Origin, distribution and transformation of authigenic carbonates in loessic soils

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Abstract

Processes of authigenic carbonates formation are component part of terrestrial biogeochemical cycle of carbon, which starts with co-accumulation of oxalic acid and Ca in Ca- oxalates. After plant decay are these biominerals slowly transformed under the influence of microbial processes into authigenic carbonates (calcites), depending on soil condition. The formation of authigenic calcites runs over in soil system where is rather high Ca and Mg concentration, presence of oxalomorphic plants and sufficient oxalotrophic stability of microorganisms. In addition to Ca- oxalates, Ca and Mg ions necessary for carbonate formation comes also from air (precipitation, dust), mineral weathering, subsurface water flow and decaying organic matter. The distribution pattern of authigenic calcites with depth, the size and shape of individual forms of calcites on loessic soils of SW Slovakia, as it is resulted from micromorphological study indicate that through the historical development of that soils as landscape units, soil water regime has played decisive role at vertical redistribution of forms (size, shape) of authigenic calcites. To this witness the depth of variation of needle calcite zones and horizons of micritic calcites occurrence depending on soil types (leaching). Needle shape calcite zones which approach closest to the soil surface, gradually coalescence to the horizons of micritic calcites with the depth. Micritic calcites are without, or with microsparitic domains. Our study concurrently support the ideas of their inorganic origin depending on evaporitic soil regime. This formations have its own historic dynamics on which depends also the preservation of calcaric nature of soils.

Keywords: Authigenic carbonates, oxalate-carbonate pathway, needle shaped calcites, micritic calcites, loessic soils, micromorphological aspects

Article Info

Introduction

Some soils are characteristic by relatively high amount of calcium carbonates. Their origin can be lithogenic (clastogene) and pedogenic (secondary, authigenic). Authigenic carbonates are those that are formed through the processes responsible for the soil development. Calcification as the process of the accumulation of authigenic carbonates in soils is dominant in many soils in arid or semiarid environments (Eswaran et al., 2000). Wherever a source of calcium exists and there is insufficient water (energy) to translocate it from the profile, secondary carbonates can accumulate.

Authigenic carbonates occur in multiple forms in soils. Calcretes, a common name for authigenic carbonates pool, can be present in a variety of discrete forms (nodules, coatings, pendant cement, pseudomycelia, calcified roots, rhizo-concretions). (Gile et al., 1966; Mermut and Arnaud, 1981). From a petrological point of

view, authigenic carbonates can be formed by needle shape, micrite and microsparite calcites. Notably, in vadose zone the most widespread forms are needle shape and micrite calcites.

Both, abiogenic sources of Ca and CO_2 (soil parent material, groundwater, precipitation, dust) and biogenic (decaying organic matter, root and rhizomicrobial respiration) are involved in carbonates authigenesis in soils. The formation of carbonate accumulations may occur in different ways: dissolution and reprecipitation of carbonates (Treadwell-Steitz and McFadden, 2000), downward movement of Ca^{2+} rich meteoric water through the soil profile (Gile et al., 1966; Monger, 2002), precipitation from upward or capillary rise of soil solutions and shallow groundwater (Sobecki and Wilding, 1983), recrystallization of lithogenic carbonates inherited from parent material (Polyakov, 1989), various biogenic processes (vital activity of bacteria, fungi, actinomycetes and yeast) (Aristovskay, 1980; Verrecchia and Verrecchia, 1994).

Accordingly, plants can have unexpected consequences on calcite accumulation in soils and therefore contribute to global carbon cycling (Garvie, 2006). More than 215 families of plants are able to form biominerals in their tissues from oxalic acid and cations taken from soil solution (Ca, Mg, K, etc.) (Franceschi and Loewus, 1995). Oxalates after decaying of plants are released to the soils. They are not degraded to the basic components, but depending on conditions are slowly transformed into authigenic carbonates. High concentration of Ca or Mg, presence of oxalomorphic plants and high oxalotrophic stability of microorganisms are required for an operating oxalate–carbonate pathway (Martin et al., 2012; Cailleau et al., 2014).

