Carbonate accumulation morphology in a soil chronosequence in the southern Pre-Ural, Russia: Significance for Holocene paleoenvironmental reconstruction

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ABSTRACT

A chronosequence consisting of paleosols buried under kurgans of the Savromatian (2,500–2,600 yr BP) and the Late Sarmatian Time (1,700–1,800 yr BP), along with the modern Dark Kastanozems was studied in a dry steppe area of the southern Pre-Ural region, Russia. We focus on morphological features of carbonate accumulations, that occur as white soft spots (WSSs) at different scales of soil mass organization, to understand their role in paleoenvironmental reconstruction. The carbonate accumulations in Bk horizons of paleosols buried within the Savromatian period and of the modern Dark Kastanozems are similar in quantity but differ slightly in their diameter. Calcic features in the Savromatian paleosols are diverse and have signs of both dissolution (calcite crystals in voids) and segregation. Only in the Savromatian paleosols, desiccation cracks have broken the WSSs into pieces. We consider highly probable that the Savromatian paleosols formed under slightly drier and more continental climate than present. The Late Sarmatian paleosols are characterized by WSSs in Bk horizons with the largest size and greatest quantity, and their diversity is great enough to divide the Late Sarmatian paleosols into two morphological groups, 'upper' and 'lower', based on signs of dissolution. The 'lower' group shows no signs of dissolution, so we conclude that the WSSs formed in stable dry climatic conditions. Establishment of a more humid climate at the beginning of the Late Sarmatian period produced signs of dissolution preserved in the 'upper' group that was buried late in this chronointerval. The WSSs in the modern soils have the clearest signs of dissolution compared with other soils in the chronosequence, which we interpret to indicate that the modern climate is likely the most humid interval of the late Holocene. Detailed investigation of morphological peculiarities of carbonate accumulations on the different scales of soil mass organization in the chronosequences of steppe soils is a valuable source of information on the paleoecological situation of Holocene climate intervals and can be successfully used for that aim.

Key words: pedogenic carbonates, soil chronosequence, Kastanozems, Holocene, Russia.

RESUMEN

Se estudió una cronosecuencia consituida por paleosuelos sepultados bajo kurgans del Savromatiano (2,500–2,600 yr BP) y del Sarmatiano tardío (1,700–1,800 yr BP), así como por Kastanozems oscuros modernos, en un área de estepa seca de la región Meridional pre-Ural en Rusia. Nos enfocamos en las características morfológicas de acumulaciones de carbonatos, presentes como manchas blancas suaves (WSSs) a diferentes escalas de organización de la masa del suelo, para entender su papel en la reconstrucción paleoambiental. Las acumulaciones de carbonatos en los horizontes Bk de paleosuelos sepultados durante el Savromatiano y de Kastanozems oscuros son similares en cantidad *pero difieren ligeramente en su diámetro. Los rasgos cálcicos en los paleosuelos Savromatiano son diversos y muestran signos de disolución (cristales de calcita en huecos) y segregación. Únicamente en los paleosuelos del Savromatiano se observa que las grietas de desecación han roto en pedazos las manchas blancas suaves (WSSs). Consideramos muy probable que los paleosuelos del Savromatiano se hayan formado bajo un clima ligeramente más seco y continental que el actual. Los paleosuelos del Sarmatiano tardío se caracterizan por tener WSSs en los horizontes Bk con el mayor tamaño y en mayor cantidad; su diversidad es suficientemente amplia para dividir a los paleosuelos del Sarmatiano tardío en dos grupos morfológicos, "superior" e "inferior", con base en los signos de disolución. El grupo "inferior" no muestra signos de disolución, por lo que se concluye que los WSSs se formaron en condiciones climatológicas secas y estables. El establecimiento de un clima más húmedo al inicio del Sarmatiano tardío produjo signos de disolución preservados en el grupo "superior", que fue sepultado tardíamente en este cronointervalo. Los WSSs en los suelos modernos muestran los signos más claros de disolución en comparación con los otros suelos en la cronosecuencia, lo que interpretamos como indicio de que el clima moderno es probablemente la fase más húmeda del Holoceno tardío. Una investigación detallada de las peculiaridades morfológicas de las acumulaciones de carbonatos en las diferentes escalas de organización de la masa del suelo, en cronosecuencias de suelos de estepa, es una valiosa fuente de información sobre la situación paleoecológica de los climas del Holoceno que puede ser usada con éxito para ese propósito.*

Palabras claves: carbonato pedogenético, cronosecuencias de suelos, Kastanozem, Holoceno, Rusia.

INTRODUCTION

The study of paleosols buried under archaeological settlements or monuments such as funeral mounds (kurgans) is widely used to reconstruct paleoenvironments of the Holocene for different world regions (Stewens and Walker, 1970; Yaalon, 1971; Limbray, 1975; Vreeken, 1975; King *et al.*, 1978; Holliday, 1989; Barba, 1994) and particularly Russia (Zolotun, 1974; Veklich *et al.*, 1979; Akhtyrtsev and Akhtyrtsev, 1986; Gennadiev, 1990; Ivanov, 1992; Demkin, 1997; Dergacheva, 1997; Alexandrovskiy, 2002). Among properties of paleosols buried under kurgans in the steppe zone of Russia, the characteristics of humus and soluble salts have been studied in detail and their paleoenvironmental interpretation is more or less similar. The researchers have also paid much attention to carbonates in these paleosols. In most cases, the depth of carbonates (established by reaction with HCl), total carbonate content, and carbonate resources in the solum (upper 1 or 2 m) as well as field morphology were used to characterize the carbonate profile.

