

# Evolution of the Carbonate State of Agrogenically Transformed Dark Gray Forest Soils in the Central Forest-Steppe

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**Abstract**—The integrated study of the carbonate state of soils, which involves all the forms of soil carbonates at different levels of the soil organization, allows exactly assessing the degree and the rate of the soil transformation due to agricultural development. The evolution of the carbonate state in agrogenically transformed soils was assessed on a site with a known land-use history and with remaining natural soils. The direction, rate, and stages of the carbonate state transformation upon the agrogenic use of dark gray forest soils were determined on the basis of the morphogenetic analysis. Agricultural development entails a significant reorganization of the carbonate profile: a dark gray forest soil evolves into a medium-thick slightly podzolic chernozem with a greater pool of carbonates. The calcareous pedofeatures and horizons evolve stepwise: in the soil of a 100-year-old plowland, the transition to another organization of the carbonate state is observed: carbonates migrate more actively, and the dissolution–precipitation conditions are most dynamic. In the upper calcareous horizons, the structure of the calcitic pedofeatures becomes more collomorphic, and this mass fills almost all the voids; in the lower calcareous horizons, calcite is predominantly segregated into calcareous pedofeatures.

## INTRODUCTION

The carbonate state, which implies the totality of all the forms of soil carbonates at different levels of their organization in the soil [3], can be used, in combination with other types of soil diagnostics, as an indicator of the soil evolution under anthropogenic (including agrogenic) use. The integrated study of the carbonate state contributes to the exact and diverse assessment of the degree and rate of the soil transformation due to agricultural development, which is one of the most rapid and powerful factors affecting the properties of pedons at all the levels of their organization.

There are insufficient data on the temporal variation of the carbonate profile of forest-steppe soils due to plowing. The carbonate state of arable chernozems is relatively well studied (suppositions were made about the transformation of the carbonate profiles involving changes in their thickness and occurrence depth, the appearance of special forms of recent carbonates, the character of the migration processes [2, 6, 7], and the changes in the mobility and content of active carbonates [1]); however, only limited data are available about the carbonate-state variation in anthropogenically transformed gray forest soils of the forest steppe. The mechanisms and temporal scales of

the carbonate variation in both forest-steppe chernozems and gray forest-steppe soils also remain unstudied.

In our opinion, the carbonate-state variation in the agrogenically transformed soils can be assessed only on the fields with a known land-use history. In addition, such chronosequences should include natural soil analogues. The carbonate state in soil (agro)chronosequences during short time intervals (tens to a few hundred years) can be used for assessing the evolution of the dissolution–precipitation–recrystallization of carbonates. The morphological variation of the calcareous pedofeatures is the most telling illustration of the carbonate state dynamics and the evolution of the temporal changes in arable gray forest-steppe soils.

The main aim of this work was to reveal the direction, rate, and stages of the carbonate-state transformation upon the agrogenic use of soils on the basis of the +morphogenetic analysis.

## OBJECTS AND METHODS

The Polyana site under study is in the Shebekino region of Belgorod oblast (Fig. 1). This area belongs to the southern part of the central forest-steppe zone (south of the Central Russian Plain). The site under study is an interfluvial slightly inclined to the southwest

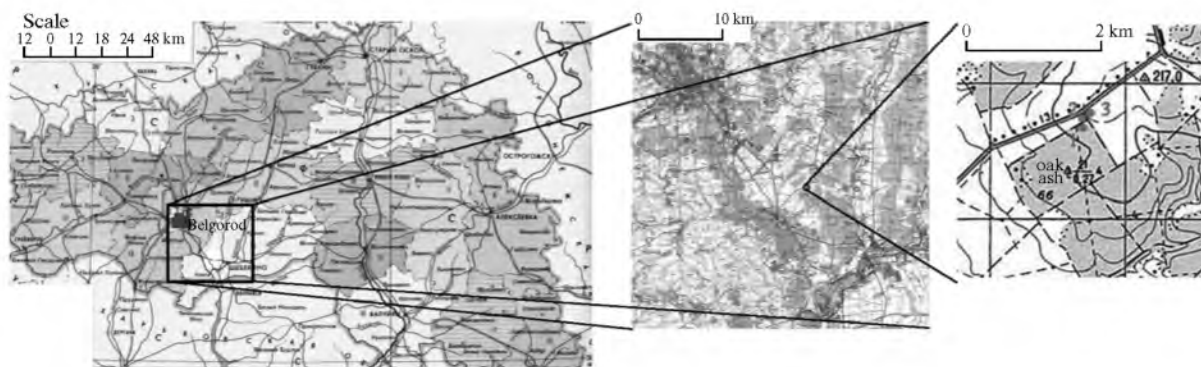


Fig. 1. The region under study and the location of the soil profiles.

between the valleys of the Severskii Donets and Koren' rivers. Before the intensive economic development (17th–18th centuries), it was completely covered by oak broad-leaved forests.

The agricultural development of the site began more than 200 years ago and stepwise covered more and more areas. According to the analysis of the land-use history, the soils were tilled with wooden plows and plows to a depth of 15–20 cm until the 1930s; the mechanical tillage of the plowland with tractors began later on. The depth of the plow horizon increased with time to reach 30–37 cm at present. The application of mineral and organic fertilizers began in the postwar years; according to the fertilization index, the soils can be classified as poorly cultivated (the application rates of manure never exceeded 5 t/ha).