Carbonates in the soil system play an important role in the global C cycle, as a pool of considerable size. An estimated 1.10^{12} to $1,7.10^{12}$ t C of authigenic carbonates is stored in the world's soils, mainly in arid and semi-arid regions (Eswaran et al., 2000). Results by Landi et al. (2003) have shown that the soils of the prairies and forests have sequestered 1,4 times more C in the form of authigenic carbonates than does organic matter. Authigenic soil carbonate pools are well known and treated in soils from several points of view (e.g. calcrete, calcaric soil subtypes) but their role in the terrestrial carbon balance is usually underestimated and rarely considered in literature.

Information about the amount and rate of authigenic carbonate accumulation also may help in understanding and describing past climatic conditions. Whereas, microscale authigenic carbonate abundance and distribution are sensitive indicators of environmental changes. They possible indicate the changes of moisture regime and dust accumulation characteristics in many cases (Becze-Deák et al., 1997; Gocke, 2010; Kuznetsova and Khokhlova, 2012; Barta, 2014). Generally, distribution of carbonates in soil profiles and along the toposequences is consistent with soil moisture flows. Downward percolation, capillary rise, and lateral flow both at the surface and within the soil play important but different roles in each landscape position (Wang and Anderson, 2000). Because of the complexity of processes involved in atmosphere–vegetation–soil–landscape relationships, there are few reliable estimates for authigenic carbonates in the world's soils (Landi et al., 2003).

In general, main aim of this topic was to elucidate authigenic carbonate accumulations in loessic soils, on the example of Trnavská pahorkatina loess hilly land (SW Slovakia) and potential source of their origin in soil profiles. We pay specific attention to the vertical differentiation and gradual transformation of forms of authigenic calcites (needle shape and micritic ones) in soil toposequences based on micromorphology and SEM study.

Material and Methods

The study site is located on Trnavská pahorkatina loess hilly land, in the southwest of Slovakia. The main study objects is based on micromorphological analysis of undisturbed soil samples. In the study area of hilly land were investigated 4 different soil types, which are abundant there to the greatest extent. The studied soil profiles herein were (classified according to WRB, 2006): Calcaric Chernozem, Chernozem, Luvic Chernozem and Luvisol (WRB, 2006). These cultivated soils were formed on the quaternary eolian sediments (loess). The study of soils thin sections were examined with the polarizing microscope and the scanning electron microscope and followed by micromorphological methodology of Stoops (2003). Some older soil thin sections were used in this study for the comparison.

Results and Discussion

We have been noticed 2 prevailing forms of authigenic carbonates in loessic soils of the studied area. Needle shape calcites occurred mostly upside and micrite calcites at the lower parts of soil profiles.

In studied soils carbonate authigenesis starts with the formation of needle shape calcites (NSC). These common feature occured in carbonate soils, calcretes and caves are also described as needle-fiber calcite or acicular calcite. They consists of a few μm wide and up to several hundred μm long elongated needles. Some authors have been described their formation as product of biogenic processes of fungi and associated higher plants. Several morphological studies suggest that needles are calcified fungal sheaths, produced by fungal biomineralization (Verrecchia and Verrecchia, 1994; Becze-Deák et al., 1997; Barta, 2014; Bajnóczi and Kovács-Kis, 2006). The second way of their origin is physicochemical precipitation from soil solution. Kuznetsova and Khokhlova (2012) described NSC crystals formation to be involved fast-changing water regimes from saturated solutions.

