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Nature and formation of interlayer fillings in clay minerals in Albeluvisols from the Carpathian Foothills, Poland

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ABSTRACT

The occurrence of interlayer fillings in clay minerals in the slightly acidic soils of humid temperate zone is a very common and characteristic feature. According to the research literature, the interlayer fillings may be composed of mineral and/or organic materials. The formation of mineral-interlayered clay minerals in soils is related to weathering, which leads to the liberation of cations from the crystalline structure of soil minerals and their subsequent sorption and fixation as a hydroxyl sheet within interlayer spaces of swelling clay minerals, or it may be due to the weathering of chlorite and partial removal of the hydroxyl sheet from interlayer spaces. The formation of organic interlayering within clays is related to interactions between organic and mineral colloids occurring in soil environment. The main aim of the present study was to determine the nature and formation of the interlayer fillings in clay minerals in four Albeluvisols from the Carpathian Foothills in southern Poland showing the occurrence of a fragipan and various degrees of bleaching due to periodic stagnation of water as well as ongoing land use (i.e. forest soils vs. arable soils). This was done using research results obtained from X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR and FTIR-ATR), and chemical analysis. The obtained results show that Albeluvisols from the Carpathian Foothills in Poland are characterized by the occurrence of clay minerals with interlayer fillings, which are the most developed in the upper soil horizons (A, AE, and E). The nature of interlayer fillings in clay minerals in the Albeluvisols studied is mainly organic; however, an additional presence of very small amounts of metal-hydroxy polymers in the interlayer space of clays cannot be completely excluded. Clay minerals with interlayer organic fillings found in the upper soil horizons are formed from swelling clays (smectite and vermiculite) due to the accumulation of organic matter in the interlayers during pedogenesis. The same pattern of clay mineral transformation (i.e. swelling clays into interlayered clays) is observed in Albeluvisols showing strong bleaching and slight bleaching and subject to different forms of land use (i.e. forest soils vs. arable soils). Most likely, this is related to quite similar physical and chemical properties of the soils as well as similar environmental conditions (except of ongoing land use). Quantity of organic matter does not play a crucial role in the formation of organic interlayered clays in soil environment. The most important is low pH (below 5.5) of soil solution and the presence of expandable clay minerals in soil material.

1. Introduction

The occurrence of interlayer fillings in clay minerals in the slightly acidic soils of the humid temperate zone is a very common feature and has been extensively studied by many soil mineralogists (e.g. Bain and Fraser, 1994; Harris et al., 1987, 1988; Nakao et al., 2009; Skiba et al., 2011; Tolpeshta et al., 2010). According to the research literature, the interlayer fillings may be composed of metal-hydroxy (e.g. Barnhisel and Bertsch, 1989; Sawhney, 1960) and/or organic materials (e.g. Bain and Fraser, 1994; Drewnik et al., 2014; Righi et al., 1995; Skiba et al., 2011; Theng et al., 1986; Yariv and Lapides, 2005). The formation of hydroxy-interlayered clay minerals in soils is related to weathering, which leads to the liberation of cations from the crystalline structure of soil minerals and their subsequent sorption and fixation as a hydroxyl sheet within interlayer spaces of swelling clay minerals (i.e. vermiculite, smectite) or due to the weathering of chlorite and partial removal of the hydroxyl sheet from interlayer spaces (e.g. Barnhisel and Bertsch, 1989; Meunier, 2007; Nakao et al., 2009; Tolpeshta et al., 2010). Harris et al. (1988) used chemical composition and morphology of mineral grains studied under a scanning electron microscope to show that hydroxy-interlayered vermiculite (HIV) found in Florida soils, was formed from mica. Weed and Nelson (1962), Harris et al. (1989), and Weed and Bowen (1990) had also suggested mica as a precursor of hydroxy-

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interlayered minerals (HIMs). According to the research literature, aluminum and iron are the most popular cations forming mineral interlayered sheets within interlayers of 2:1 clays (e.g. Nakao et al., 2009; Righi et al., 1993; Tolpeshta et al., 2010; Weed and Nelson, 1962). Rich (1968) stated that soils showing slightly acidic pH (4.5–6.0), low content of organic matter (below 4.0%), and frequent cycles of wetting and drying are the most favorable environments for the formation of hydroxy-interlayered clays. On the other hand, Malcolm et al. (1969) and Harris et al. (1987) showed that in very acidic soils containing high amounts of organic matter, HIMs are decomposed due to the removal of the metal-hydroxy sheet from interlayer spaces and are transformed into smectite and/or vermiculite.