The Polyana site consists of the following lands: natural broad-leaved forests and plowlands 100 and 150 years in age in the place of a broad-leaved forest. The considered lands occur under similar lithological–geomorphological conditions (a very gentle watershed slope of no more than 2°) on calcareous loess-like heavy loams and light clays (Fig. 2). On each land site, paired soil profile pits were dug 10 m from each other. These profiles can be considered as an agrochronosequence: soils unaltered by agricultural use, soils under agricultural use for 100 years, soils under agricultural use for 150 years.

The content of carbonates was determined by acidimetry. The density of the soil material was determined in situ in each of the profiles studied. The reserves of  $C_{CaCO_3}$  were calculated separately for the 0–100 and 0–200-cm layers. The morphology of the carbonates was studied for the upper and lower calcareous horizons (BtC<sub>Ca</sub>–BC<sub>Ca</sub>) of all the soils. Undisturbed soil monoliths taken from the calcareous horizons were studied with a polarization microscope. The morphology of small fragments from these monoliths was studied using a JEOL JSM-6380LA scanning electron microscope. For this purpose, the samples were covered with a thin metal (Au) layer to create electrical conductivity using an Eiko IB-3 ion coater.

The elemental composition of the separate segments of the samples under study was determined using a JED-2300 energy-dispersion spectrometer.

## RESULTS AND DISCUSSION

The studied background soil was located on a natural land occupied by an ash–maple forest with oaks and forest herbs. The soils under the forest have the following set of morphological horizons: A1 (0–17 cm)–A1A2(E) (17–28 cm)–A1A2(E)Bt (28–42 cm)–A2(E)Bt (42–59 cm)–Bt1 (59–84 cm)–Bt2 (84–119 cm)–BtC<sub>Ca</sub> (119–150 cm)–BC<sub>Ca</sub> (150–183 cm). The thickness of the humus horizon is 17 cm; the thickness of the humus profile is 42 cm. In the 17- to 42-cm layer, the podzolization zone determined from the grayish coating of skeleton is superimposed on the humus profile. In the lower part of the illuvial profile (the BtC<sub>Ca</sub> horizon), the processes of illuviation (forming brown organomineral cutans) and carbonatization (forming dispersed micellar carbonate forms) are superimposed. The effervescence is frequently observed from a depth of 126 cm. From its morphogenetic properties, the background soil was classified as a dark gray forest soil.

Soil profiles on the 100-year-old plowland were established 70 m from the background profiles. The soil under the 100-year-old plowland has the following set of genetic horizons: Ap (0–34 cm)–A1A2(E)Bt (34–45 cm)–A2(E)Bt (45–56 cm)–Bt1g (56–75 cm)–Bt2g (75–109 cm)–BtC<sub>Ca</sub> (109–140 cm)–BC<sub>Ca</sub> (140–185 cm). The plow horizon was formed by mixing the original A1, A1A2, and (partially) A1A2Bth horizons of the natural soil. Because of the plowing, which compacted the upper horizons and destroyed the structure of the soil, and the periodic wetting–drying, fine (0.5–1 cm) vertical cracks were formed in the profile of the arable soil, which are channels for the removal of humified suspensions from the upper part of the profile; their thin films on the walls of the cracks are observed down to depths of 100–110 cm (at the level of the lower Bt2g horizon). The size of the eluviation zone decreases due to the