With the increase of NSC volume in soil a gradual micritisation is observed until continuous micritic (calcic) horizons are formed beneath. Micrite is a term used for calcite crystals less than 4 μm in size. Micrite crystals can be formed by precipitation of carbonates in the pores. This process called sparmicritization (Kahle, 1977).
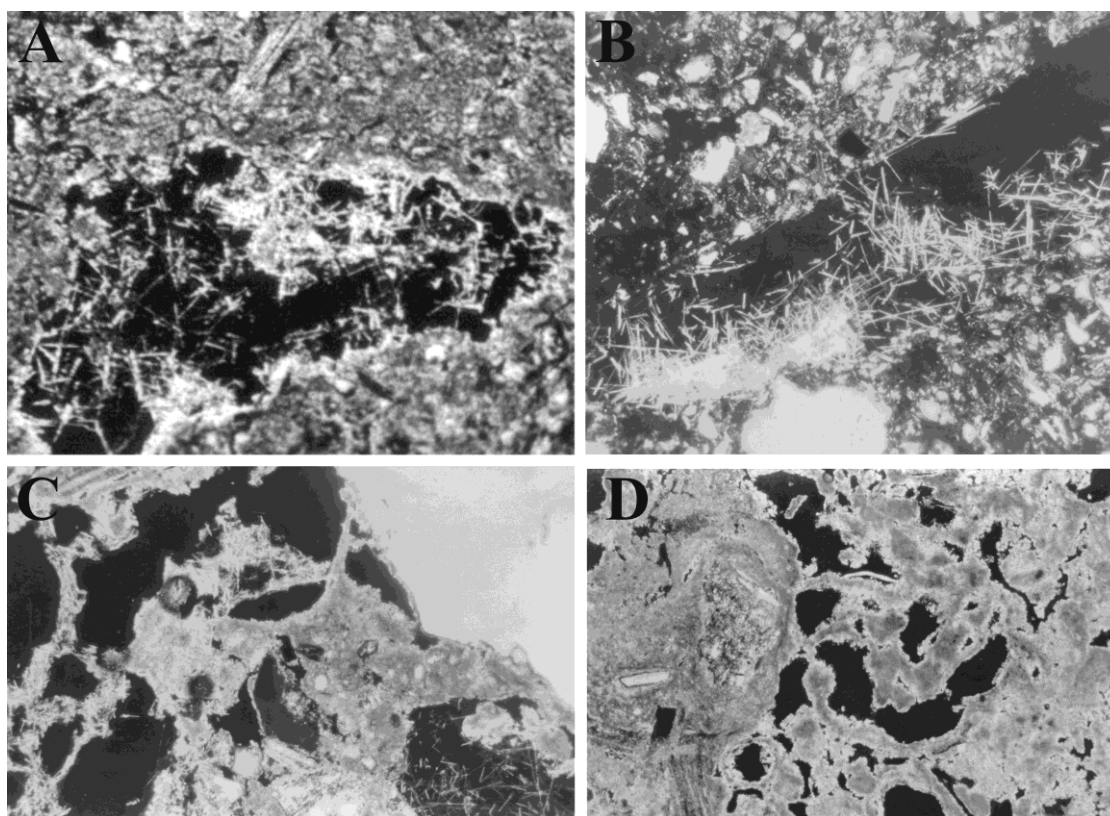

Figure 1. Gradual transformation (coalescence) of needle shaped calcites into micritic ones in the upper part of calcic horizon in loessic soil, A) needle shape calcites with the weak signs of coalescence, B) needle shape calcites with the coalesced domains in the lower part, C) advanced coalescence of needle shape calcites into micritic ones; needle calcites still visible in one biopore (bottom right), D) almost complete micritization (coalescence) of needle shape calcites, only with few needles in porous system.

