

## GENESIS OF AUTHIGENIC CARBONATES IN QUATERNARY SEDIMENTS AND SOILS OF DANUBE LOWLAND I.

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**Citation:** Čurlík, J., Kromka, M. (2022). Genesis of authigenic carbonates in Quaternary sediments and soils of Danube Lowland I. *Pedosphere Research*, vol. 2, 2022, no. 2, pp. 106–118. NPPC – VÚPOP 2022. ISSN 2729–8728.

### Abstract

Carbonates authigenic is epigenetic geochemical process which leads to the excretion (neof ormation) of carbonates in host sediments and soils independent on their genesis. It is applied on places where are sufficiently high contents of calcium in pore- or groundwaters, and suitable evapotranspiration landscape potential. Due dual approach to their study (pedological and geological) is one of the causes of many ambiguities around nomenclature, classification, interpretation of the genesis of authigenic carbonates and in recognition of their pedogenetic and geochemical significance. An essential factor of authigenic carbonates formation is sufficiently high concentrations of calcium in pore- and groundwaters and suitable climatic conditions that affect water evaporation. The role of authigenic carbonates is discussed; the majority of authigenic carbonates is a mixture of several morphological, or transitional types. Soil classification and spatial distribution of soils (soil toposequences on loess), as well as soil pedogenesis in alluvial and loess parent material is processes with proposal on the new classification criteria involvement.

**Keywords:** authigenic carbonates nomenclature, classification, sources of calcium, models of formation, loess, calcic horizons

### INTRODUCTION

For authigenic carbonates we consider those carbonates that were formed at the place of their current occurrence. On the contrary, clastogene, which are brought with mineral mass, or represent unweathered remains of underlying carbonate rocks (limestone and dolomite fragments). Authigenic carbonates play very significant role in supergene zone. They are component part of many surface deposits (loess, deluvial, fluvial sediments). Soils with contents of authigenic carbonates cover about 20 million km<sup>2</sup> on the Earth surface which is approximately 13% of the entire Earth surface (Yaalon 1967). They are found in Aridisols, Mollisols, Salt-affected soils, Rendzinas, (USDA Soil taxonomy 1999), Fluvisols, Vertisols (IUSS Working Group WRB 2022) etc. As follows from the work of Chen *et al.* (2002), in Australia, carbonatic soils cover up to 21% of the entire continent, that is significantly more than the world average. This is related to the aridity of the climate on this continent. Carbonates play an extremely important role in terms of the overall carbon cycle and its sequestration on the continents. In soils of arid and semiarid regions in the world are stored 1.10<sup>12</sup>-1.7.10<sup>12</sup> t of carbonates (Eswaran *et al.* 1999)

Some authors argue that prairie soils and forest soils sequester 1.4 times more carbon in carbonates than in soil organic matter (Landi *et al.* 2003). Since they are often component part of sediments and soils, have long been the subject of extensive research by soil scientists and geologists in the world. Soil scientists interpret their origin as a part of pedogenesis and geologists as first stage of diagenesis. This dual approach to their study is one of the causes of many ambiguities around nomenclature, classifica-

tion, interpretation of the genesis of authigenic carbonates and in recognition of their pedogenetic and geochemical significance. Unlike abroad, the research of authigenic carbonates and carbonate systems in Slovakia, did not attract enough attention. Information about regional distribution of authigenic carbonates in Slovakia are scarce, no maps and other presentations are available, and their genetic interpretations are missing.

This does not contribute to the knowledge of deposits and their changes under the influence of pedogenesis. They are considered in Quaternary geology and soil science for random phenomena and do not attribute the necessary genetic significance to them. In an effort to contribute to bridging of a certain gap in this area of research, we present this contribution, which discusses several of the mentioned problems.

#### *Problems of nomenclature and classification of authigenic carbonates*

Carbonates that are brought with mineral mass, or inherited from the weathering of the underlying carbonate parent rocks (debris limestones and dolomites) are referred to as „primary“. Various authors they classify also as *allotigene*, *clastogene*, *geogenic*, *lithogenic*, or *inherited*. In foreign literature, outside of America, secondary carbonates are collectively referred to as „calcretes“ (Lamplugh 1902, Wright & Tucker 1991). Based on the works of Netterberg (1980), Watts (1980), and Goudie (1983) they defined them as „near-surface, terrestrial, accumulations of predominantly calcium carbonates, which occurs in a variety of forms; from powdery to nodular to highly indurated. It results from the cementation and displacive and replacive introduction of calcium carbonate into the soil profiles, bedrock and sediments, in areas where vadose or shallow freatic groundwater is saturated with respect to Ca-carbonates“. Calcretes should be to varying degrees solid, but gradually there were placed more friable materials (Netterberg 1980, Goudie 1983). According to some authors, to the calcretes should be placed only to those accumulations of carbonates with minimal content  $\text{CaCO}_3$  in host materials 10-15%, although much larger proportion (40-50%) is expected (Chen *et al.* 2002). The main characteristic of calcretes is the presence of carbonate components in the studied formation (horizon) in which they form the dominant morphological phenomenon (Achyuthan *et al.* 2012).