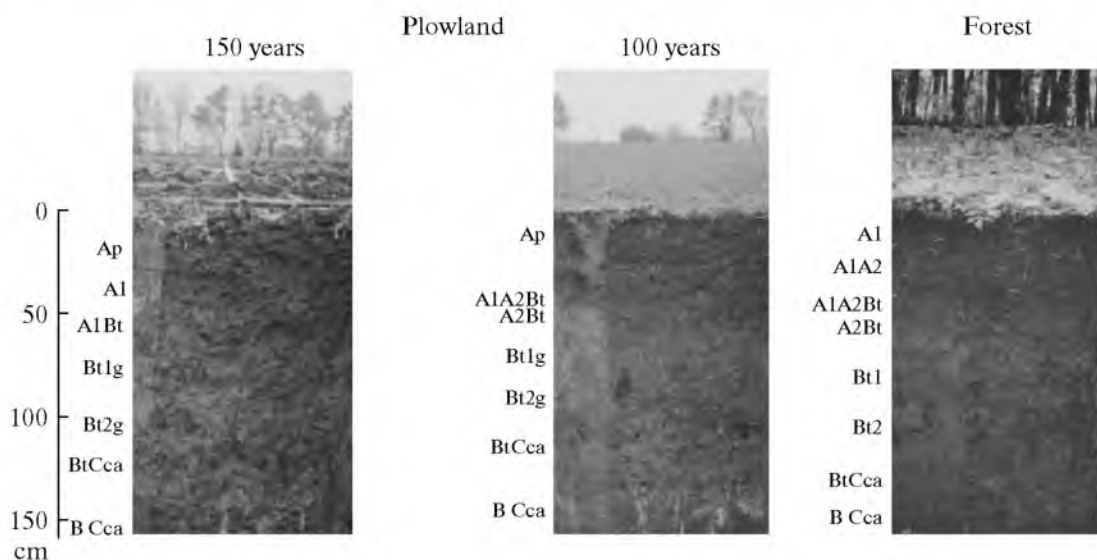
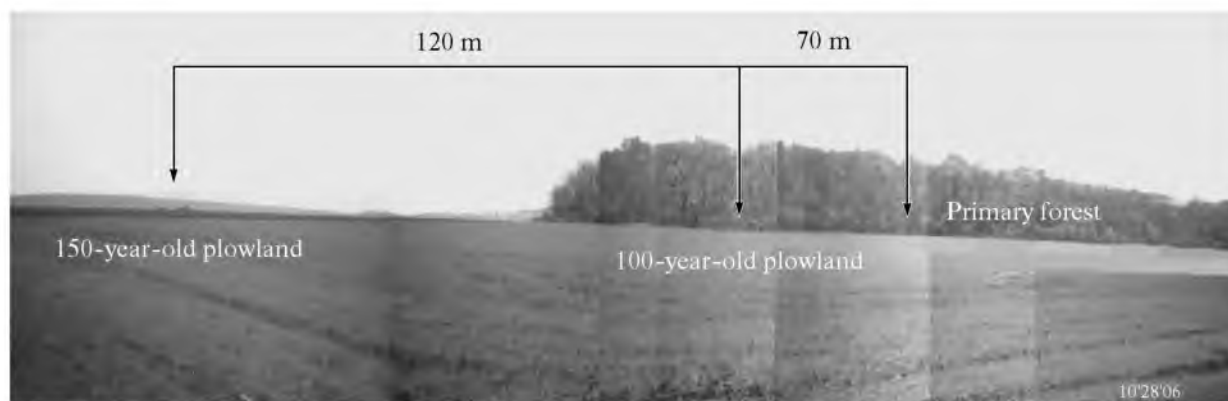


Fig. 2. The agrochronosequence: the soils under the forest and the 100- and 150-year-old plowlands.

formation of the plow horizon. At the same time, the redistribution of the skeleton, which are concentrated around the main cracks, is observed. The enhancement of leaching and suspension transfer could occur in these zones due to the more intensive infiltration of atmospheric precipitation. The illuvial horizons acquired a nonuniform color because of the appearance of slightly gleyed dovish brown zones; the content and size of the iron–manganese coats increase. The carbonate profile underwent the following macro-morphological changes: abundant whitish yellow mycelia-like veins of carbonates scattered in the soil material were observed in the BtC<sub>Ca</sub> and BC<sub>Ca</sub> horizons; marly carbonate accumulations appeared in the main cracks, which formed cutans covering the surfaces of prismatic aggregates.

The soil of the 100-year-old plowland was referred to as an arable surface-gleyic dark gray forest soil.

120 m to the northeast, soil profiles on the land under agricultural development for 150 years were studied. The soil has the following set of genetic hori-

zons: Ap (0–37 cm)—A1 (37–49 cm)—A1Bt (49–63 cm)—Bt1g (63–94 cm)—Bt2g<sub>Ca</sub> (94–127 cm)—BtC<sub>Ca</sub> (127–140 cm)—BC<sub>Ca</sub> (140–183 cm). An increase in the zone of humification and a decrease in the distribution zone of skeleton occurred in the profile of the old arable soil. Uniformly distributed carbonate veins and accumulations up to 0.5-cm-thick line the main cracks from a depth of 100 cm. Below 150 cm, separate aggregates are covered with vertically oriented whitish yellow carbonate accumulations; rare carbonate nodules are found. The soil of this land is a medium-thick slightly podzolized chernozem.

The level of effervescence in the soil of the 100-year-old plowland is reliably higher than that in the natural soil; no reliable difference in the occurrence depth of the carbonates was found between the old arable soil and the background (forest) soil. This variation is most probably not occasional, because a similar tendency (an increase in the effervescence line in the recently developed soil and a decrease in the old developed soil) was revealed in the study of the agrogenic evolution of dark gray forest soils on another site

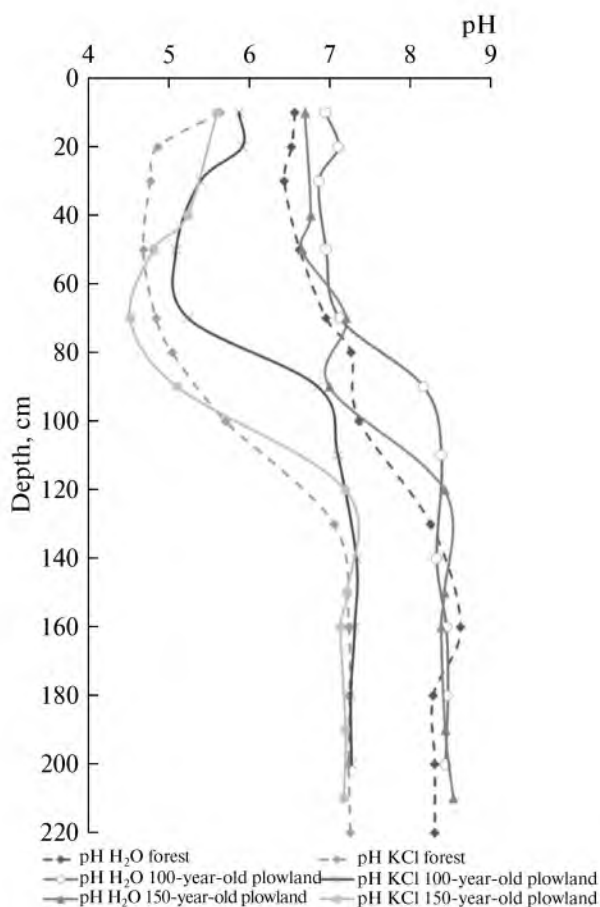


Fig. 3. The pH in the profiles of the agrochronosequence soils.