At the same time, it may be assumed that the morphological peculiarities of pedogenic carbonate accumulations studied at different scales of soil mass organization have not been used for paleoecological reconstructions, but their study may be highly informative and should be considered. This assumption is based on some previous studies where the morphology and rate of carbonate accumulation in modern soils and paleosols seem to be connected with certain environmental conditions of a region and/or chronointerval studied, as shown in a number of soil climo- and chronosequences in semiarid and arid regions (Kubiena, 1938; Gile *et al.*, 1966; Wieder and Yaalon, 1982; Birkeland, 1984; Reheis, 1987; West *et al.*, 1988; Polyakov, 1989; Gile, 1993, 1995; Verrecchia and Verrecchia, 1994). Detailed morphological studies of carbonate neoformations proved useful in paleoclimatic interpretation of Pleistocene paleosols in loess-paleosol sequences (Kemp, 1995; Becze-Deak *et al.*, 1997) and of Holocene Chernozems (Khokhlova *et al.*, 2001).

The main aim of this work was to study the morphological features of carbonate accumulations on different scales of soil mass organization in a soil chronosequence in the dry steppe area of the southern Pre-Ural, and to understand the utility of these characteristics for paleoenvironmental reconstruction.

OBJECTIVES AND METHODS

The study site is located near Pokrovka village in Sol'-Iletsky district, Orenburg region (50°55'N, 54°33'E). Geomorphologically, this territory belongs to the Poduralskoje Plateau, in the southeastern end of the Southern Ural mountain range (Figure 1). Relief is slightly rolling with predominant heights of about 100–300 m. The climate is continental; mean January temperature is -10°C, July +28°C. Mean annual precipitation is about 300 mm, potential evaporation is two times higher than precipitation. Natural vegetation of the research area has been totally destroyed by agricultural tillage. The predominant modern soils of the area are Dark Kastanozems that formed in stratified alluvial loams.

The key site of our study is the Pokrovka 10 burial ground situated on the true surface of the first terrace of the Ilek and Khobda rivers (tributaries of the Ural river), two kilometers south of Pokrovka village. Archaeological excavations of this ground with more than 100 kurgans have

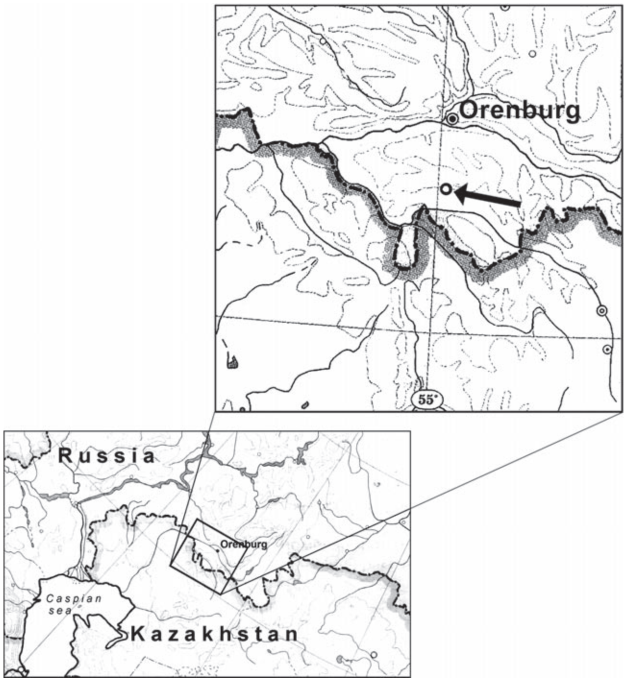


Figure 1. Map of the research area. Arrow shows the location of the study site near Pokrovka village in Sol'-Iletsky district, Orenburg region.

been carried out since 1995 under the leadership of Prof. L.T. Yablonsky (Institute of Archaeology, RAS, Moscow).

We studied a chronosequence consisting of paleosols buried under kurgans of the Savromatian (2,500–2,600 yr BP) and the Late Sarmatian (1,700–1,800 yr BP) periods, along with the modern Dark Kastanozems (surface soil not ever buried under a kurgan). The kurgans have been dated archaeologically and provide the age of burial and cessation of pedogenesis that has been continued for the modern Dark Kastanozems (a pre-incisive chronosequence in the sense of Vreeken, 1975). Details of morphological and some chemical properties of the soils in the chronosequence have been described previously (Khokhlova and Khokhlov, 2002).

The only carbonate accumulations found in the soils of the chronosequence are white soft spots (WSSs). The depth of occurrence in each soil profile varied vastly in connection with the variability of parent rock texture and location of each soil profile in mesorelief, so that we could not logically study the regularity of changes in WSSs depths in each age group of paleosols. In the field, the quantity and diameter of WSSs in Bk horizons of all soils in the chronosequence were determined in 10 x 10 cm squares by means of morphometric analysis. Then, the average quantity and diameter of WSSs were estimated for the Bk horizon as a whole in each soil.

For the morphological investigation, duplicate samples of WSSs, inlcuding surrounding soil mass, with undisturbed structure, were collected. From one sample, thin sections were made for examination under the polarizing microscope. The other sample was investigated under a binocular microscope and the most indicative areas were studied under a scanning electron microscope (SEM).

