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Quantitative clay mineralogy of a Vertic Planosol in southwestern Ethiopia: (DCrossMark Impact on soil formation hypotheses

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ABSTRACT

Planosols, characterised by a bleached, silt-textured surface horizon abruptly overlying a dense, clayey subsoil, are a very common soil type in Ethiopia. The origin of the abrupt textural change is still often debated in literature. One of the processes frequently put forward to explain the coarse textured material in the topsoil is 'ferrolysis': an oxidation–reduction sequence driven by bacterial decomposition of soil organic matter, resulting in the destruction of open 2:1 clay minerals. Recent studies of representative profiles of Vertic Planosols in south-western Ethiopia indicate that these soils are composed of a weathered volcanic ash layer deposited on top of a deflated vertic subsoil, which refutes the ferrolysis hypothesis. To strengthen the geogenetic origin of these profiles, a quantitative mineralogical analysis of the clay fraction was undertaken.

Results of a sequential fractionation revealed a strong aggregation of clay particles in the bleached horizon, while the effect of aggregation was far more limited in the vertic horizon. This is believed to be related to the dispersed, impregnative nature of iron oxides in the bleached horizon, compared to the segregated nature of the sharp, nodular concretions found in the vertic horizon. The annealing XRD analysis revealed only minor changes in dehydroxylation temperatures of kaolinites and 2:1 minerals between untreated and DCB-treated samples, indicating that the pretreatment did not significantly alter the mineral lattices. Multi-specimen, full-profile fitting of XRD patterns revealed no large quantitative differences between sub-fractions of the bleached and vertic horizons, although a net increase of 1:1 layers over 2:1 layers towards the top of the profile can be observed in the bleached horizon. This could be interpreted as the result of neo-formation of kaolinite. The main mineralogical differences between the bleached and vertic horizons of the $< 2 \mu m$ fraction are mainly a result of the different proportions of sub-fractions. Interestingly, the $< 0.05 \mu m$ fraction seems to be dominated by a complex assemblage of kaolinite and smectite mixed-layer minerals. The obtained detailed view on the mineralogical composition of the clay fraction of a typical Vertic Planosol has provided new insights in the complex nature of these duplex soils, confirming ferrolysis not to be at the origin of the abrupt textural change.

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1. Introduction

Phyllosilicates are considered among the most interesting mineral phases in soils to understand and study, for a multitude of reasons (e.g. their (trans)formation(s), reactivity, abundance, properties, and function) (Hubert et al., 2012; Lado and Ben-Hur, 2004; Velde and Meunier, 2008). Phyllosilicates are also omnipresent in the clay fraction, which controls the physical and chemical properties of soils to a large extent (Agbenin and Tiessen, 1995; Boivin et al., 2004; Caner et al., 2010; Lado and Ben-Hur, 2004; Molina Ballesteros and Cantano Martin, 2002; Righi et al., 1999). Therefore, accurate, quantitative mineralogical

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analysis of phyllosilicates is very useful when trying to understand soil formation processes.

Because of their inherently small size, X-ray diffraction still is the primary tool for analysing phyllosilicates. However, quantifying them accurately is a difficult task as clay mineral assemblages, especially in soils, are often complex mixtures of several species, each having their own variability in terms of crystal size, morphologies and composition, and all too often, mixed-layer clay minerals are present as well (Caner et al., 2010; Righi et al., 1999). Therefore, in routine analysis, at best a qualitative interpretation can be made, and only the more crystalline, well-ordered clay phases present in soils are positively identified, while mixed-layer minerals are not detected that easily. This has mistakenly led to the conclusion that mixed-layer minerals are not that common in soils. However, recent studies applying a quantitative approach to analyse X-ray diffraction profiles for clay fractions in soils (Caner et al., 2010; Hubert et al., 2009, 2012; Righi et al., 1999) have





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proven that mixed-layer minerals are much more common in soils than originally thought.

The Vertic Planosols in south-western Ethiopia are characterised by a bleached surface horizon with a stagnic colour pattern and periodic water stagnation abruptly overlying a dense, slowly permeable, heavy clay subsoil, and are in that sense typical examples for the Reference Soil Group of Planosols in World Reference Base (Driessen et al., 2001; Van Ranst et al., 2011). The origin of the abrupt textural change is still often debated in literature. Previously a process called 'ferrolysis' – an oxidation–reduction sequence driven by chemical energy derived from bacterial decomposition of soil organic matter able to destroy the lattices of open 2:1 clay minerals (Brinkman, 1970) – was held responsible for the formation of these soils.

However, a more recent study has proved that these Vertic Planosols are more likely formed by the deposition of a (reworked) ash layer on top of a deflated Vertisol, which refutes the ferrolysis hypothesis (Van Ranst et al., 2011). The study of Van Ranst et al. (2011) focused primarily on chemical, physical and (micro-) morphological analysis and a qualitative mineralogical study using X-ray diffraction and optical microscopy. They concluded that the silt and sand fractions of the Vertic Planosol contain a large amount of amorphous material - identified as being a mixture of volcanic glass and silt-sized phytoliths - as well as quartz, feldspars and iron oxides. No significant differences in relative composition were observed when comparing sand and silt fractions of vertic and bleached horizons. On the other hand the clay fraction exhibits a striking difference in mineralogical composition: the bleached horizon dominated by kaolinite and illite, while the vertic horizon contains significantly more smectite, with lower amounts of kaolinite and illite compared to the bleached horizon.