of typical forest-steppe in the Korocho district of Belgorod oblast [5].

The agricultural development of the dark gray forest soils resulted in the alkalization of the profiles, especially in the lower part of the soils studied (Fig. 3); the content and reserves of pedogenic carbonates also increased. The content and profile distribution of the carbonate CO<sub>2</sub> in the agrochronosequence is shown in Fig. 4. The horizons with the maximum accumulation of carbonates can be distinguished under the plow horizons at a depth of 100–150 cm in both soils; the content of carbonates above and below these horizons decreases. The highest content of carbonates was observed in the soil under the 100-year-old plowland; in the soils under the forest and the 150-year-old plowland, the content of carbonates is lower. This distribution of carbonates in the agrochronosequence well agrees with the reserves of CO<sub>2carb</sub> calculated for the different layers (Fig. 5). In the 0- to 100-cm layer, the appearance of CO<sub>2carb</sub> was noted only in the arable soils: the reserve of this layer was 12.6 t/ha in the 100-year-old plowland and slightly decreased to 8.6 t/ha in the 150-year-old plowland. At the same time, the reserve of carbonates in the 0- to 200-cm layer of the

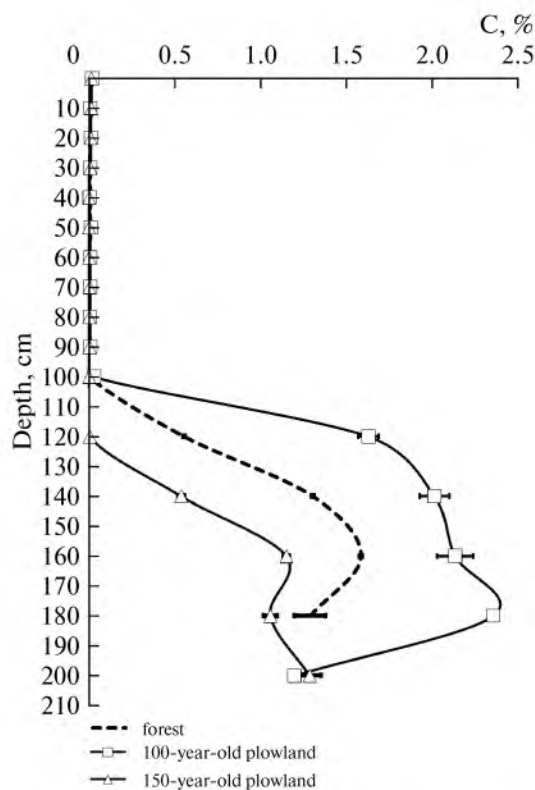


Fig. 4. The content and the horizon distribution of the carbonate CO<sub>2</sub> in the agrochronosequence.

soil under agrogenic development abruptly increased from 520.9 t/ha in the soil under the forest to 668.3 t/ha in the 100-year-old plowland and remained stable at the further agricultural use.

The carbonatization of the profiles of the arable dark gray forest soils is most probably related to the changes in the temperature and water regimes of the soils at the conversion of the forest to plowland. The

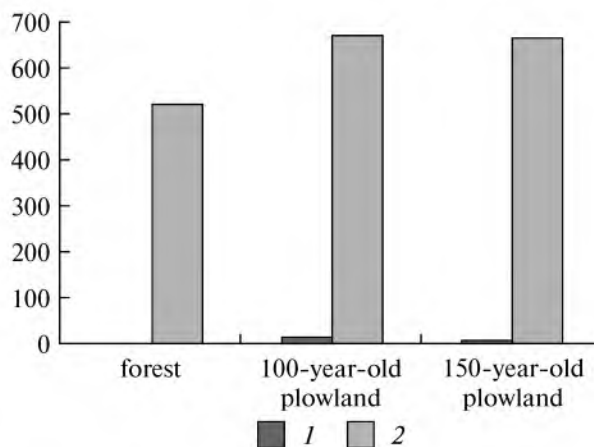
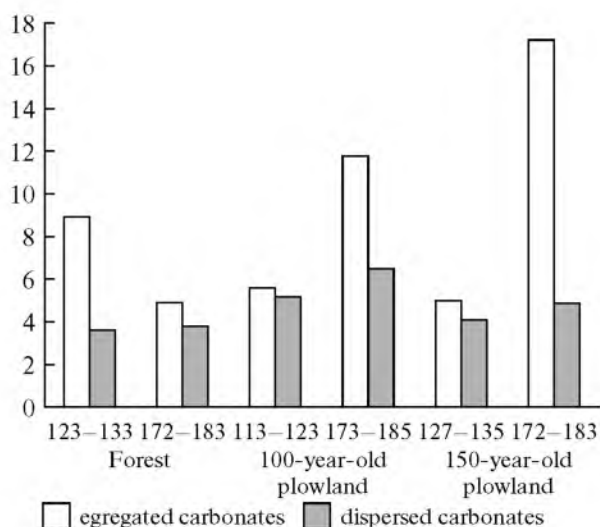


Fig. 5. The CO<sub>2carb</sub> reserves (t/ha) in the different layers of the agrochronosequence soils: (1) 0–100 cm; (2) 0–200 cm.