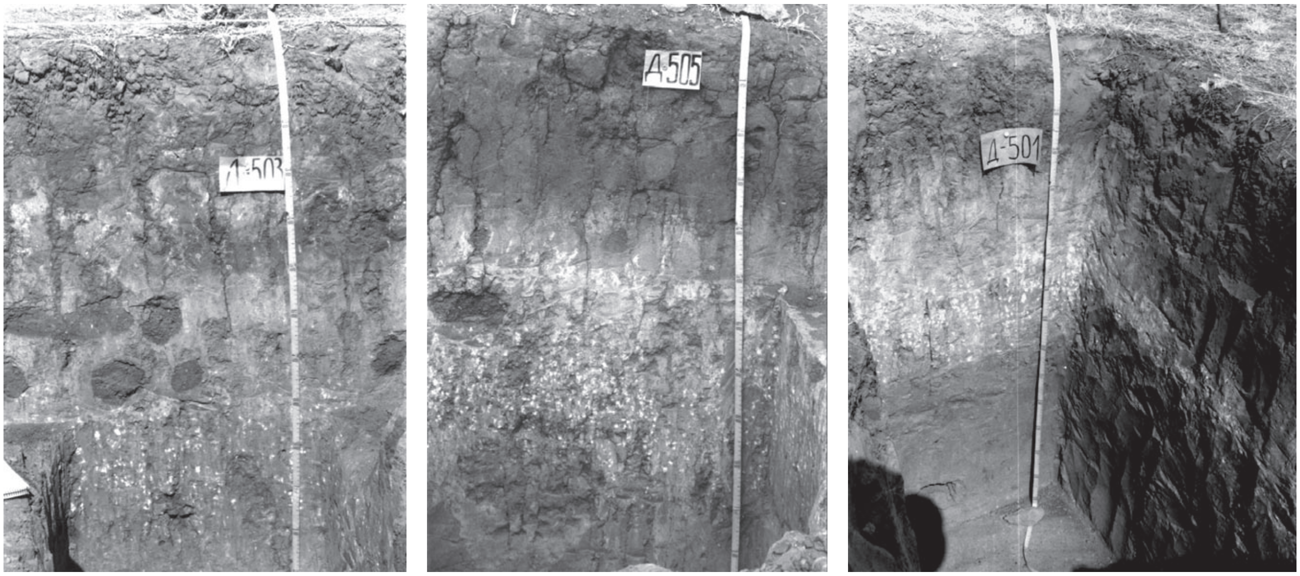
In addition, samples of WSSs and of soil mass without visible carbonate accumulations (SM) were collected from the walls of all pits with a knife. The mineralogical composition of WSSs and SM was analyzed by means of differential thermal analysis and X-ray diffraction. The thermal analysis was used to determine the carbonate content and the characteristics of calcite lattice in the WSSs.

RESULTS

During the study of carbonate profiles of buried paleosols, we first had to detect diagenetic carbonates formed after burial. In the paleosols of the chronosequence, these carbonates are situated only in the uppermost buried horizon A1, 0–20(25) cm. Morphologically, they are represented by gray faint filaments on the pit walls and differ considerably from the WSSs. Nowhere, diagenetic carbonates and WSSs occurr at the same horizons. WSSs are separated from the diagenetic carbonates by a 20–40-cm thick layer with no visible carbonate accumulations. Because of this, the diagenetic carbonates do not interfere with the study of the carbonate profile in the Bk horizons of the paleosols.

The characteristic soil profiles of each chronointerval are presented on the field photos of the pits studied (Figure 2). The most important result of morphometric analysis of WSSs in Bk horizons is the occurrence of considerable differences in the patterns of paleosols buried during the Late Sarmatian Time (1,700–1,800 yr BP). The WSSs in Bk horizons of paleosols buried at that time are larger and more abundant than in the Savromatian paleosols and in the continuously forming modern Dark Kastanozems (Figure 3). In addition, considerable heterogeneity in the size and quantity of WSSs in the Late Sarmatian paleosols as a group was observed. On the basis of the diameter and quantity of WSSs in Bk horizons, the Late Sarmatian paleosols have been subdivided into an 'upper' and a 'lower' group (Figure 3). The soils with WSSs in larger quantity, most uniform, and with the largest diameters are referred to as the 'upper' group, and the soils with WSSs in lesser quantity and extremely heterogeneous diameters as the 'lower' group. The WSSs in Bk horizons of paleosols buried within the Savromatian period and of the modern Dark Kastanozems occur in similar quantity but differ slightly in their diameter. The chronology and patterns of average morphometric characteristics of WSSs in Bk horizons in the soil chronosequence are shown in Figure 4.

In thin section, compact calcic features can be observed in the Bk horizon of the Savromatian paleosols. Some of these features have homogeneous texture and absolute undisturbed fabric, whereas others show signs of dissolution and recrystallisation on their periphery. Some



a) b) c)

Figure 2. Field photographies of the pits studied. a) Savromatian paleosol; b) Late-Sarmatian paleosol; c) modern Dark Kastanozem.

large calcic features consist of many smaller size features. Boundaries between the small-size calcic features are marked by mobile microcrystalline calcite. All this diversity of calcic pedofeatures can be found in the same horizon of the Savromatian paleosols (Figure 5a, b). The soil mass is considerably impregnated by calcite grains but the boundaries between calcic features and plasma are abrupt (Figure 5c). Under the SEM, the calcic features in the Savromatian paleosols look as a compact homogeneous mass of crystals with small rounded hollows on the feature surface (Figure 5d). Calcite crystals have different size, imperfect habit, and some planes formed at different phases of crystal growth. Some of the crystals have etching pits (Figure 5e). The most characterizing peculiarity of calcic features morphology that occurs only in the Savromatian paleosols is the presence of desiccation cracks that divide a feature into parts (Figure 5f).