The observed difference in mineralogy is one of the reasons why the ferrolysis process was originally put forward as a 'probable explanation' for the formation of this soil. However, since the observations are still qualitative in nature, a quantitative mineralogical analysis of the phyllosilicates in the clay fraction was undertaken to further test the proposed geogenetic origin of these soils. Additionally, Cornelis et al. (2014) proposed that under the current pedological conditions the sources and sinks of silica in the Vertic Planosol of southwestern Ethiopia are partially controlled by neoformation of kaolinite. More detailed mineralogical insights may help to confirm this. Furthermore, this work has tested whether the routinely made dithionite–citrate–bicarbonate (DCB) and H_2O_2 pretreatments have any detrimental mineralogical effect.

2. Material and methods

2.1. Environmental setting

The Gilgel-Gibe catchment in southwestern Ethiopia covers an area of about 5500 km² and is located in the Oromiya region, Jimma zone about 260 km from Addis Ababa (latitude 7°22′72″–7°34′84″ N; longitude 37°21′05″–37°28′80″ E). The mountainous study area is characterised by steeply incising, V-shaped river valleys in the catchment flanks and fairly flat plains at the centre of the catchment and wider river valleys. The Borè site is located in the middle of this plain some 200 m from the Gibe river, some 30 m above its present alluvial plain. The mean annual rainfall and temperature are 2097 mm and 17.2 °C, respectively. The rainfall is mainly distributed between May and September.

The study area is situated on the Ethiopian plateau (1096 to 3259 m a.s.l.), south-west of the rift valley. The outcropping geology of the catchment is dominated by Eocene, Paleocene and possibly Holocene magmatic materials (a.o. basalts, trachytes, rhyolites, tuffs, ignimbrites and ash deposits) and is inherently complex (Tadesse et al., 2003). Lower landscape positions are filled with alluvium and lacustrine sediments.

2.2. Materials

The sampling site, located in the Borè valley, was carefully selected based on a terrain study using aerial photographs and on-site observations. In general, the Vertic Planosols in the catchment have an abrupt textural change at about 40 cm depth separating the bleached, silty topsoil from a buried, heavy clay Stagnic Vertisol, which exhibits gilgai and well developed slickensides. In this vertic material, wide cracks often form during the dry season in which bleached, topsoil material fall. Bulk samples were taken at fixed depth intervals (of every 5 cm down into the vertic material up to 75 cm below the soil surface, while taking care to sample just above and below the textural break). For a complete description of the soil profile, reference is made to Van Ranst et al. (2011). A subset of 5 samples at depth intervals of 10–15 cm, 20–25 cm, 30–35 cm, 40–45 cm and 70–75 cm was selected for this study.

2.3. Laboratory procedures

Soil textural analysis was done on the fine-earth fraction (<2 mm) of samples after removal of organic matter with H₂O₂. The sand fraction (2000–63 µm) was separated from the silt and clay fraction by wet sieving, and the silt fraction (63–2 µm) was separated from the clay fraction (<2 µm) by successive sedimentation using repeated syphoning of supernatant clay suspensions after dispersion of clay using Na₂CO₃. NaCl was used as the flocculating agent. The recovered clay fraction was thoroughly washed to remove excess Cl⁻ (until testing negative with AgNO₃), while centrifuging at 3500 rpm after each step.

To better characterise the mineralogical composition of the clay fraction, an additional sequential fractionation was done on the <2 μ m fraction in order to obtain four sub-fractions (2–0.2 μ m, 0.2–0.1 μ m, 0.1–0.05 μ m and <0.05 μ m) according to the centrifugation method as described in Laird et al. (1991). This was performed on 1 g of the total <2 μ m fraction without further pretreatment and on 1 g after treating with 5% H₂O₂ at 40 °C and DCB (Dahlgren, 1994) in order to remove any remaining organic carbon and iron oxides respectively.

To obtain compositional limits (e.g. structural iron), the DCBextractable amounts of Fe, Al, Si and Mn were measured using atomic absorption spectroscopy (AAS), the total elemental composition of the untreated clay fraction (<2 μ m) was determined after fusion with Li₂CO₃ and H₃BO₃ at 1000 °C and dissolution in HNO₃-, and loss of ignition (LOI) was determined as the weight loss after ignition at 850 °C for half an hour. Concentrations were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

After sequential fractionation, the total <2 μ m fraction and the four sub-fractions for both the untreated and pretreated samples were saturated with Ca²⁺. Excess electrolytes were removed by washing twice with deionized water and centrifugation after which they were transferred to a dialysis tube and placed in a beaker with distilled water. Dialysis was continued until no more Cl⁻ could be detected using AgNO₃, after which the samples were transferred to a beaker and dried.

Oriented samples of all fractions were prepared by transferring a suspension using a pipette on glass slides. The suspension was prepared as such that the surface density of the sample on the glass slide is at least 10 mg/cm³. For each slide an X-ray diffraction pattern is recorded in air-dried and glycolated state on a Philips X'PERT SYSTEM with a PW 3710 based diffractometer equipped with a Cu tube anode, a secondary graphite beam monochromator and a proportional xenon filled detector. The incident beam was automatically collimated. The secondary beam side comprised a 0.1 mm receiving slit, a soller slit, and a 1° anti-scatter slit. The tube was operated at 40 kV and 30 mA, and the XRD data were collected in a θ , 2 θ geometry from 3.00' onwards, at a step of 0.020°2 θ , and a count time of 10 s per step.

In addition to regular X-ray diffraction, an annealing process was performed on oriented samples prepared in a similar way as described Download English Version:

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