In studied soils cumulating amount of NSC composes distinctive zones. These white coloured pseudomycelium (remind of mold) occur in discrete pores (cavities, biopores, channels). In consequence of readily dissolved NSC is a depth of their occurrence in soil profile most probably function of repreciptation and soil moisture regime. Under the NSC zones were always observed continuous horizons of micritic calcites. Our investigation brought an evidence of gradual transformation (coalescence) of NSC into micritic calcites (Figure 1). Formation of micritic calcites horizons in soils is result of a long term dynamic changes of soil and land (dissolution, migration, precipitation). In this case we assume lateral inflow, which is related to topographical positions, as a main factor responsible for the character of these horizons in soils. This statement is confirmed by high carbonate content (20-30%) in calcic horizons present already at the depth of 60–80 cm in Chernozems while in Luvic Chernozems and Luvisols which exit at higher altitudes, calcic horizons are present at the depth 90-120 and 120-150 cm, respectively. Thus, carbonate accumulation within each soil profile is closely related to the major movement of soil moisture on landscape segment. For

upper slope positions, downward flows dominate moisture movement in the soils. Therefore, carbonate enrichment in the upper slope soils involves dissolution of carbonates near the surface, followed by carbonate-enriched soil solution moving down from the surface, and precipitating at a depth related to the average depth of infiltration (Brown, 1956).

In studied soil types on loess of Trnavská pahorkatina hilly land we noticed presence of NSC zones and micritic calcites horizon in different depth of soil profiles. Zones of NSC were closest to the soil surface in Calcaric Chernozems (20–60 cm), followed by Chernozems (40–65 cm), Luvic Chernozems (70–90 cm). Finally in Luvisols were situated under luvic horizon in depth 100–120 cm. The distinct size of needles was also confirmed. The size of needles is 1–2 μm wide and 10–100 μm long in chernozems and in luvisols may exceed 4 μm wide and 120 μm long. The zones of NSC continuous merge into micritic calcites horizons in Calcaric Chernozems unevenly in depth 60–80 cm and evenly under the 80 cm of soil depth. In Chernozems are occurred in 65–85 cm, followed by Luvic Chernozems (90–120 cm) and Luvisols (120–140 cm). Hereby, nodules of calcite occurred to a great extent in these horizons, which are also an accompanied by precipitation and recrystallization of carbonates in depth (Figure 2). Moreover, domains of sparitic calcites were observed in micritic matrix. Probably, their formation is due to recrystallization of micritic forms of calcite and is more abundant in older loesses beneath, sometimes in association with the crystic fabrics.
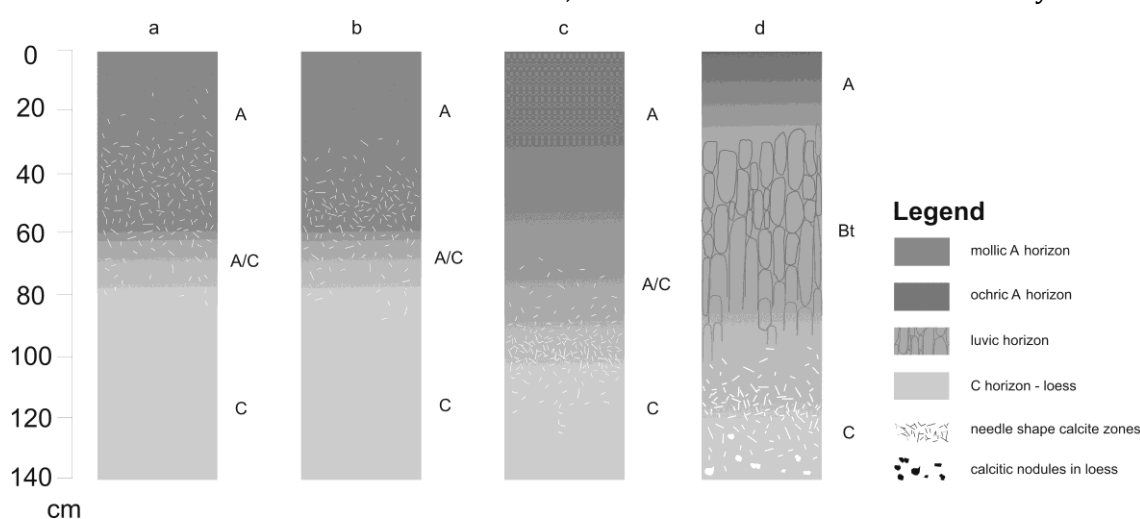

Figure 2. Schematic presentation of the needle shape calcite zones in loessic soil a) Calcaric Chernozem, b) Chernozem, c) Luvic Chernozem, d) Luvisols, (note the depth of occurence of needle calcites zones).