The morphological habit of WSSs of the 'upper' and

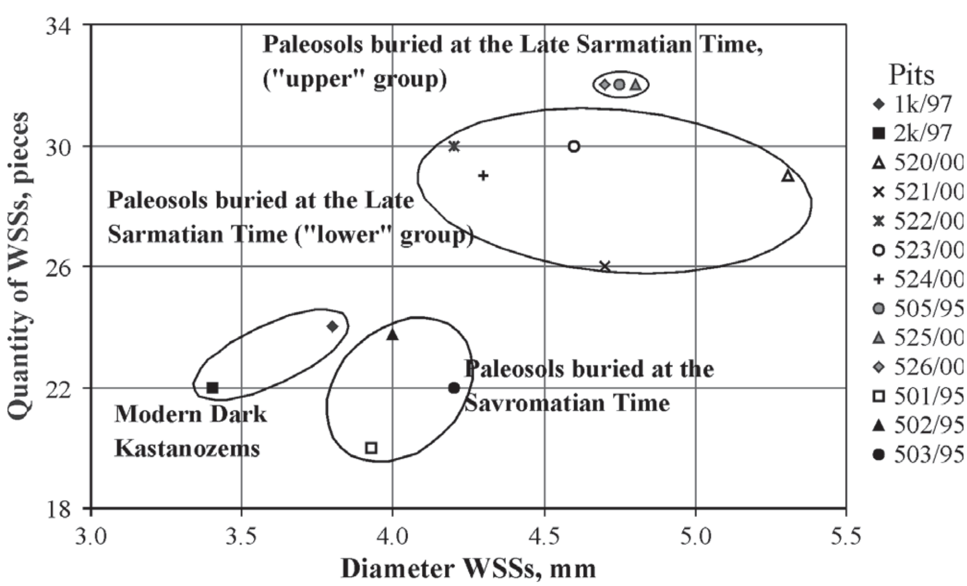


Figure 3. Morphometric data of carbonate accumulations (white soft spots, WSSs) occuring in Bk horizons from modern Dark Kastanozems and from paleosols buried at different time.

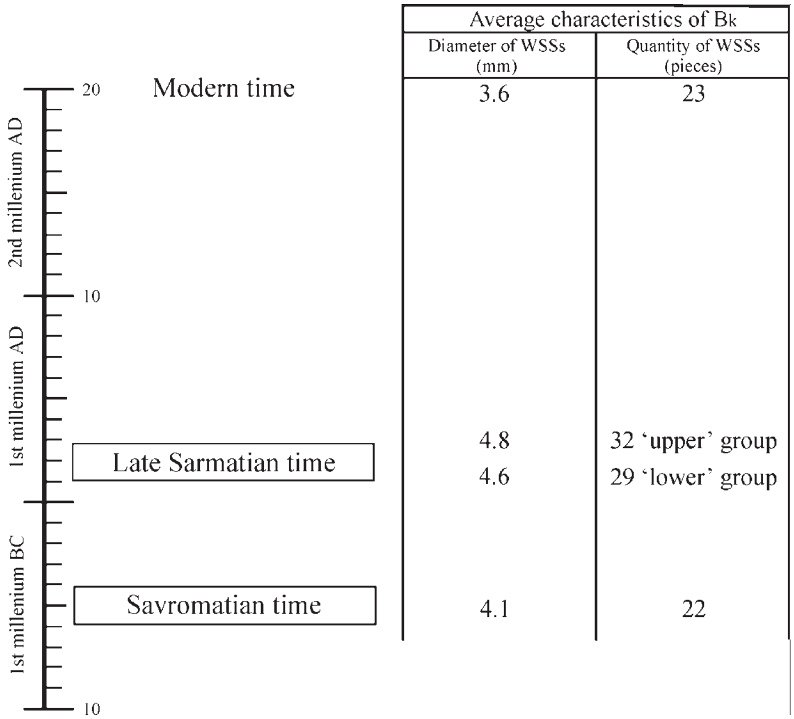


Figure 4. The chronology and pattern of average WSSs characteristics in Bk horizons in the soil chronosequence.

'lower' groups of the Late Sarmatian paleosols differs clearly, as shown in Figure 3. Mesomorphologically, the WSSs in the paleosols of the 'upper' group are surrounded with a halo of dissolved and redeposited calcite crystals whereas the WSSs of the 'lower' group mostly do not have such halos.

In thin section, the samples of the 'lower' group of Late Sarmatian paleosols show relatively homogenous internal fabric of calcic features, weakly expressed cracks, clusters of microcrystalline calcite located in few voids (Figure 6a), and abrupt boundaries between features and soil mass (Figure 6b). Under the SEM, the surface of features in Bk horizons of the 'lower' group is homogenous, without cracks, and covered with a thick layer of equal, elongated, and perfect calcite crystals (Figure 6c, d). In these paleosols, the process of a new calcic feature developing on a grain of another mineral was observed. The other mineral grains were observed partially covered with calcite crystals (Figure 6e) or completely covered (Figure 6f).

In the samples of the 'upper' group of Late Sarmatian paleosols, the large calcic features are conglomerates of small bounded features. These conglomerates are rather compact and, while rare, voids with separated microcrystalline calcite grains may occur inside (Figure 7a). Large calcic features consisting of loose packed small ones and without microcrystalline calcite inside of voids are also present (Figure 7b). The calcic features have clear signs of dissolution: some 'scours' and cracks occur on the surface of features, and calcite crystals have irregular indented edges and etching pits (Figure 7c, d).