In the American literature, instead the term *calcrete* another general term is used the term „caliche“ (kǎ-lē-chē) (Zhou & Chafetz 2009). In France, they are marked as „croûte calcaire“ (Voght 1984), in Africa (and the Near East), we meet also „kankar“, „kunkar“, „nari“, „capstone“, etc. (Goudie 1983, Reeves 1976). Especially in soil science, other common names are also used: *pedocretes*, *duricrusts*, *hardpan* (Netterberg 1980, Milnes & Hutton 1983), but those include a wider group of specific neoformations in the soil, such as *dolocretes* (formed by dolomites), *gypcrete* (gypsum), *silcretes* ( $\text{SiO}_2$ ), *ferricretes* (with Fe oxides), *manganocretes* (with Mn oxides). Goudie (1983) considered calcretes as a certain form of *duricrusts*. Due to accumulation of calcretes (caliche) in soil, calcic and petrocalcic horizons are formed.

Many of the mentioned terms can be understood as synonyms, used for near-surface terrestrial accumulations of Ca-carbonates. However, upon deeper analysis, we find that some of them also have a special connotation. For example, „clastogene“, „allotigene“, need not be the same as „primary“. Even „calcretes“ can be, and often are, transported by wind, fluvial, or colluvial processes and deposited on others places as „clastogene“. They do not need to have „primary“ structure. A typical example is loess. It can be carried multiple times by the wind (deflation). Wind transport includes all loess components, i.e. „primary“(allotigene) and „secondary“ carbonates (calcretes). Similarly, carbonates redeposited by fluvial activity can also have a „primary“ or „secondary“ structure. During an erosion, with soil components could be redeposited carbonates, the structure of which can be *lithogenic*, but also *pedogenic* (secondary). Terminological confusion is then reflected in the diversity of opinions about their genesis and classification.

Based on the hydrological conditions of formation, *carbonates-calcretes* were divided into three groups namely:

- a) *pedogenic*, which are formed by pedogene-illuvial translocation of calcium (and Mg) from upper to lower soil horizons and precipitated in lower horizons (calcretes in the soil moisture zone) (Gile *et*

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al.1966, Reeves 1976, Klappa 1983, Mack *et al.* 2000, Monger 2002, Zhou & Chafetz 2009, Chen *et al.*2002, Alonzo-Zarza & Wright 2010).

- b) *groundwater calcretes* (which many authors designate as *nonpedogenic*) (Carlisle 1983, Goudie 1983, Wright & Tucker 1991) which form on places where shallow groundwater tables laying close to the surface, capillary rissing, evaporate and carbonates precipitated of them („calcretes in *capillary fringe zone*“)
- c) *phreatic calcretes* which are formed during non-pedogenic processes in the phreatic zone (directly from water solutions) e.g., water of springs, caves, rivers, lakes and other water bodies formations (Monger 2002 and others). They are the most contrasting forms in relation to pedogenic calcretes. They are formed by the precipitation of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ions from laterally transported water. Khadkikar *et al.* (1998) used similar principles of classification when distinguished
- a) *pedogenic carbonates*, which are formed during pedogenic-iluvial translocation of calcium (and Mg) from surface horizons and its (re)precipitation in lower horizons („calcretes in the soil moisture zone“) (Gile *et al.* 1966, Reeves 1970, 1976, Mack *et al.* 2000, Monger 2002),
- b) *groundwater calcretes*, („non-pedogenic“) (Carlisle 1983, Goudie 1983, Wright & Tucker 1991) are formed in places where groundwater lies close to the surface, capillaries rise up, evaporate and carbonates „calcretes in the zone of capillary rise“ are formed,
- c) *conglomerate calcretes* – the last term is non-genetic because it does not represent group, but only morphological forms of calcretes.

Later, (Zamanian *et al.* 2016) used completely different division principles when they singled out three groups of carbonates in soils: *geogenic*, *biogenic* and *pedogenic*. Geogenic carbonates are considered inherited from parent rocks or brought with mineral mass to the place of their occurrence (limestone fragments and dolomites). They consider *biogenic* group as shells fragments, skeletons of animals, calcified tissues of plants and biominerals. In fact, in both cases these are not calcretes *sensu stricto*, but „allotigene“ (clastogenic) carbonates. According to some authors, pedogenic carbonates are formed in soils by the transformation of geogenic, biogenic or pedogenic carbonates which were formed in the previous development cycles. As we will see in the following, this is also not entirely based on truth. It can be seen from the overview that nomenclature and classification of carbonates is contradictory, and it is not possible to draw a clear boundary between the separated groups. Among the most common problems associated with the classification of carbonates (calcretes) we conclude the following:

- Division of calcretes into „pedogenic“ and „*non-pedogenic*“ is currently widely and uncritically used (Netterberg 1980, Alonzo-Zarza & Wright 2010). This cannot be accepted without any doubts. Pedogenesis is a process that includes the formation of both, *automorphic* and *hydromorphic* soils. If groundwater lies close to the surface, it hydromorphically affects the development of soils. *Groundwater calcretes* that are formed from laterally migrating groundwater are sometimes found in the entire soil profile (Calcaric Fluvisols, Phaeozems, Gleysols). They intervene in the soil profile, so they are part of pedogenesis. How they can be marked as „non-pedogenic“?
- *Clastogene* („primary“, geogenic, lithogenic, inherited) and *authigenic* („secondary“) carbonates (calcretes) oftenly occur together. When co-occurring, cannot be unequivocally labeled as „*primary*“, or „*secondary*“ carbonates. The designation „secondary“ is not appropriate in cases of repeated formation (reprecipitation) of carbonates. This is understandable, because in places where the conditions for the formation of carbonates are found, there are also possibilities of preserving the clastogene „primary“ ones. Sometimes the presence of calcretes- „secondary“ forms can also be distinguished by the appearance of nodular, rhizoconcretionary and laminar forms, or as carbonate coatings on gravel boulders (Čurlík 1985, 1993, Čurlík & Mejeed 1996). Under the microscope, these forms can be distinguished based on microstructure, shapes, and other features. Our micromorphological studies of carbonates in fluvial sediments and loess confirmed co-occurrence of both clastogene and authigenic forms of carbonates.
- Calcretes- „secondary carbonates“ are found in deposits (fluvial, eolian, deluvial and eluvial) as well

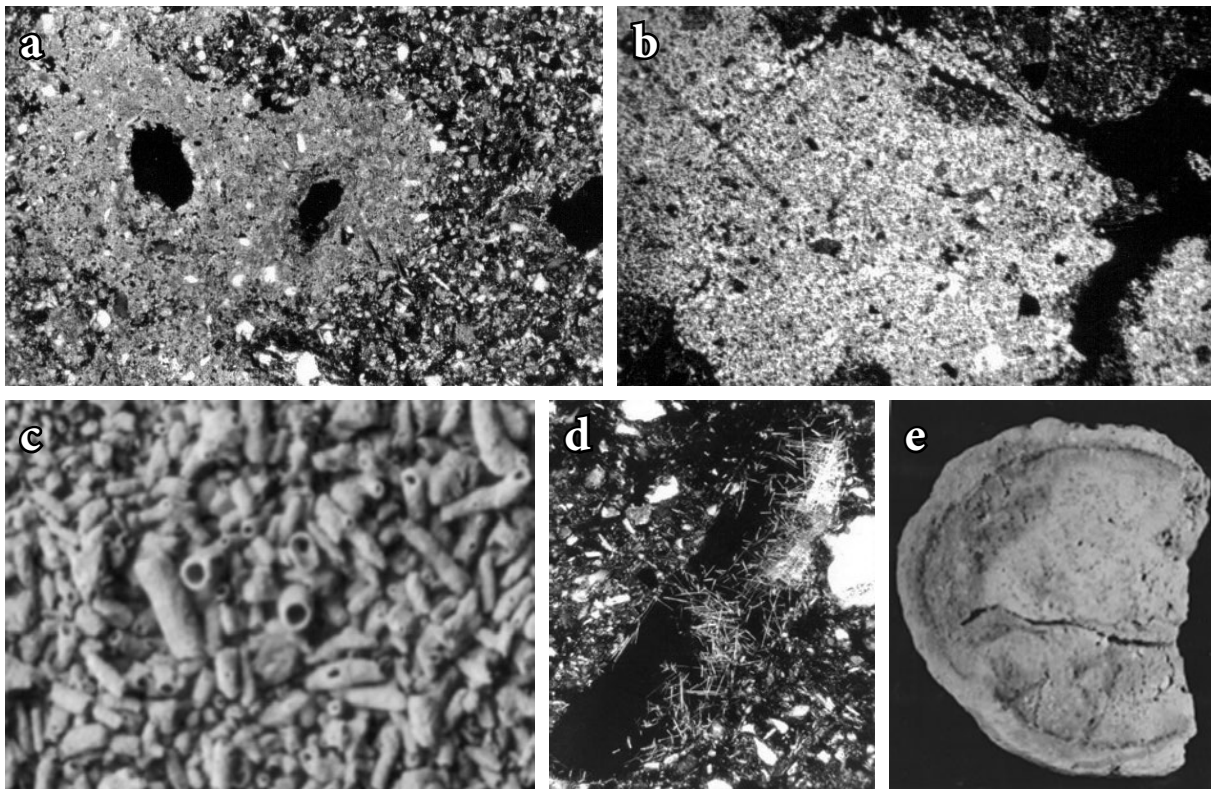
as in soils. Pedogenesis, which takes place on of these parent materials disrupts forms and distribution of „secondary“ carbonates in the soil profile. For example, in loess soils, depending on climate and topography, carbonates can be leached, Ca and other ions migrate on- or under the surface, from higher to lower hypsographic levels. There they can re-precipitate.

These are the primary reasons for which we use in the presented contribution wider, less specific term „*authigenic carbonates*“ instead extended „calcretes“ or „caliche“. This term was used also in several others works (e.g., Sehgal & Stoops 1972, Folk 1974, Sobecki & Wilding 1983, Łącka *et al.* 2009, Kolesár & Čurlík 2015).

