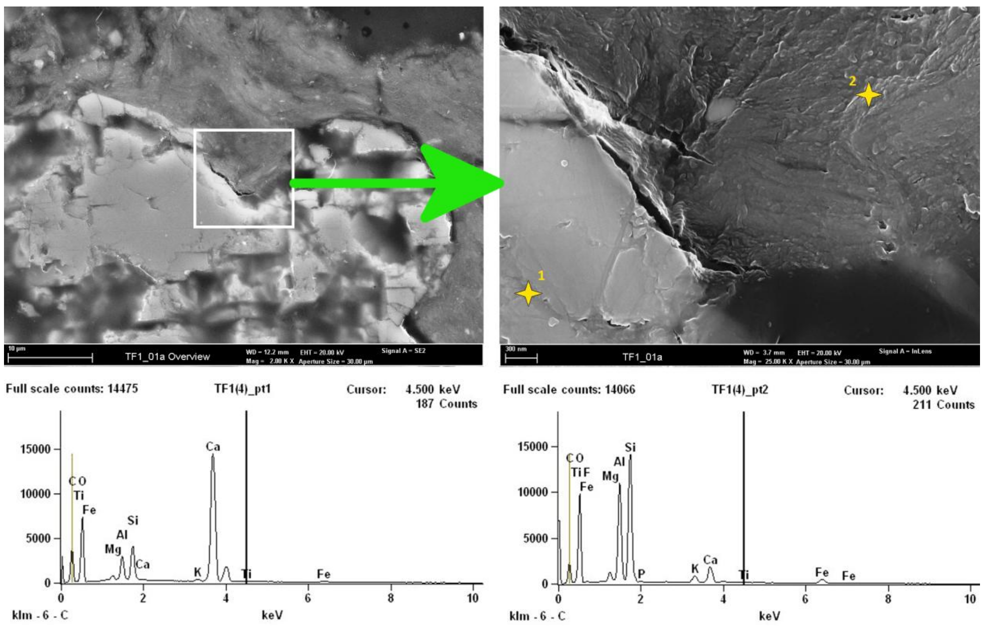

Figure 7: Calcite grain starting to be replaced by clay in the rock-soil transition zone of the Terra Fusca in the profile "Schwaighauser Forst". Right is an enlargement of the square marked on the left. The geochemical composition determined by EDS is shown at the bottom for point 1 (left) and point 2 (right), indicating that clay formation started inside small cracks of the calcite grain, although chemically still dominated by Ca (point 1). In contrast, the soil matrix in the larger fissure is characterized by a further increase of Si, Al, and Fe, while Ca was diminished (point 2).

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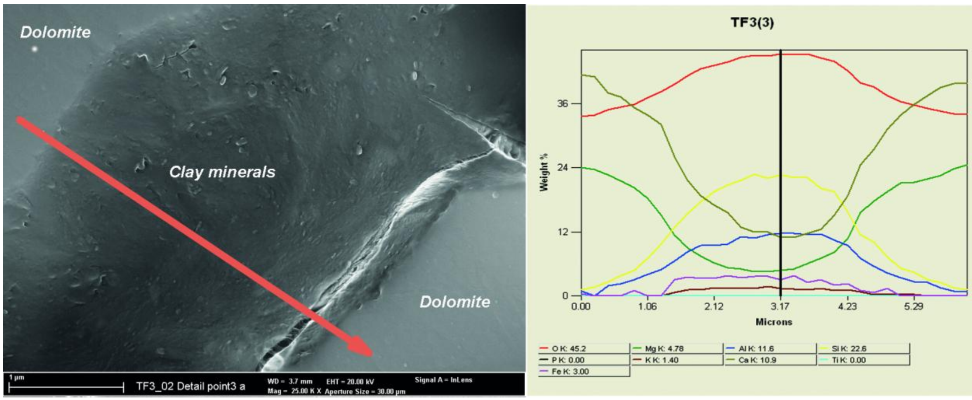

Figure 8: SEM cross-section using EDS to determine element composition along a section of a dolomite grain in the rock-soil transition zone of the Terra fusca in the profile "Schwaighauser Forst". The graph to the right shows the weight % of the studied elements along the section marked by the arrow to the left. As can be seen, there is a gradual increase of Si, Al, and Fe towards the darker area of the dolomite grain, while Ca and Mg are reduced, pointing to gradual isovolumetric replacement of the dolomite by clay minerals.