Micromorphologically, the modern Dark Kastanozems show signs of total calcic feature dissolution in the upper part of Bk horizons. Many calcite crystals are present in voids and the boundaries between calcic features and soil mass are diffuse (Figure 8a). Internal fabric of calcic features is characterized by the presence of large cracks with dissolving calcite crystals and small cracks that are just marked (Figure 8b). In the lower part of the Bk horizon, the process of calcic features decomposition is observable. The boundary between the feature and soil mass is diffuse (Figure 8c), but no mobile calcite crystals are observed in the voids of the SM (Figure 8d). Under SEM, the modern soil has the largest scours and cracks, and fell into separate pieces, in contrast with the compact calcic features observed in the Savromatian and Late Sarmatian paleosols (Figure 8e). Under the largest magnification, calcite crystals on the surface of the feature have different sizes plus etching pits on the edges (Figure 8f).

The thermal analyses demonstrate that the highest calcite contents in WSSs and the lowest in the SM occur in the Late Sarmatian paleosols (Table 1). Decomposition temperatures of WSSs in the Savromatian paleosols are the lowest, indicating that calcite crystalline lattice of the WSSs is imperfect and disordered compared to the Late Sarmatian paleosols and modern Dark Kastanozems. On the contrary, the WSSs of the Late Sarmatian paleosols showed the highest temperatures at the end of structural decomposition, which indicates a more perfect structure of calcite lattice.

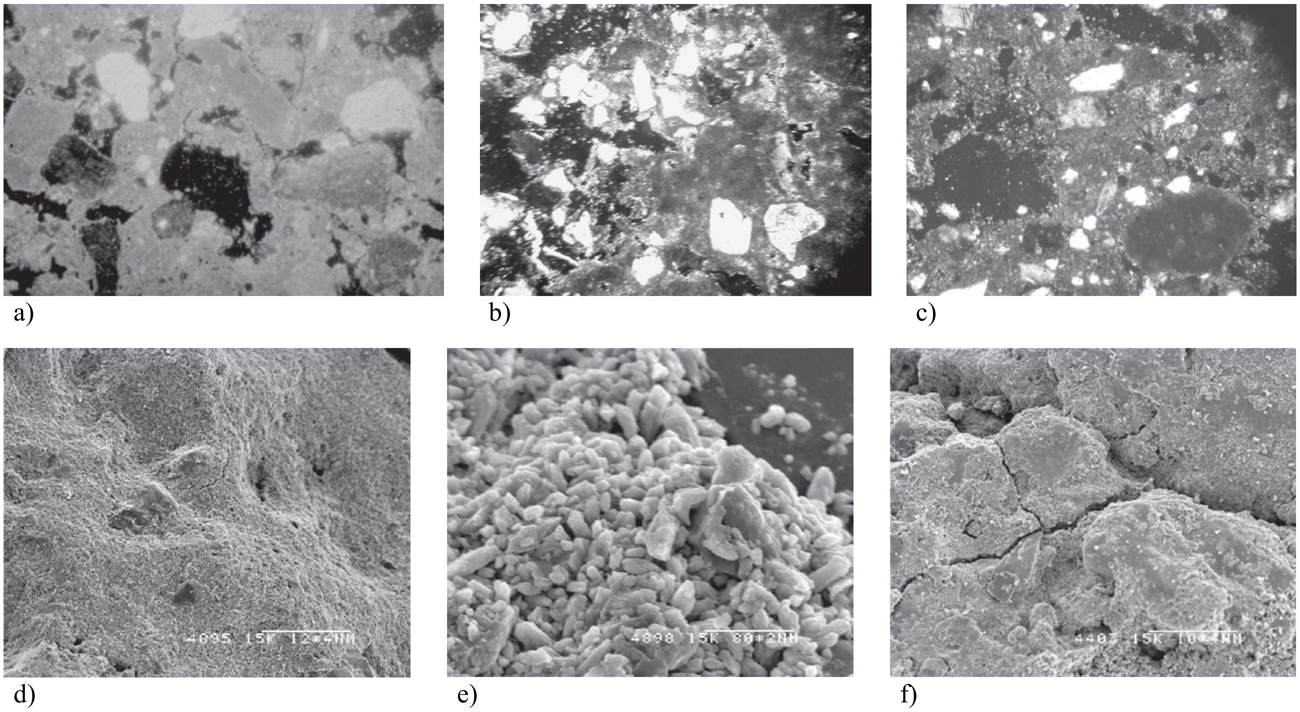


Figure 5. Microstructure and submicrostructure of calcic features in the paleosols buried at the Savromatian time. a) compact calcic features of undisturbed fabric with signs of dissolution on periphery, XPL; b) small size calcic features form a large one with mobile microcrystalline calcite between them, XPL; c) abrupt boundary between a compact undisturbed calcic feature and plasma impregnated by calcite, XPL; frame width of photos a–c is 3.4 mm; d) compact homogeneous mass of calcite crystals with small rounded hollows on the feature surface, 250x; e) calcite crystals of different size, imperfect habit, crystals with planes formed at different phases of crystal growth, and rare etching pits on crystal edges, 3800x; f) dessication cracks dividing a feature into parts, 300x.