Formation of authigenic carbonates (*calcification*) is epigenetic geochemical process during which carbonates are excreted (newly formed) in host materials at the place of their current occurrence, regardless of genesis. It applies wherever, there are sufficient sources of calcium and evapotranspiration potential exceeds the amount of precipitation. Is therefore dominant in cover deposits and in arid and semi-arid soils, with a primary lack of moisture. (e.g., Millot *et al.* 1977). This characteristic distinguishes them from those carbonates which are precipitate directly from solution (in springs, caves, rivers, and in other water systems-phreatic calcretes). They form an independent group of carbonates, which we will not deal with, although, due to morphology, they cannot be reliably separated from others forms, especially if these have undergone postdepositional changes (e.g., Wright & Tucker 1991).

#### *Morphological classification of authigenic carbonates*

It is based on the visible signs that can be describe directly in the field. They are needle shaped, powdery, nodular, pisolitic, tubular, laminar, honeycomb, layered, conglomeratic and others (Čurlík 1993, Paquet & Ruellan 1997, Chen *et al.* 2002, Stoops *et al.* 2010, Alonso-Zarza & Wright 2010, and others). *Powdery*



*Figure 1.* Authigenic carbonates in loess: a – micritic hypocoatings around the biopores in loess (magn. 28×, cross polar.), b – irregularly distributed micritic calcites in the loess matrix (magn. 28×, cross polar.), c – tubular forms of calcites (rhizoconcretionary) obtained by wet sieving of loess (magn. 8×), d – needle-shaped calcites in pores, e – fragment of macronodule (septaria) from loess Trnava Loess hilly land (Loc. Senec)

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*forms* are fine (micritic), usually friable, dispersed, or clustered in the soil matrix. *Nodular* carbonates are composed of discrete, friable to solid, irregular (nodular) forms. Their size, shape, degree consolidation and the content of  $\text{CaCO}_3$  in nodules, as well as their purity is variable. *Carbonate clusters* are formed by precipitation in the pores and then expanded into the matrix. *Pisolitic* forms are similar to nodular, but they are concentric and have a regular isometric shape. *Tubular*, rhizoconcretionary forms are developed most often around former roots, channel-like pores, and cavities. Their size is very variable and can reach up to several tens of centimeters, in the case excretion from groundwater (Klappa 1983, Semeniuk & Meagher 1981, Čurlík & Mejeed 1996) (Fig. 1).

Development various features such as nodules, pedotubules (tubes), clusters, relate to processes of dissolution, leaching and recrystallization (Chen *et al.* 2002). *Laminar* forms occur in places where powerful positions of calcretes are present, which they did not undergo significant pedogenic modification. The main process of their creation is plant root activity (e.g., Wright & Tucker 1991). Layered, conglomeratic and boulder forms were also described by Alonso-Zarza & Wright 2010). „Hardpan“ (hardpan calcrete) is a designation for continuous layers of solid cemented authigenic carbonates in the host materials that have a micritic microstructure. They were studied in the Žitný ostrov area (Čurlík & Mejeed 1996). The majority of authigenic carbonates is a mixture of several morphological, or transitional types, but their detailed classification is not processed. From the petrological point of view, the authigenic carbonates are formed by needle-shaped, micritic and microsparitic calcites (Čurlík & Mejeed 1996).

#### *Soil classification and spatial distribution of soils*

Soil-forming processes on loess always mean a minor or major intervention in the very nature of the loess. The smallest intervention to the loess has *chernozemic soil process*. It relates to the accumulation and stabilization of organic substances on- and under the surface, without changing the mineral composition and fabric of the loess. Sufficient calcium content causes the stabilization of organic substances (humus) in the form of calcium humates and the formation of a *mollic humus horizon* (Poljakov 1989, Nash & Smith 2003, Altermann *et al.* 2005, Eckmeier *et al.* 2007). Typical representative of these soils is Calcaric Chernozem (IUSS Working Group WRB 2022). In these soils thanks to relief, low amount of precipitation, and strong evaporation rate, precipitation evidently evaporates to the soil surface and leaves the salts content. This maintains the calcaric nature of the soils. Humus is aggregated and in the humus horizons zones of needle-shaped calcites are formed. Oftenly can be recorded as mold-like in-fillings between aggregates, known as “pseudomycelia”. They add gray shades of color to the humus horizon (Kolesár & Čurlík 2015). Under the microscope, we observe them as *zones of needle-shaped calcites*. They are a reflection of evaporative processes. The quantities of needle-shaped calcites increase with depth, where they gradually transited into zones of micritic carbonates, similar as we find in the loess itself (Kolesár & Čurlík 2015). As soon as precipitation increase, or the relief is changes, the humus can be destabilized, organic and inorganic colloids dispersed and can migrate. The depth of needle-shaped calcites zones is also changing – lowering, through the *Haplic Chernozem* to *Cambic Chernozems*, where they are located several tens of centimeters below the surface. The fabric of loess and stability of authigenic carbonates are gradually disturbed, their amounts and forms in soil profiles changes. Depending on the climate and topography (relief), carbonates can be leached from the surface, calcium, and other ions, migrate in the soil profile, vertically or laterally, from the higher to lower hypsographic levels. Carbonates can here re-precipitate. The relocation of loess material also occurs.