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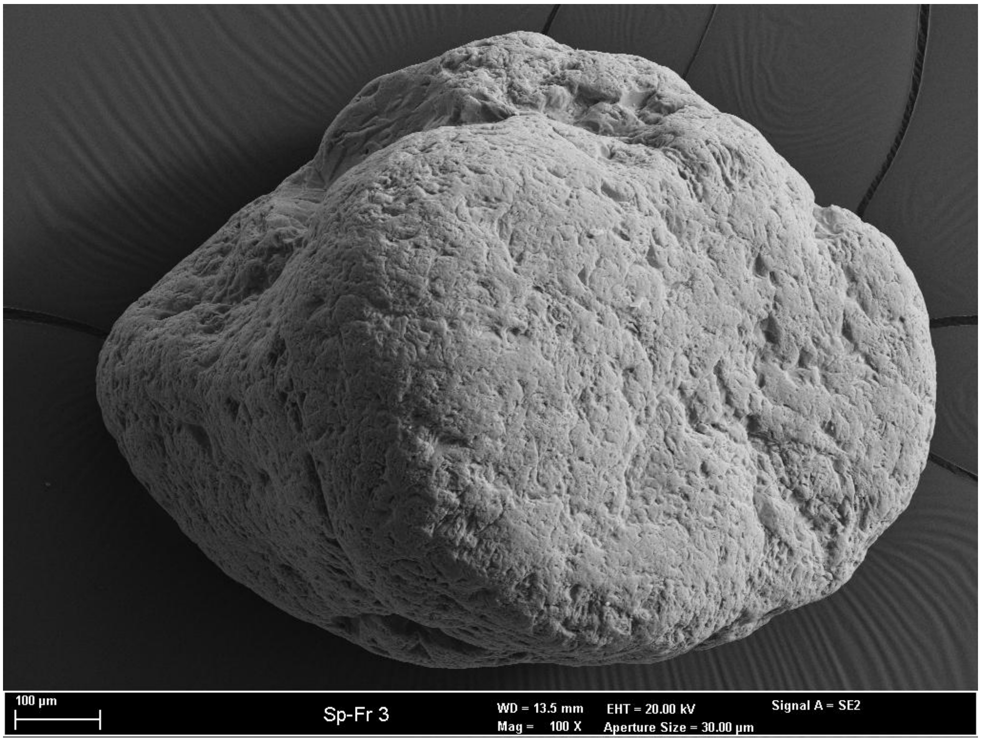

Figure 9: Quartz grain of the coarse sand fraction of the red fill in the limestone crack of the Fricke profile. Note the densely set small V-shaped marks typical for aeolian transport during loess deposition.