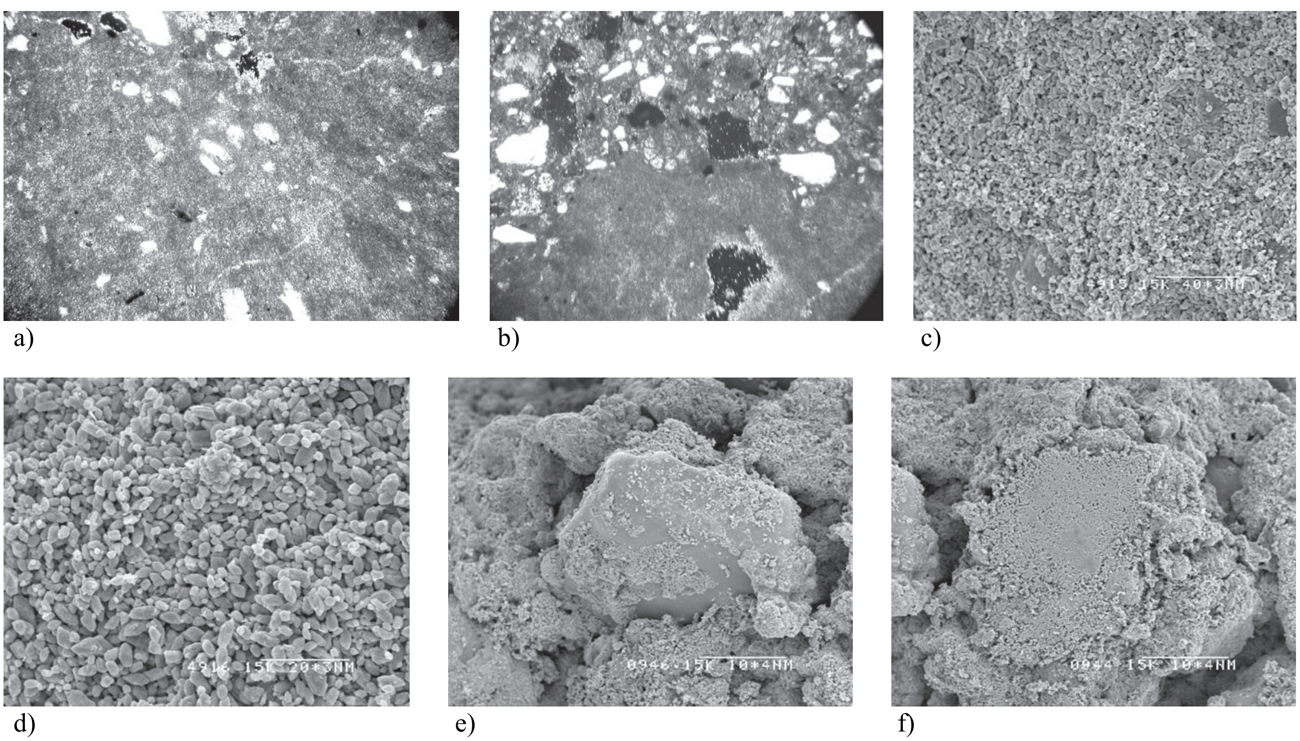


Figure 6. Microstructure and submicrostructure of calcic features in the paleosols buried at the Late Sarmatian time ('lower' group). a) homogenous fabric of calcic feature with weakly expressed internal cracks, XPL; b) abrupt boundary between calcic feature and plasma, XPL; frame width of photos a and b is 3.4 mm; c) homogenous surface of a calcic feature without cracks, 750x, d) thick layer of equal, elongated and perfect calcite crystals on the feature surface, 1500x; e) non-calcite mineral grain partially covered with calcite crystals, 300x; f) non-calcite mineral grain completely covered with calcite crystals, 300x.