The gray-black colour of the humus horizons and the morphology of the soil profiles is changing. Humus horizons of *ochric type* are formed. Humus is dispersed, and in humus and clay depleted- *eluvial horizons*- and in humus and clay enriched *illuvial – (luvic) horizons* are formed. Three-phases (A-B-C) soils of *Luvisol types Luvisols (Cutanic) – Albic Luvisols (Cutanic) – Albic Luvisols* are formed, from two-phases Chernozemic (A-C) soils. The entire soil profile (120-150 cm) is non-calcaric. Decalcified (Bt-E) horizons usually overlap horizons with signs of carbonate enrichment in the subsoil-the *calcaric horizons* (according to IUSS Working Group WRB 2022) they are  $\geq 15$  cm thick,  $\geq 15$  wt.%  $\text{CaCO}_3$ ,  $\geq 5$  wt.% more  $\text{CaCO}_3$  than the underlying horizon or  $\geq 5$  wt.% authigenic carbonates, which are formed by disso-

lution of Ca in surface horizons, its migration and carbonates reprecipitation, in the lower horizons. The degree of decalcification depends on the relief and climate conditions. (to climatic conditions) (Yaalon 1967, McBride 2001, Birkeland 1999, Kolesár & Čurlík 2015). Decalcification determines the thickness, but also the CaCO<sub>3</sub> contents in calcic horizons. Some of these horizons with a higher carbonate content solidify (petrify) and form the so-called *petrocalcic horizons* (Rabenhorst & Wildig 1986, Wright 1991). They appear to be more resistant to erosion and therefore, may play an active role in the erosional modification of the youngest forms of relief on loess hills (Ruellan 1968).

The most decalcified (leached) in this series are Cutanic Albic Luvisols. The entire soil profile (120-150 cm) is non-calcaric, the humus is degraded, eluvial (albic) and illuvial (luvic) horizons are formed. Pedogenesis has disrupted the structural composition of authigenic carbonates and caused dispersion and translocation of colloids. The most important factor in this differentiation is relief. Even weak recurring climatic fluctuations in the Holocene, with a suitable slope in the landscape are sufficient, to cause lateral migration of soluble components. At the same time, it is a “one-way road” with no return. As a result *soil-geochemical zonation* was formed on the loess hills of the Danube Lowland, as a reflection of the post-depositional changes of the loess.

Our findings confirmed that even in the majority of interglacial paleosols that developed in the early Pleistocene under of intense weathering conditions (rubified soils), complete loess decalcification did not occur. It is known (Frechen *et al.* 1999, Li *et al.* 2013) that maximum infiltration depth of precipitation in the loess, does not exceed 5 m. Since the total thickness of the loess often exceeds this depth, some loess positions may remain intact since their formation. This insight has various implications; in particular, ideas about loess decalcification, about the thick loess loam formation, opinion on soil zonation need to be more thoroughly revised.

Bedrna (1964), who studied recent soils on the loess of the Trnava Loess hilly land, found that they have a zonal character. He identified a topographical series of soils on the loess, which included: *Calcaric Chernozem*, gradually at higher level *Haplic Chernozem – Cambic Chernozem – Luvic Chernozem – Luvisol*, on the highest hilly levels *Albic Luvisol (Cutanic)– Fragic Albic Luvisol – Planosol – Gleyic Retisol* (IUSS Working group WRB 2022). Development of this cascade system was attributed by Bedrna & Mičian (1967) to the *bioclimatic influence of the mountain range* on the adjacent hills. They came up with a new concept called *soil piedmont zonation*, which was based on the assumption that with approaching to the mountains, the humidity of the climate increases, which is associated with gradually higher, and higher degree, of soil leaching. They believed that mountain ranges are the main factor that determines the distribution of rainfall over the adjacent loess hills. This apparently led the mentioned authors to the idea that piedmont zonation is a special phenomenon „climofunction“, which does not fit into the ideas about the *vertical soil zonation*. Some other authors (Linkeš 1976, Hraško & Linkeš 1988) questioned the existence of *piedmont zonation*. They argued, for example, that on hilly areas, which have a completely different position in relation to mountain ranges, zonation is not a function of the distance from the mountain range.

The series of different but co-evolving soil units on a slope (cascade), that reflects the complex relationships between soil units and relief forms Milne (1935) called *catena*. It means that on the same substrate and on a certain form of slope (landscape unit) a paragenese sequence of soil units is formed, with one-way exchange of substances and energy. Milne thereby laid the foundations for the study of the relationships between soils and landscape forms, and at the same time, of the new discipline - *soil geomorphology*, which studies the evident genetic relationships between soils and landscape forms.