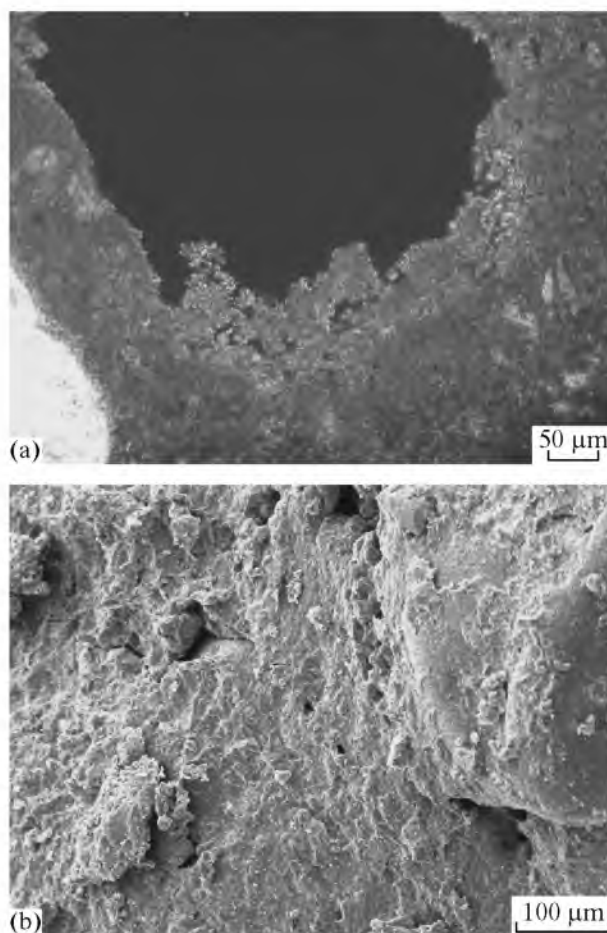
**Fig. 6.** Distribution of the segregated and dispersed carbonates (%) in the agrochronosequence; the numbers under each pair of samples indicate the depths of the sampling from the upper and lower calcareous horizons.

absence of permanent plant cover on the surface of the plowland results in its desiccation and the input of old carbonates with colloidal solutions from the subsoil layers, as was shown earlier for the chronosequences of paleosols buried under kurgans [4]. This migration of carbonates apparently increased their content in the agrologically used soils.

The distribution of segregated and dispersed carbonates, an important indicator of the carbonate state's dynamics, was also studied (Fig. 6). The most interesting fact is that the calcareous pedofeatures are dispersed and desegregated in the upper calcareous horizons during the agroevolution, while a tendency toward the consolidation of the calcareous pedofeatures is observed in the lower calcareous horizons. A similar tendency in the dynamics of the carbonates in the entire soil material was also revealed in the micro- and submicromorphological studies of monoliths from the upper and lower calcareous horizons of all the soils.

No migration of calcite is observed in the pores of the upper calcareous horizon of the soil under the forest; the pores are almost empty. Small and medium fragments of lithogenic detritus are found. The plasma is highly saturated with carbonates; there are well-shaped small contractions in the plasma and microzones with different degrees of carbonate saturation (Fig. 7a). The carbonate concentrations are very loose; collomorphic carbonate films, although thin, imitate the relief of the silicate material; the pores are empty. All the calcareous pedofeatures have traces of in situ etching (Fig. 7b).

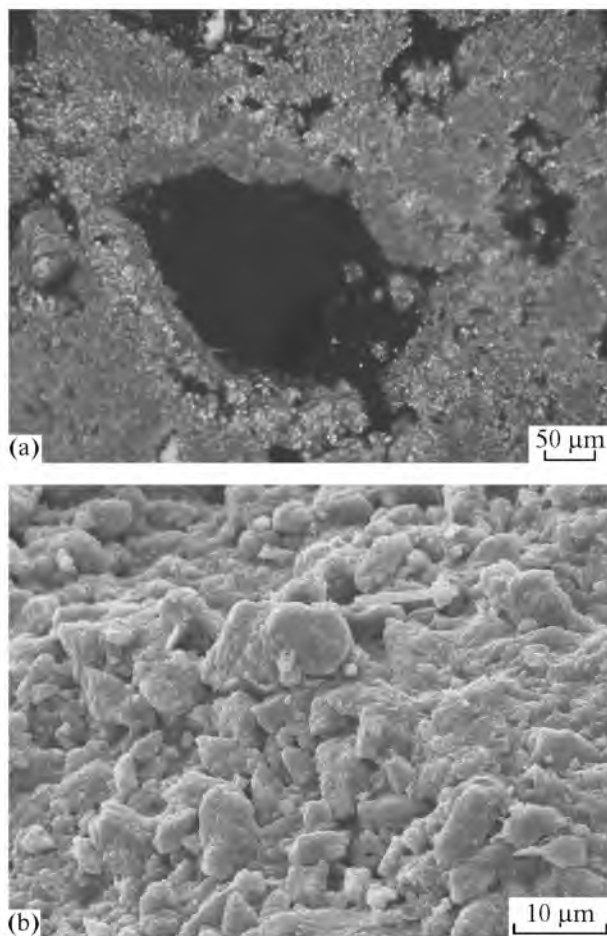
In the lower calcareous horizon of the soil under the forest, the saturation of the plasma with carbonates is lower than in the upper sample. Concentrations in