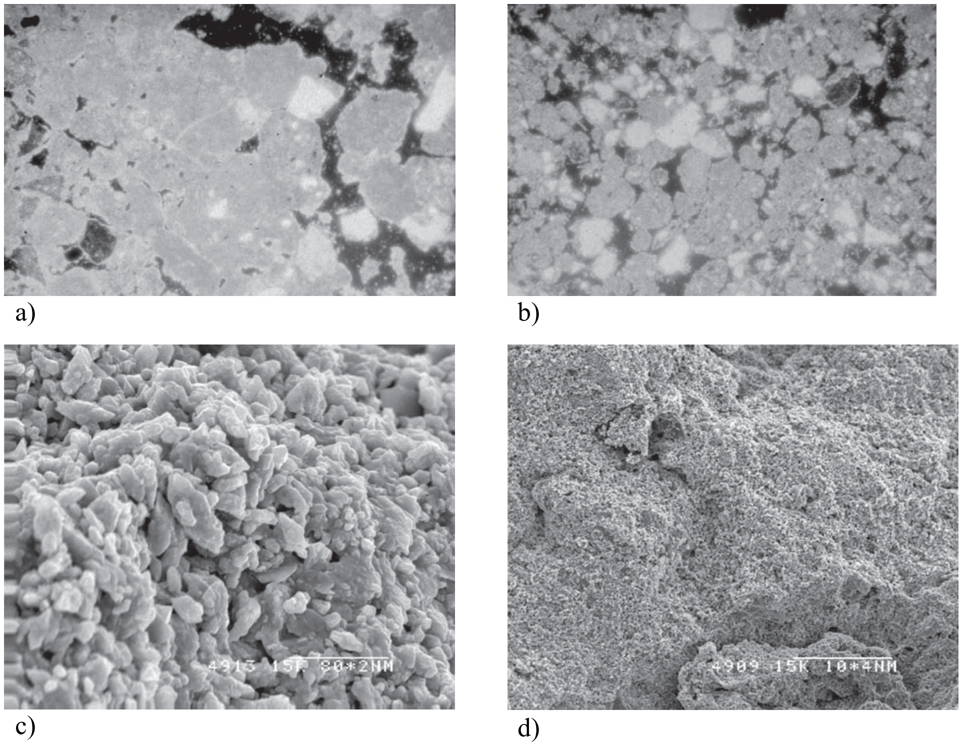


Figure 7. Microstructure and submicrostructure of calcic features in the paleosols buried at the Late Sarmatian time ('upper' group). a) rather compact large feature consisting of small ones, rare microcrystalline calcite grains in voids, 'splicing' of small features in a large void, XPL; b) large calcic feature consisting of loose packed small ones and without microcrystalline calcite inside the voids, XPL; frame width of photos a and b is 3.4 mm; c) calcite crystals with irregular indented edges and etching pits, 3800x; d) some 'scours' and cracks on the surface of a calcic feature, 300x.

DISCUSSION AND CONCLUSIONS

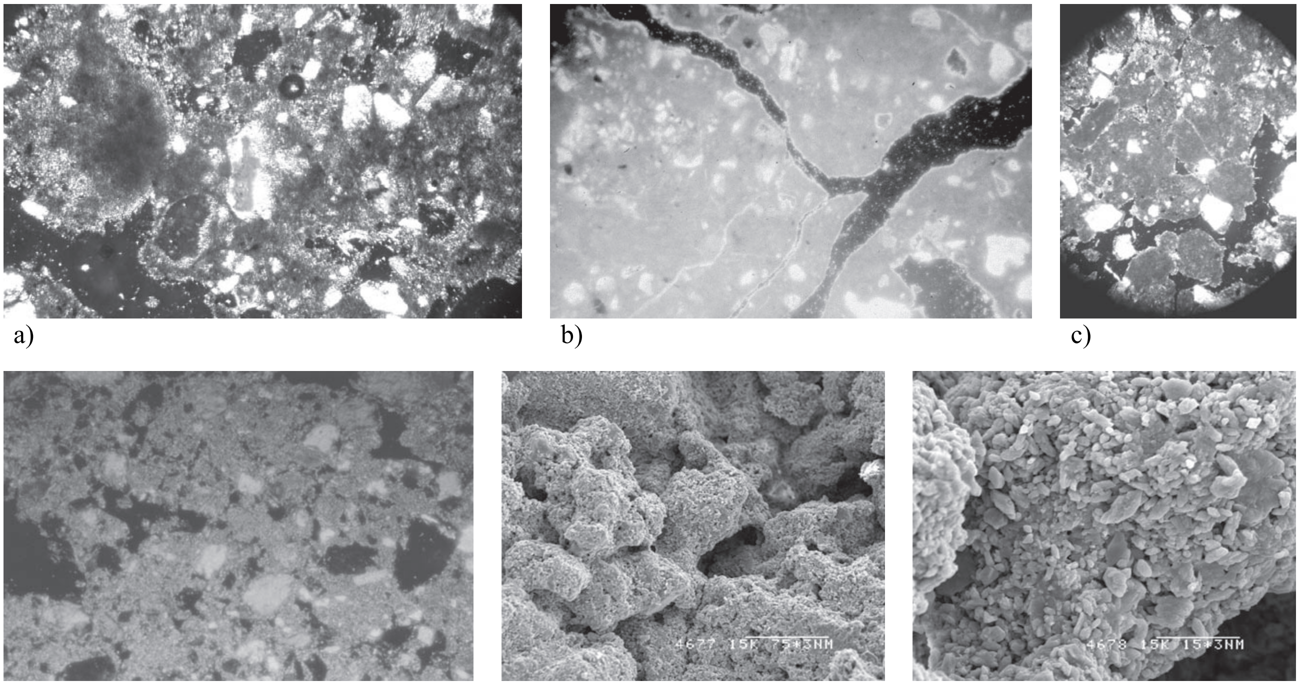
Based on these observations we tried to reconstruct the environmental conditions in different chronointervals of Early Nomads Age in the Southern Pre-Ural. The paleosols buried at the Savromatian time and the modern Dark Kastanozems have similar quantity of carbonate accumulations in Bk horizons but they differ slightly in diameter. The calcic features in the Savromatian paleosols are diverse and have signs of both dissolution (calcite crystals in voids) and segregation. Only in the Savromatian paleosols, desiccation cracks that had broken the WSSs into pieces occur. On the basis of such evidence, it is highly probable that the paleosols of the Savromatian time formed under slightly drier, and more continental and contrasting climate than that in the modern time.

The WSSs in Bk horizons of paleosols buried at the Late Sarmatian time are the largest in size and quantity of all soils in the chronosequence. In addition, on the basis of considerable heterogeneity in diameter and quantity of carbonate accumulations in those horizons, the Late Sarmatian paleosols have been divided into two groups: 'upper' and 'lower'. The morphology of the WSSs in paleosols of these two groups also differs by signs of dissolution. There are no signs of dissolution in the WSSs of the 'lower' group, only the process of new calcite crystal growth on the surface of carbonate accumulations or other minerals was observed. The WSSs of the 'upper' group are in the initial stage of dissolution.

We suggest that the WSSs of the 'lower' group of Late Sarmatian paleosols formed in stable dry climatic conditions. At the beginning of the Late Sarmatian time, the more humid and mild climatic conditions became established. Some Late Sarmatian paleosols with clear signs of WSSs dissolution ('upper' group in Figures 3 and 4) were likely buried at a later time than other paleosols of this chronointerval ('lower' group in Figures 3 and 4).