The mentioned soil zonation is not only a reflection of the climate, but as we mentioned, it is significantly influenced by the relief (the energy of the relief). It directs the transport of substances in the gravitational field, i.e., from higher to lower positions, from autonomous (eluvial), to geochemically subordinate – *elemental geochemical landscape*. With the same input of energy into the system, the highest (convex) landscape units are gradually decalcified, the lowest-geochemically subordinate, on the contrary, recalcified. The relief also affects the erosion and degradation of loess, the relocation of soil sediments and the

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formation of secondary loess (Caidong *et al.* 2003). In landscape geochemistry we say that convex forms of relief, can play the function of transeluvial, and concave, transaccumulative elementary geochemical landscapes (Glazovskaja 1986). Lithology (geological composition of rocks) determines which substances, and how quickly, they are released and translocated during weathering, and in which direction their migration takes place. Vegetation, on the other hand, inhibits the yield of substances and supports the upward movement of calcium, by removing calcium from the soil and accumulating it on the soil surface after it decays. During soils formation, the possible influence of capillary, gravity and sorption forces, the dissolution of substances and the participation (contribution) of living organisms, must also be considered.

Knowledge from the geochemical study of loess has also shown that different types of landscapes are present in one and the same climatic zone. The boundaries of climatic zones and boundaries of geochemical landscapes are most oftenly different. Therefore, geochemical zonality cannot be understood as the existence of separate bands or zones. Perelman already in 1975, explained this inconsistency in the *law on geochemical zonality*, in which he stated that “*geochemical zonality does not means that the areas occupying certain landscape units (natural formations) have the form of belts or zones, but in the fact, that the landscape (the soil) depends on the climate*”. The concept of piedmont zonality of soils, which is based only on the climatic principle (climofunction) (“increased humidity and leaching, as you approach the mountain range”), as presented by Bedrna & Mičian (1967) is not generally valid.

Bedrna (1964), as mentioned earlier, included into the same loess-soils sequences Planosols. These soils are characteristic by the illuviation of colloids and oxidation-reduction phenomena. Contain iron-manganese coatings, nodules, and concretions. They do not contain carbonates in the entire profile. They occur on the edges of hills at the foot of the mountains. The parent material of these soils is old-Pleistocene colluvial sediment (Maglay *et al.* 2018). It follows from that they may not represent the one chain of soil toposequence on loess. At this stage of knowledge, we consider them rather as pre-Holocene relict soils, although their further differentiation during the Holocene is understanding. During the Holocene, depending on the relief, altitude and climate, the following soil toposequence on the young Pleistocene loess is clearly demonstrated: *Calcic Chernozem – Haplic Chernozem – Luvic Chernozem – Luvisols (Cutanic)– Albic Luvisol (Cutanic)*. In this sequence carbonates are gradually leached, humus and colloids dispersed and translocated. The soil toposequences on loess, during the Quaternary (Pleistocene) has changed, as evidenced from the occurrence of rubified paleosols on loess hills of the Danube Lowland. Soil paleosequence and paleozonality is not known.

### *Pedogenesis on alluvial sediments of lowland rivers*

The sedimentary cover of the river floodplains in this area is made up by Holocene deposits. Among them sandy and clay loams, displaced loesses, and flooding loams alternate, sometimes with admixture of gravels.

Soils are very uneven in terms of texture. Heavy clayey soils alternate with light sandy soils. On floodplains *Calcaric Fluvisols*, *Gleyic Calcaric Fluvisols*, *Calcaric Fluvisols*, *Gleyic Calcaric Fluvisols*, *Calcaric Gleyic Fluvisols* are present. These soils are the function of mechanical composition of parent material and the depth of groundwater table (Societas pedologica slovacica 2014). On floodplains and aggradation terraces *Calcaric Fluvisols* are present. In alluvial soils clastogene carbonates prevail on authigenic. Mollic *Fluvisols* and subtypes, are soils with deep mollic horizons, seasonally under hydromorphic influence mostly on places with shallow groundwater tables. With stronger hydromorphic influence they locally transitioned to *Gleysols*, mostly on heavy clayey sediments of floodplains. The original vegetation there consisted of various swamps and moist communities. In relation to hydromorphic influence soils developed under meadows. The main soil-forming processes are calcification and gleyization in alkaline conditions. This process differs from typical gleyization in acid environment. From typical gley processes is different by the fact that in *calcaric gley proces* iron and manganese oxides does not completely reduce. Soils have an alkaline reaction, different content of clastogene and authigenic carbonates. In such conditions, iron and manganese migrate poorly and are excreted in gley horizons mostly as oxides. Such conditions are

not pleasant for Fe and Mn migration. In wet depressions and in the dead arms of rivers peats were developed (Jurský Šúr, Modranský Šúr, Pusté Uľany, Hájske).

Pedogenesis on that young Holocene River sediments is typical by the interruptions of pedogenesis due to sedimentation (redeposition) of new material during torrential rains. Soils are more a set of superposed layers of sediments, as individual genetic horizons.

#### *Pedogenesis on the alluvial sediments of Žitný ostrov*

The development of recent soils on Žitný ostrov is linked to the Holocene history of pedogenesis. *Calcaric Chernozems* have developed on the old Holocene calcaric sediments that cover the Pleistocene gravels of the Žitný ostrov core. These automorphic soils indicate that this part of the territory was not flooded in the past and the soils were formed without hydromorphic influences. Those are often shallow soils, given that the underlying gravels in the upper Žitný ostrov lie only a few tens of cm below the surface. The formation and persistence of Chernozems on the alluvial deposits of Žitný ostrov is influenced by relief and climate. During field study, we discovered that these Chernozems in the vicinity of the Malý Dunaj river (e.g., Most na Ostrove), are overlain by the Young Holocene fluvial deposits. They are therefore older, and their formation falls within the temperature optimum of the Holocene (Atlantic), i.e. roughly in the period before 6,000-7,000 thousand years ago.