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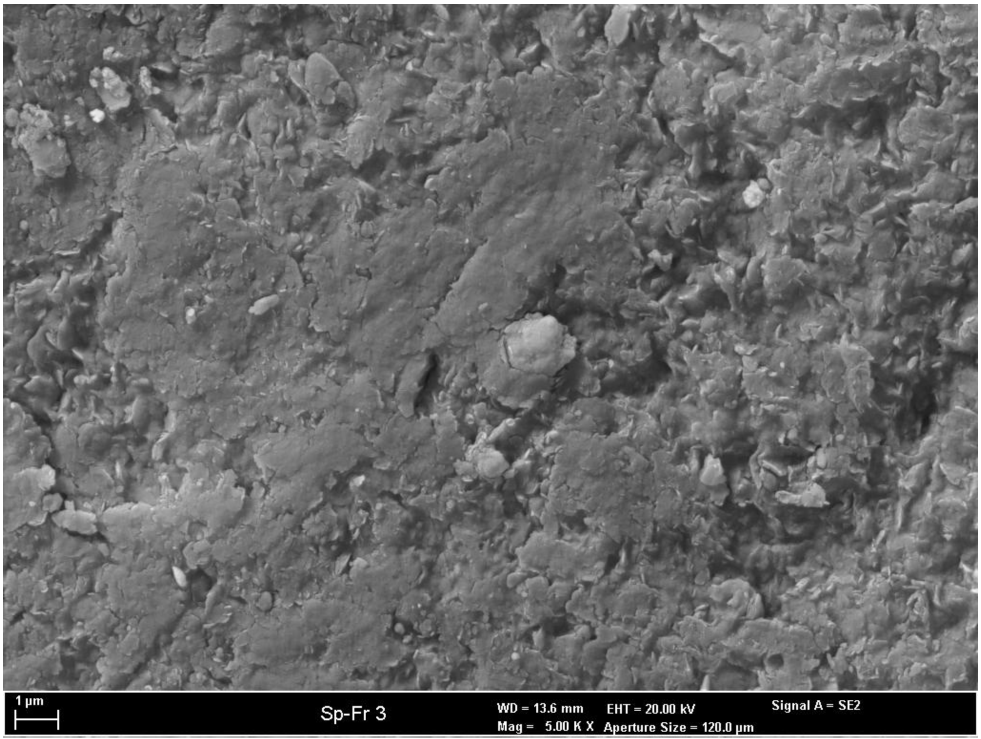

Figure 10: Grain from the fine sand fraction of the red fill in the limestone crack of the Fricke profile. It is completely covered by clay, possibly representing a pseudosand aggregate largely consisting of clay (and silt).

Table 1: Results of bulk soil analyses of the profiles "Fricke" and "Schwaighauser Forst". The Fe (d/t) ratio describes the ratio of dithionite-soluble iron (Fe_d) to total iron contents. Increasing redness is reflected by smaller values in the index according to Hurst (1977). The dolomite content of the bedrock at the Schwaighauser Forst profile was calculated according to the residue mass after the rock's dissolution with HCl.

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Sampling depth [cm]	Sample	Munsell dry	RR after Hurst (dry)	Oxalat-soluble silicium [mg/g]	Dithionit-soluble iron [mg/g]	C_{org} %	pH	$CaCO_3$ %	Clay %	Silt %	Sand %	Fe(d/t)	Ti/Zr
Profile FRICKE													
0-25	**Ah**	10 YR 6/3	40	0.01	11.5	3.08	4.5	2.1	27	69	4	0.49	9
25-90	**Bv**	10 YR 6/4	30	0.14	17.5	0.28	4.7	1.5	36	61	3	0.47	11
90-125	**II TBv**	10 YR 6/4	30	0.03	19.1	0.32	5.5	0.5	45	52	3	0.43	12
125-200	**II TCv**	10 YR 6/4	30	0.07	26.6	0.35	6.7	0.6	59	38	3	0.54	15
370	**III Tu (1)**	5 YR 4/4	15	0.77	33.6	0.13	7.7	2.1	65	22	13	0.5	18
520	**III Tu (2)**	5 YR 4/4	15	0.75	33.0	0.12	7.6	1.6	66	21	13	0.49	15
500	**mcC**	10 YR 5/3	33	-	-	-	-	98.1	75	24	1	-	20
Profile SCHWAIGHAUSER FORST													
0-5	**Ah**	10 YR 6/3	40	0.02	10.1	3.80	6.5	4.6	39	39	22	0.38	11
5-35	**Tv**	10 YR 6/4	30	0.04	14.3	1.10	7.6	3.2	57	28	15	0.43	13
>35	**TCv**	10 YR 7/4	35	0.06	9.9	1.40	7.6	35.2	67	23	10	0.49	21
>50	**mcC**	10 YR 4/2	40	-	-	-	-	(99.99)	86	13	1	-	11

Table 1: Results of bulk soil analyses of the profiles "Fricke" and "Schwaighauser Forst". The Fe(d/t) ratio describes the ratio of dithionite-soluble iron (Fe_d) to total iron contents. Increasing redness is reflected by smaller values in the index according to Hurst (1977). The dolomite content of the bedrock at the Schwaighauser Forst profile was calculated according to the residue mass after the rock's dissolution with HCl.