The WSSs in the modern soils have the clearest signs of dissolution compared with all other soils in the chronosequence. The climate of modern time is likely to be the most humid of the studied chronointervals (Savromatian and Late Sarmatian).

Our conclusion on the paleoenvironmental conditions of the chronointervals before and during the Late Sarmatian time in the Southern Pre-Ural region agrees with the data of other researchers of Holocene paleosols in the steppe zone of Russia. Several authors consider the period before the Late Sarmatian time was hot and dry, and that at the beginning of the Late Sarmatian time, it changed to milder and wetter paleoenvironmental conditions (Ivanov, 1992;



a) b) c) d) e) f)

Figure 8. Microstructure and submicrostructure of calcic features in the modern Dark Kastanozems. a) indistinct boundary between calcic feature and plasma, XPL; b) internal fabric of calcic feature, large cracks with mobile microcrystalline calcite inside and cracks just marked, XPL; c) decomposition of large calcic feature, XPL; d) entire impregnation of plasma by calcite, absence of mobile calcite in voids, XPL, frame width of photos a–d is 3.4 mm; e) large 'scours' and cracks on the feature surface, 400x; f) calcite crystals of different sizes and with etching pits on their edges, 2000x.

Ryskov and Demkin, 1995; Pesochina and Zaitsev, 1996). As for the climatic conditions in the Savromatian time, they are considered to be similar to the modern time. In particular, the same conclusion was made previously by us on the basis of the usual (field morphological observation and some analytical characteristics) properties of the soils in this chronosequence (Khokhlova and Khokhlov, 2002). The study of morphological features of the carbonate accumulations in the chronosequence allowed us to obtain more specific and unique information on the climatic conditions of the Savromatian Time.

Morphological analysis of the WSSs on different scales of soil mass organization allows us to consider the mechanism of their segregation–desegregation under the changing environmental conditions in this region at the different intervals of the last 2,500 years of the Holocene. With increasing aridization, the WSSs become larger due to consolidation of the small calcic features into larger ones; the quantity of WSSs in the Bk horizon increases as a result of their formation on new centers of crystallization. At the beginning of a humid stage, the sizes of WSSs grow slightly due to the looser packing of calcite crystals under recrystallisation and to the formation of halos around WSSs. In our opinion, this process takes place in a short time interval, perhaps 10s to 100 years. We suppose this process to be 'rapid' because of our observations in the paleosols under kurgans of a single relatively short archaeological period (for example, the Last Sarmatian time continued not more than 200 years). Then, parts of a calcic feature break away and a large feature disintegrates producing small ones. The smallest features are most likely to dissipate (or disperse) completely. These processes lead to decreasing sizes and quantity of WSSs in Bk horizons, however we consider this probably occurred over thousands of years. This process is considered to be relatively 'slow', because its results could not be seen in the paleosols of a single period but observed in the soil chronosequence as a whole.

In that range of the reconstructed climatic variation in the soil chronosequence, the processes of segregation–desegregation of carbonate accumulations (white soft spots, WSS) in the Dark Kastanozems of the southern Pre-Ural took place within the Bk horizon. We must recall that the loss of carbonate material outside this horizon was not observed morphologically. Data from thermal analysis supports this morphological observation; in the Late Sarmatian paleosols, subjected to the process of carbonate segregation, the $CaCO_3$ contents are high in the WSSs and low in the soil mass (SM), while in the modern Dark Kastanozems, subjected to carbonate desegregation and dispersion, the relationship patterns are reversed.

Our study shows that a detailed study of the morphological peculiarities of carbonate accumulations on the different scales of soil mass organization in the chronosequences of steppe soils is a valuable source of

Table 1. $CaCO_3$ content, thermal characteristics, and parameters of calcite lattice.

Pit, horizon	Sample	$CaCO_3$ (%)	Thermal analysis Temperature (°C) of structural decomposition			X-ray diffraction patterns
			begining	maximum	end	d_{104}
Paleosols buried at the Savromatian time (2,500 – 2,600 yr BP)						
D527/00, B1k	WSSs*	46.4	760	820	880	0.037
-II-	SM**	24.1	750	780	850	0.037
Paleosols buried at the Late Sarmatian time (1,700 – 1,800 yr BP)						
D517/97,B1k	WSSs	64.9	760	870	900	0.037
D518/97,B1k	WSSs	62.1	790	860	910	0.037
D522/00,B1k	WSSs	60.3	790	870	920	0.037
D524/00,B1k	WSSs	53.4	770	860	900	0.037
D525/00,B1k	WSSs	53.4	790	860	900	0.037
D526/00,B1k	WSSs	62.3	770	860	900	0.037
D517/97,B1k	SM	23.1	770	810	850	0.037
D518/97,B1k	SM	21.2	760	820	850	0.037
D522/00,B1k	SM	19.9	760	790	850	0.037
D524/00,B1k	SM	17.6	750	810	850	0.037
D525/00,B1k	SM	22.1	770	790	850	0.037
D526/00,B1k	SM	21.3	760	790	850	0.037
Modern Dark Kastanozems						
2K/97, B2k	WSSs	57.7	770	870	890	0.037
D519/97,B1k	WSSs	49.2	770	870	900	0.037
2K/97, B2k	SM	26.1	790	820	860	0.037
D519/97,B1k	SM	23.7	770	820	850	0.037

Note. *WSSs: carbonate white soft spots; **SM: Soil mass without visible carbonate accumulations

specific and unique information on the paleoecological conditions of different Holocene climatic intervals and can be successfully used for that aim.

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