**Fig. 7.** Micro- and submicromorphology of the upper calcareous horizon in the soil under the forest: (a) empty pores and small carbonate concentrations in the plasma; (b) thin collomorphic films imitating the relief of the bulk soil mass.

the pores are clearly distinguished from the plasma slightly saturated with carbonates (Fig. 8a). Visually, the carbonate concentrations are more massive: the crystallomorphic forms are distinct and large, but the sample is completely covered with a collomorphic film, which is thicker than in the upper sample and smoothes the relief more (Fig. 8b). Lithogenic detritus is also found.

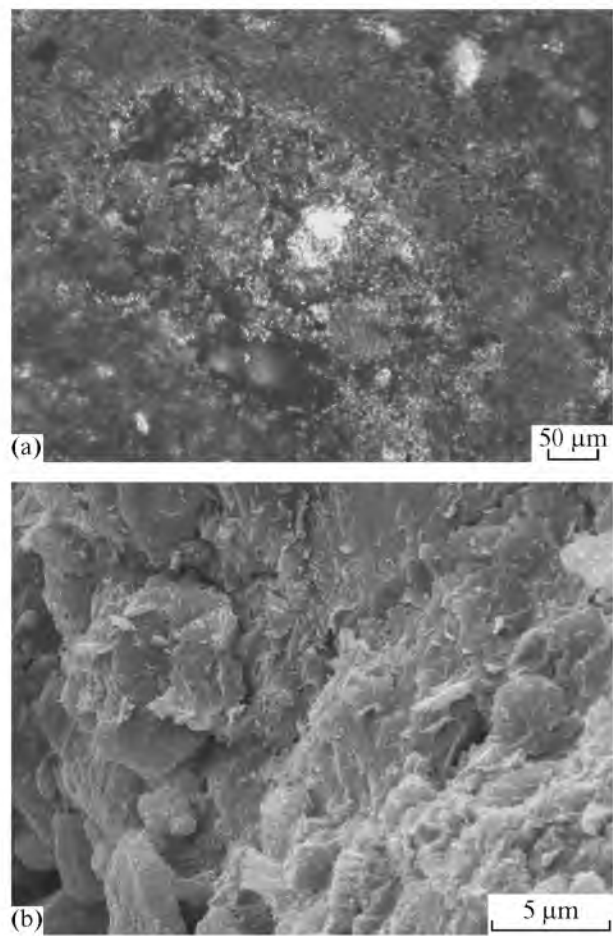
In the upper calcareous horizon of the soil under the 100-year-old plowland, there are acicular calcite and multiple carbonate concentrations in the pores. The stages of intrusion of acicular calcite into the plasma are visible; even the grains of lithogenic carbonate detritus are sometimes surrounded by such calcite; there are microzones of skelsepic plasma fabric (Fig. 9a). The carbonate concentrations are fine-crystalline; there are imperfect acicular shapes. The collomorphic calcite is well pronounced (Fig. 9b). This sample illustrates the early stage of pore filling with calcareous material.



**Fig. 8.** Micro- and submicromorphology of the lower calcareous horizon in the soil under the forest: (a) plasma not very saturated with carbonates; (b) more massive collomorphic film.

In the lower calcareous horizon of the 100-year-old plowland, the plasma is highly saturated with carbonates, carbonate concentrations are found in the pores and plasma, and microzones with skelsepic plasmic fabric are observed. Lithogenic carbonate detritus is recrystallized at the periphery; completely recrystallized fragments are also found (Fig. 10a). Various shapes of calcite crystals were revealed: large, small, acicular, rodlike, and flaky ones. The soil material is covered with calcite films of different thicknesses. The pores are almost completely filled with crystallomorphic carbonates (Fig. 10b).