Eutric Fluvisol (*Chiernitza*) and its subtypes represent a group of weak (or seasonally) hydromorphically influenced soils on *calcaric parent material*, with a deep mollic horizons. Unlike Chernozems, the humus horizon is much thicker, it has weak hydromorphic features in the form of coatings and nodules of Fe and Mn oxides. With the increase of hydromorphic influence, they transit to subtypes with the manifestation of gleyic features. In places where the groundwater tables lie close to the surface, and hydromorphically influenced the soil development, Gleysols were formed. Hydromorphic influence of soils by groundwater does not mean only wetting of the soil profile, but usually complex effects associated with the excretion of certain substances on the one hand, leaching on the other, as well as influencing the water, temperature, and air regimes of soils (Fulajtár *et al.* 1998). Silty soils are most often present on coarse-grained alluvial sediments and in terrain depressions. The original vegetation there consisted of various swamps and humid communities. They are widespread especially on the Middle and Lower Žitný ostrov, or in depressions, where the groundwater levels merge closer to the surface and thus historically hydromorphically more and more influenced the development of soils. The main soil-forming process is the *gley carbonatic process*, characterized by the accumulation of organic substances, the formation of deep humus horizons and the manifestation of gley processes, the intensity of which depends on the depth of the groundwater levels. The carbonate gley process differs from typical (acidic) gley processes, as it stated earlier, that it is developed in a alkaline (carbonatic) environment. In such conditions, iron and manganese migrate poorly and are also excreted in gley horizons mostly as oxides (Fe and Mn). The gleyic horizons are not gray as in typical Gleysols, but mottled, with alternating oxidation and reduction signs. Such gley horizons are typical for all alluvial areas of the Danube Plain, developed on carbonate substrates. The iron (and Mn) oxides often coprecipitate with the authigenic carbonates. This gives soils and sediments a mottled appearance. These features have not been analyzed separately in the field and their classification in the group of clayey soils was done more according to morphological features.

*Calcaric Fluvisols* were formed on early Holocene fluvial sediments (aggradational mounds) along the Danube and L. Danube. In the upper part of the island, the width of the Holocene belt reaches 15 km, in the lower part it is 4-6 km, or it emerges in the form of Žitný ostrov. They are undifferentiated A-C soils. Depending on the inundation, the profiles of these soils tend to be layered, while the individual layers can be heterogeneous in grain size. Fluvisols with a darker humus horizon (referred to as “dark alluvial soils” in older terms) were developed on older Holocene substrates, undisturbed by sedimentation. In the terrain depressions and overgrown dead branches of rivers, *Histosols* (peat) are developed (Dunajská Streda, Veľký Meder). Locally, especially on the Lower part of Žitný ostrov, there are salt-affected soils present (between Komárno and Veľký Meder, near Dunajská Streda, Zlatná na Ostrov, etc.).

From this overview, it can be seen that the geochemical structure of the soils of Žitný ostrov is a reflec-



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tion of *geological (geomorphological), climatic, and hydrogeological conditions* of the territory. The migration of substances takes place from higher hypsometric levels to lower ones, in proportion to the flow of the groundwater of the Danube. With the gradual change in the mineralization of groundwater, different hydrogeochemical zones are formed in this supraquatic landscape (Čurlík 2005). Elements that migrate in groundwater are redistributed in the solid phases of aquifer horizons. Carbonates (and salts) are secreted from them on evaporative geochemical barriers. An essential factor in their formation is a sufficiently high content of Ca (Mg) in pore and underground waters. Water vapor is needed to achieve this concentration, so another condition is the climatic factor. Fe and Mn oxides are excreted from them at oxidation-reduction barriers.

Gradual lowering of the relief (in the SE direction) resulted in an increase in hydromorphic influence of soils and in the formation of a special *hydrogeochemical soil zonality*. It starts from hydromorphically unaffected (automorphic) *Calcic Haplic Chernozem* to *Gleyic Calcic Chernozem*, *Calcaric Phaeozem*, *Gleyic Calcaric Phaeozem* to *Calcic Gleysol* in depressed areas. At the edges of the Island, there are young Fluvisols. A special phenomenon is the covering of soils with redeposited material of the former humus horizons of soils excavated from the places of the supply channels of the waterworks, which were spread over the soils in various depressed positions. They can be recognized based on the unnatural soil structure and the thickness of the humus horizons (e.g., Gabčíkovo). These processes resulted in the development of a special geochemical structure of Žitný ostrov soils, which is schematically presented on the geochemical maps (Čurlík 2005). There is abnormally depicted a depression on the island SE from Dunajská Streda. This depression is characteristic by the high content of authigenic carbonates and by the high correlation between the Fe and Mn oxides and trace elements content that are bound to them (co-precipitated, sorbed). The nature of the lateral differentiation of elements in this cascade landscape-geochemical system is related to the different hydromorphic influence of soils and sediments.