Generally, distribution of carbonates in soil profiles and along the toposequences is consistent with soil moisture flows. Downward percolation (*per descensum*), capillary rise (*per ascensum*), and lateral flow both at the surface and within the soil play important but different roles in each landscape position (Wang and Anderson, 2000). This contention we have been confirmed in respect to the variable depth of NSC zones and horizons of micritic calcites occurrence depending on soil types (leaching). Important is to note a fact, that the accumulation rates of authigenic carbonates in soils are not simply a function of the dissolution and precipitation rates of calcite, but depend on water availability in the soil profile which in turn results from rainfall and soil permeability (Arkley, 1963). We suppose that rainfall and dust as the main sources for Ca^{2+} influx and oxalate–carbonate pathway are responsible to control accumulation rates of calcretes in loessic soils, because weathering of primary minerals is slow and weak, but the exchange of water and solids between soil and atmosphere is rapid

Because calcic horizons form slowly and can persist in landscapes for a long time intervals, the depth to the calcic horizon is also a function of paleoclimate. Interest in authigenic carbonates as an archive for paleoclimatic reconstructions in soils of arid and semiarid climates has increased during recent decades (Barta, 2014; Becze-Deák et al., 1997; Gocke, 2010; Kuznetsova and Khokhlova, 2012). Although, a particular form or type of secondary carbonate can be ascribed to a certain climate, the correspondence is not always assured. Many calcretes have been transformed, reworked and eroded in due time. Hence, their shape and size could be modified by impact of several processes (dissolution, coalescence, micritization, destruction) and their accumulation may be controlled also by lateral flow in different landscape, is just very difficult to

interpret the distribution and forms of authigenic carbonates in soil from a paleoenvironmental point of view (Alonso-Zarza et al., 1998; Čurlík, 1985; Gocke, 2010).

Conclusion

Authigenic carbonates contribute an abundant amount of loessic soils in SW Slovakia and in many cases they give rise of the calcic horizons. They are formed mostly by calcites, which are found in a great deal as needle shape or micritic calcites. To a lesser extent nodules and rhizo-concretions can also be present. Our study supports the ideas on inorganic origin of needle shape calcites zones. The most frequently it starts with the evaporation of pore waters, decreasing of partial CO_2 pressure in soil air, or with increasing input of calcium or magnesium ions. The needle shape calcites zones gradually transited (coalesced) into micritic horizons. Thereafter, continuous horizons of micritic calcites (calcic horizons), with or without microsparitic calcite domains are formed in soil profiles.

Microscale analyses revealed that needle shape calcite zones are situated always in the uppermost parts of soil profiles but at different depth, depending on soil types. In Calcaric Chernozem from 20 to 60 cm, in Chernozem from 40 to 65 cm, in Luvic Chernozem from 70 to 90 cm. In Luvisols needle calcite zones are present at the depths 100 to 120 cm and length of needle is higher than in former soils. Micritic (calcic) horizons are formed always beneath the needle shape calcite zones.

Most decisive role in formation distribution and accumulation of calcretes in loessic soils has moister soil regime, CO_2 partial pressure, abundance of Ca^{2+} or Mg^{2+} ions, plants and microorganisms (oxalate–carbonate pathway). Rainfall, dust, wheathering of primary minerals, subsurface water flow and decaying organic matter provide Ca^{2+} ions and plants and decaying organic matter in soil mostly provide CO_2 for the formation of authigenic carbonates. Top-down movement derives from the infiltration of meteoric water, resulting in leaching, bottom-up movement evolves from capillary rising groundwater through evaporative pumping and lateral flow are the most responsible factors for the authigenic carbonates distribution in different soil types on loess.

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