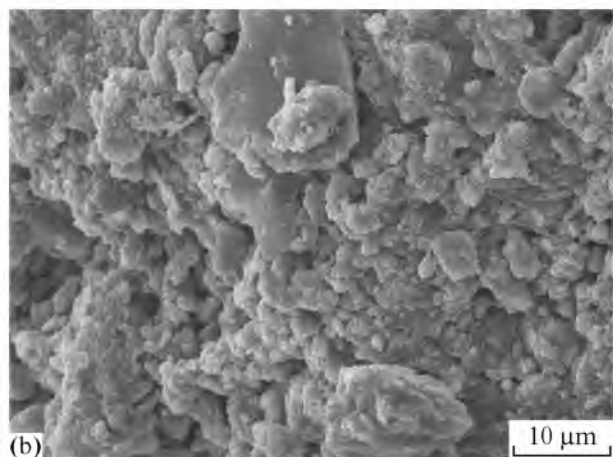
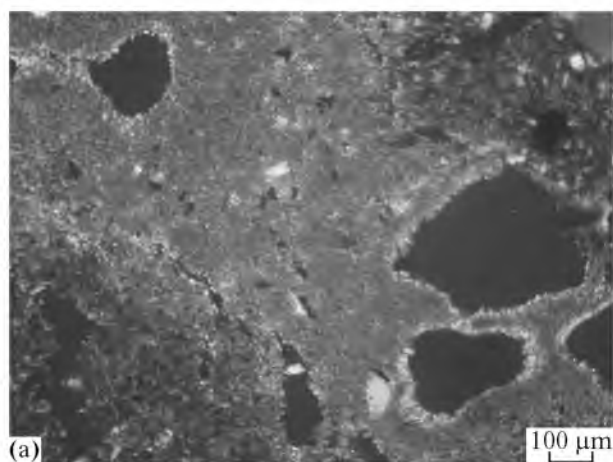
The upper calcareous horizon of the 150-year-old plowland is characterized by the lattisepic fabric of the clay-carbonate plasma and rare microzones of skelsepic orientation of carbonates. The grains of the mineral skeleton are coated with the carbonate plasma; they are sunk in it; no crystallized carbonates are visible (Fig. 11a). Only rare pores with intergrown needles remain. The submicromorphology of the carbonates is characterized by large sinter formations smoothing the



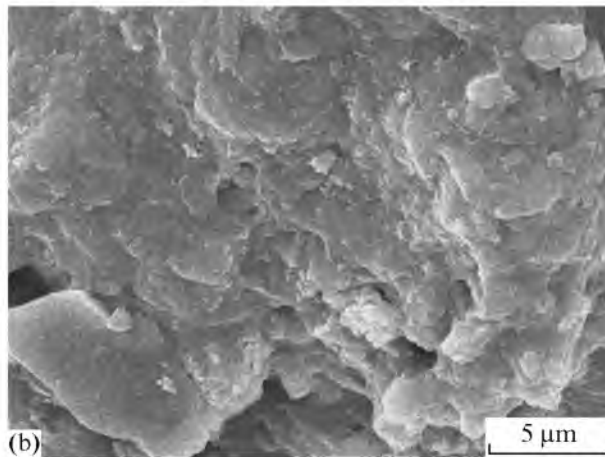
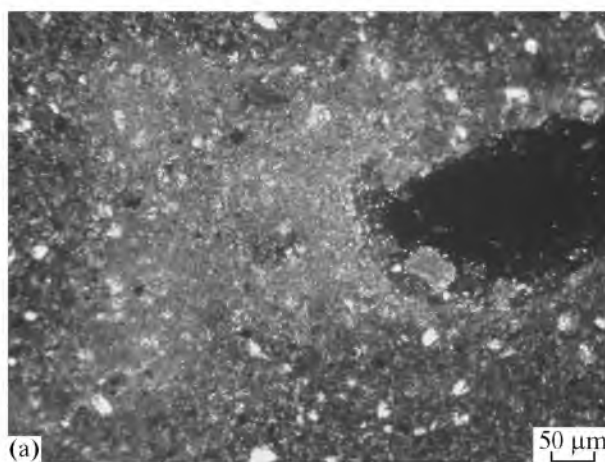
**Fig. 9.** Micro- and submicromorphology of the upper calcareous horizon in the soil under the 100-year-old plowland: (a) intrusion of acicular calcite into the plasma; (b) small crystals on the collomorphic film.

relief and filling the pores. Separate crystals are observed on the surface of the films (Fig. 11b).

The lower calcareous horizon of the 150-year-old soil is characterized by the presence of very large disintegrated carbonate concentrations in the plasma; the translocation of separate calcite grains and fragments of carbonate concentrations in pores can be seen. The stages of the concentration ingrowth into the plasma, as well as the clear separation of the carbonate concentrations and plasma, are visible (Fig. 12a). There are unrecrystallized grains of lithogenic carbonates, as well as ferrugination spots on the surface of the carbonate plasma. In submicromorphological terms, the carbonate concentrations in this horizon are the most crystalline in the agrochronosequence studied; their morphology is similar to that of the calcareous pedofeatures in steppe soils, e.g., *beloglazka* (white soft nodules). The calcite crystals have clear growth faces. Collomorphic calcite fills the pores, which are almost closed (Fig. 12b).



**Fig. 10.** Micro- and submicromorphology of the lower calcareous horizon in the soil under the 100-year-old plowland: (a) plasma highly saturated with carbonates containing very large concentrations in pores; (b) different crystals and thin collomorphic films.



**Fig. 11.** Micro- and submicromorphology of the upper calcareous horizon in the soil under the 150-year-old plowland: (a) mineral skeletal grains coated with carbonate plasma; (b) large sinter formations smoothing the relief and filling the pores.