The formation of interlayered fillings inside interlayer spaces strongly affects the properties of swelling clays, leading to a reduction in their cation exchange capacity, selectivity of cation fixation, thermal stability, mineral solubility, and swelling ability (Klages and White, 1957; Nakao et al., 2009; Rich, 1968; Weed and Nelson, 1962). In consequence, swelling clay minerals could be transformed into chlorite if the interlayered sheet is complete or hydroxy-interlayered minerals if the interlayered sheet is not fully developed (Barnhisel and Bertsch, 1989). According to the research literature, clays with mineral fillings in interlayers may form mainly in the upper part of the soil profile (A, AE, and E horizons) due to weathering near the soil surface (Bain and Fraser, 1994; Karathanasis, 1988; Klages and White, 1957; Sawhney, 1960; Tolpeshta et al., 2010; Weed and Bowen, 1990; Weed and Nelson, 1962). The relative enrichment of the hydroxy-interlayered clay minerals in surface horizons may be related to preferential eluviation of other clays (Kaplan et al., 1997; Seta and Karathanasis, 1996, 1997) and/or less source materials for formation of other clays due to leaching of weathering products (Harris et al., 1989). However, in some cases, such minerals may also occur in illuvial B horizons (Harris et al., 1987; Karathanasis, 1988; Malcolm et al., 1969; Nakao et al., 2009; Righi et al., 1993). The main diagnostic feature of hydroxy-interlayered minerals (HIMs) is a lack of full collapse after heating due to the blocking of interlayer spaces by interlayered polymers (so-called gibbsitic or brucitic "islands") (Barnhisel and Bertsch, 1989; Rich, 1968; Weed and Bowen, 1990). The swelling ability of HIMs is related to the quantity and degree of development of polymers. The degree of filling may be estimated based on the shift of the basal reflection (~14.0 Å) to the lower d-spacing (between 14.0 and 10.0 Å) after heating. In effect, the higher the shift of the basal reflection to 10 Å, the lower the quantity and/or lower thermal stability of the interlayer fillings (Barnhisel and Bertsch, 1989).

Interactions between organic matter and minerals in the soil environment are widely discussed (e.g. Chenu and Plante, 2006; Laird, 2001; Laird et al., 2001; Perez Rodriguez et al., 1977; Schmidt et al., 2000; Schulten et al., 1996). According to the above mentioned literature, organic matter may be adsorbed not only on the external surface of clay minerals, but also within their interlayer spaces. As Schmidt et al. (2000), Kaiser and Guggenberger (2003), and Chenu and Plante (2006) have shown, the occurrence of such clay–organic complexes in soils leads to the protection of organic matter against decomposition. Thus, the formation of organic–mineral complexes is a very important process in carbon and nitrogen sequestration in the context of global warming.

The main aim of the present study was to determine the nature and mode of formation of interlayer fillings in clay minerals in four Albeluvisols from the Carpathian Foothills in southern Poland showing the occurrence of a fragipan and various degrees of bleaching due to the periodic stagnation of water as well as various forms of land use (i.e. forest soils vs. arable soils). This was done using results obtained from X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR and FTIR-ATR), and chemical analysis.

2. Materials and methods

2.1. Study area

The present research was carried out in the Rożnów Foothills, which are the central part of the Carpathian Foothills in southern Poland. The study area is built of interstratified layers of sandstone, shale, and siltstone of turbiditic origin (so-called Carpathian flysch). Carpathian flysch is mantled by a thick loess cover, which does not contain carbonates and was deposited during the last phase of glaciation in the Pleistocene (Klimaszewski, 1967). The climate of the study area is moderately humid with the mean annual temperature between 6 and 8 °C and precipitation between 700 and 900 mm per year (Hess, 1965). In the past, the Carpathian Foothills were covered by deciduous forests

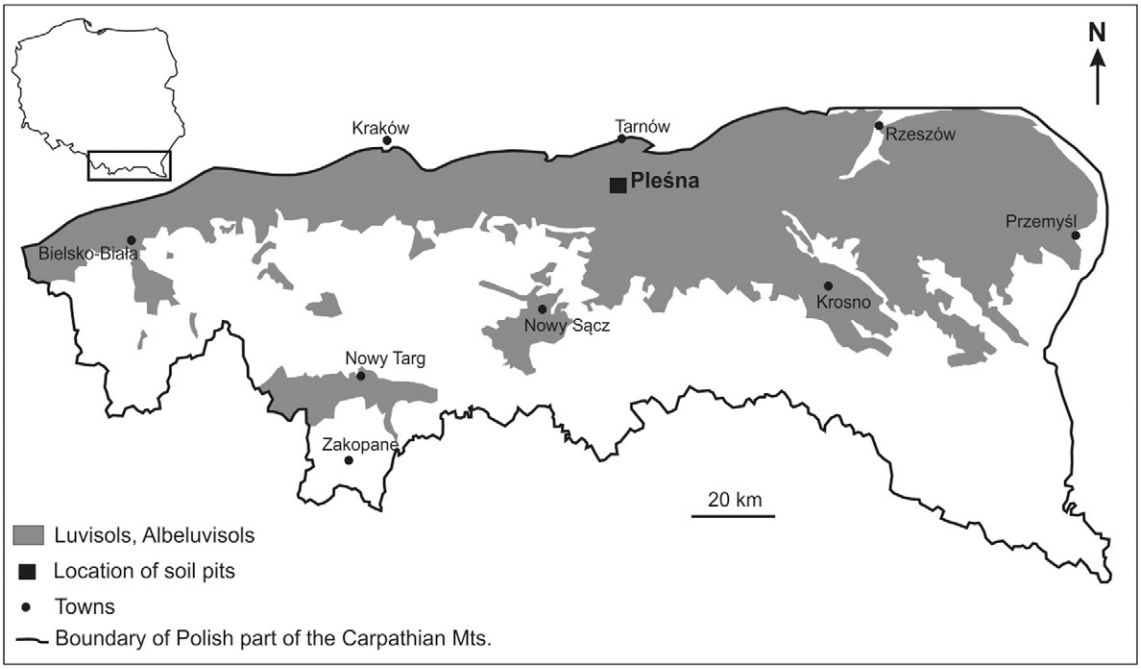

Fig. 1. Location of the studied soil profiles and occurrence of Luvisols and Albeluvisols (based on Skiba and Drewnik, 2003) in the Carpathian Foothills (Poland).