### *Authigenic carbonates and soil classification*

Carbonates influencing many soil properties, as pH, soil texture, humus stability, nutrient content, chemical elements mobility and others (Bockheim & Douglas 2006). In spite of the facts, that the content of diagenetic carbonates in soils is an accidental phenomenon connecting with the occurrence of calcaric parent material. In our soil science, it is supposed to be such an important factor that their presence in soil is determining specific *soil types (Rendzic Leptosols and subtypes)*. On the other side the content of authigenic carbonates, as we outlined, is a legitimized component of soil forming processes in certain pedo-geochemical systems. In our soil classification system are reflecting on different levels. For instance, in Chernozemic soils, which has developed in the Danube Lowland on loess and carbonatic fluvial sediments (Žitný ostrov) the presence of authigenic carbonates is reflecting only at low level. Central concept (locus typicus) for Chernozems in our soil classification system (Societas pedologica slovacica 2014) is *Haplic Chernozem*. Rest of *subtypes* are approaching to this central concept (*Luvic Chernozem, Salic Chernozem*). Chernozems with authigenic carbonates are classified only on the *soil varieties level* (*Haplic Calcic Chernozem – ČMm<sup>c</sup>*). Similarly, non-correct principles were applied for the classification of other soil types (Fluvisol, Arenosol, Vertisol, Planosol, Gleysol, Solonetz). We suppose this as confusing, non-correct approach. For example, in German soil classification a separating class of „black soils“ (Schwarzerden) is distinguishing with two *soil types Tchernosems* and *Calcic Chernosem* (Kalktschernosem) (Altermann *et al.* 2005). On the other hand, *Cambisols* and *Umbrisols*, which sometime contain carbonates, but with lower impact on soil properties are divided on subtypes level (Societas pedologica slovacica 2014). In a new approach to soil classification system of Slovakia, this should be remembered to improve these criteria.

## CONCLUSIONS

- Despite huge works in the world devoted to authigenic carbonates problems, still exist many unsolved problems and misconceptions. In the nomenclature, different terms are used for the description of similar phenomena and vice versa, the same terms, to describe very different. Classification criteria are inconsistent. Contradictory opinions are reflecting in non-correct genetic interpretation. One of the

reasons is a dual approach of soil scientists and sedimentologists to their study. The first are interpreting their origin as a part of pedogenesis, the second, as a part of diagenesis. Presented discrepancies are also the reason why we used in the title of our contribution non-genetic term – *authigenic carbonates*.

- In loesses and alluvial sediments are present two groups of carbonates *clastogene* („primary“, detritic, allothigene, lithogene, geogene, inherited) and *authigenic* („secondary“, *calcrets*, *kaliche*, *croûte calcaire*, a. o.). To the nomenclature, classification, genetic interpretation and understanding of their pedogenetic and geochemical significance is devoted more space in the introduction.
- Among most important carbonatic systems of the Danube lowland belongs *loess and carbonatic alluvial sediments*. Both systems have individual history of origin, variable ratio of chemical elements, different forms and ways of migration as well as different geochemical barriers on which carbonates precipitated. Loesses are older and their origin is connected with forest-steppe and meadow steppe conditions of glacial periods of Pleistocene. Alluvial sediments, especially soil cover, are mostly Holocene. Their origin relates to fluvial activity of rivers in conditions of evapotranspiration regimes of groundwaters.
- Our study proves, that in agreement with many authors, precondition of loess formation is *loessification* in the condition of aridic to semi-aridic climate, which is typical for steppes, deserts and semi-deserts landscapes, for which is typical low humidity (low annual precipitation) and relatively rapid water evaporation.
- On the young Pleistocene loesses verifiable was created the following soil-geochemical catena: *Calcic Chernozem – Haplic Chernozem – Cambic Chernozem – Luvic Chernozem – Luvisol*.
- The most important factor of soil differentiation is relief. At suitable slope, a weak recurrent climatic fluctuation in the Holocene are sufficient for the lateral migration of dissolved substances.
- Pedogenetically conditioned depth of carbonates distribution in soils is a reflection of the degree loess decalcification, humus degradation and illuviation of inorganic and organic colloids. Dissolved calcium (hydro-carbonates) and other ions which were leached out of the loess migrated vertically or laterally from higher to lower hypsographic levels. However, there was no complete loess decalcification occurred.
- Carbonates content is influencing many soil properties (pH, structure, humus stability, nutrients content, chemical elements mobility a. o.). In Slovak soil classification system, the content of authigenic carbonates is reflecting only on the level of soil *varieties*. Such approach is not reflecting their real meaning, nor the mission of classification system. We suppose as necessary in a new approximation of soil classification system to put it on higher classification level.
- Obtained results of our study offers a set of possible implications for understanding of loess, calcaric deposits and soil development. Very valuable information was obtained about the development of the landscape during the Quaternary.
- The study of the presence and spatial changes in the contents of authigenic carbonates in soil toposequences on loess and on fluvial loess and fluvial sediments of Danube Lowland, should attract more attention. From the vertical bonds analysis in soil profiles, is recommended to learn landscape systems, the integrity and functionality of which, depends on matter-energy flows in the landscape.

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