The predominant trends in the changes of the calcareous pedofeatures and the horizon morphology under the agrogenic use are generalized for the upper and lower horizons in the table. Arrows indicate the increase or decrease of the parameters in the agrochronosequence.

In generalizing the changes in the morphology of the calcareous pedofeatures during the agrogenic evolution, we can note the following trends (separately for the upper and lower calcareous horizons).

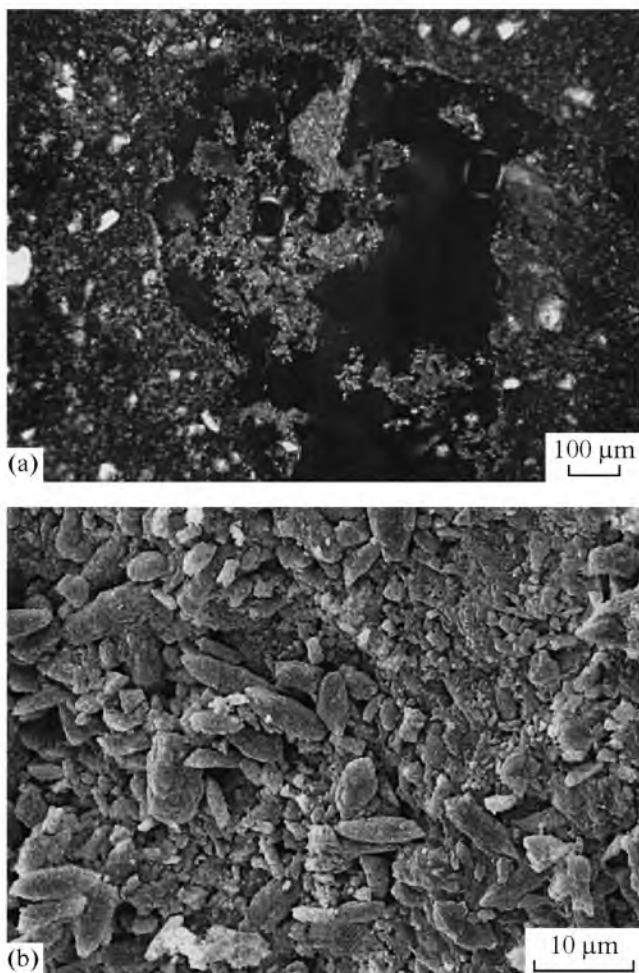
**The Upper horizons:** The total carbonate content (morphologically pronounced visually) increases, as well as the content of collomorphic forms, which tend to fill the pores and smooth the relief of the bulk soil mass. The collomorphic films become thicker; the crystallomorphic formations also become more distinct and well-shaped. Carbonates migrate from the calcareous pedofeatures to the bulk soil mass; the mild in situ recrystallization involving the transition into a colloidal solution and precipitation almost without translocation take place rather than the total dissolu-

tion of  $\text{CaCO}_3$  in the molecular solution followed by translocation.

**Lower horizons:** The contents of the collomorphic and crystallomorphic formations are greater. The general tendency is the further crystallization and segregation.

Trends and dynamic changes in the processes and properties of the carbonate profiles of the soils of the agrochronosequence studied

| Parameter                               | Upper calcareous horizon | Lower calcareous horizon |
|---|--------------------------|--------------------------|
| Total carbonates                        | ↗                        | ↗                        |
| Collomorphic forms                      | ↗                        | ↘                        |
| Sharpness of the crystal forms          | ↗                        | ↗                        |
| Calcite migration to the bulk soil mass | ↗                        | ↘                        |
| Crystallization rate                    | ↘                        | ↘                        |



**Fig. 12.** Micro- and submicromorphology of the lower calcareous horizon in the soil under the 150-year-old plowland: (a) movement of separate calcite grains and concentration fragments in pores and the stages of intrusion of carbonate concentrations into the plasma; (b) calcareous pedofeatures with well-shaped crystals.

tion of the calcareous pedofeatures. They pass the stage of different crystallization conditions, when different crystal forms and collomorphic calcite are created simultaneously. Under the soil cultivation, conditions for slow crystallization are created in the lower horizons, while, in the soil under the forest,  $\text{CaCO}_3$  is mainly precipitated from the colloidal solutions.

## CONCLUSIONS

The significant reorganization of the carbonate profile occurs in the dark gray forest soils of the central forest-steppe zone during their extensive agricultural development. The natural dark gray soil evolves into a medium-thick slightly podzolized chernozem with larger reserves of carbonates.

In the series of the evolution of arable soils from dark gray forest soils to podzolized chernozems, the calcareous pedofeatures and horizons evolve stepwise. The 100-year-old plowland is the stage of transition to another organization of the carbonate state in the agrochronosequence considered. In the 100-year-old plowland, the migration of carbonates is more active, and the dissolution–precipitation conditions are more dynamic than not only in the virgin soil but also in the soil of the 150-year-old plowland.

In the upper calcareous horizons, the structure of the calcareous pedofeatures becomes more collomorphic; this material fills almost all the voids; i.e., rapid precipitation occurs from the saturated solutions. In the lower calcareous horizons, calcite is predominantly segregated into calcareous pedofeatures, and slower crystallization occurs from the unsaturated solutions.

## ACKNOWLEDGMENTS

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