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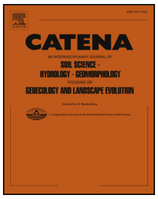

Morphological and isotopic study of pedogenic carbonate coatings from steppe and forest-steppe areas of Baikal region, South-Eastern Siberia

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ABSTRACT

In this study we investigated different age carbonate coatings in the surface steppe and forest-steppe soils and paleosols of the Baikal region and its relationship with environmental fluctuations of the Late Pleistocene and Holocene. The ^{14}C age of thin pedogenic carbonate laminae indicate four periods of coating formation: the second half of MIS-3 (24.1–23.3 and ~34.0–35.0 kyr BP), from the warm phases of the Late Glacial to the Middle Holocene (12.9–4.6 kyr BP) and the final of the Middle Holocene (3.6–3.3 kyr BP). Thus, studied carbonate coatings are mainly relict feature of the previous epochs of pedogenesis and Middle Holocene stage of surface soil formation. Paleoecological conditions reconstructed for the identified stages of formation of carbonate coatings correlate well with the trend of climatic changes in the Baikal region and adjacent areas. They reflect the effect of temperature and moisture fluctuations on the dynamics of soil-forming processes. Distinct δ^{18}O and δ^{13}C values suggest that the coatings of Transbaikalian steppes and forest-steppes of Fore-Baikal region have been formed under contrast environmental conditions. It is assumed that the formation of pedogenic carbonates in Transbaikalia is mainly confined to the summer season, when the soil is most warmed up, and the plants actively consume water and emit a large amount of CO_2. This agrees well with the slightly higher temperatures of the warm season and the greater aridity of this region. In turn, carbonate precipitation in Fore-Baikal region occurred during the degassing of soil solutions in the course of periodic freezing and thawing, alternation of phases of snowmelt and rainwater infiltration into the soil and its subsequent freezing, which can be observed in the region in spring and autumn. A significant $CaCO_3$ content in the studied soils contributed to the high growth rates of pendants. Holocene coatings are characterized by maximum growth intensity, which correlates with the highest carbonate content in the slope sediments where they are found. At the same time, MIS-3 coatings formed mainly on significantly less carbonate-rich alluvial deposits, which apparently affected their lower growth intensity. Based on an analysis of the growth rates of coatings, comparison of the isotopic composition of different age groups of pendants and soil micromorphology the more humid climatic conditions of the MIS-3 is assumed in comparison with the Middle Holocene. The temperature conditions of pedogenesis may be similar. Both for the Middle Holocene and for the MIS-3 relatively low temperatures of pedogenesis and long-term seasonal soil freezing are supposed.

1. Introduction

The accumulation of carbonates is one of the most prominent soil forming processes in arid to sub-humid environments. The formation of secondary carbonates is related to the vertical, horizontal or *in situ* replacement of carbonates during pedogenesis in the soils and sediments (Monger, 2002). The existence of pedogenic carbonate not only reveals the nature of the soil forming processes of the soil in a particular area but also serves as the main reservoir of soil inorganic carbon in the terrestrial ecosystem and plays a significant role in the carbon exchange between soil and atmosphere and affects global climate (Eswaran et al., 2000; Zamanian et al., 2016 and references therein).

Secondary carbonates are sensitive indicators of paleoenvironmental moisture conditions (Becze-Deák et al., 1997). In general, the existence of carbonate at certain depths is related to the amount of annual precipitation and biotic factors (Arkley, 1963; Retallack, 2005). Earlier (Machette, 1985; Marion et al., 1985) and more recent (Egli and Fitze, 2001; Royer, 1999;) studies have developed numerical models to

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relate the depth of carbonate accumulation to climatological data.

Occurrence and morphology of pedogenic carbonates, including size, shape, and distribution are valuable indices of pedoenvironments and pedogenic processes (Chadwick et al., 1989; Kovda et al., 2003; Khokhlova, 2008; Durand et al., 2018). Isotopic composition of secondary carbonates can provide information on paleoclimatic conditions, the composition of paleovegetation (Cerling, 1984; Dworkin et al., 2005; Pustovoytov et al., 2007; Monger et al., 2009; Quade et al., 2013; Oerter and Amundson, 2016) and the landform dynamics (Kovda et al., 2006; Quade et al., 2007; Barta et al., 2018). A variety of methods applied for dating pedogenic carbonates allows us to solve the geochronological problems (Singhvi et al., 1996; Sharp et al., 2003; Pustovoytov et al., 2007; Khokhlova et al., 2013; Oerter et al., 2016).

Microlaminated and laminated coatings or pendants are especially promising type of secondary carbonate accumulations. Their formation is generally similar to the formation of speleothems (Brock and Buck, 2005), considered in recent years as one of the most promising paleoclimatic proxy on the continents (Fairchild and Baker, 2012). Layered carbonate coatings are micro-sedimentation systems within the soil profile and are formed by processes of intra-profile migration of substances in true, colloidal solutions, in suspensions, and their deposition on geochemical and mechanical barriers (Bronnikova et al., 2017). Differences in the composition of solutions and suspensions, in conditions of migration and deposition, lead to the formation of coatings differing in their composition and morphology. Thus, layered carbonate coatings can shed light on the direction, intensity and sequence of processes of intra-profile migration and accumulation of matter, as well as environmental conditions that determine these processes (Courty et al., 1994; Pustovoytov, 2002; Golubtsov et al., 2014; Oerter et al., 2016; Zamanian et al., 2016; Bronnikova et al., 2017).

Our studies in recent years have shown the widespread occurrence of carbonate coatings in the soils of the Baikal region (Golubtsov et al., 2014; Golubtsov et al., 2019). However, despite their high potential, there is no information about morphology, age, origin and stable isotope geochemistry of carbonate coatings in the regional soils.

This work aims to reveal the morphology and stable isotopic composition of different age carbonate coatings in the soils and paleosols of the steppes and forest-steppes of the Baikal region depending on environmental fluctuations of the Late Pleistocene and Holocene.

2. Materials and methods

2.1. Study area: geographical localization and landscape characteristics

The Baikal region is a vast area in the South-Eastern Siberia that is highly heterogeneous in terms of physiographic conditions. The highest carbonate content is observed in the soils of steppes and forest-steppes. Taiga is a major landscape of the Baikal region. Steppe and forest-steppe landscapes are distributed discontinuously here (Fig. 1). Those are a part of the belt of island steppes and forest-steppes of the South-Eastern Siberia. This belt extends from the north-west to the southeast for almost two thousand km. It is located at the southern boundary of the permafrost zone and along the northern borders of the arid Central Asia. Such a geographical location should determine the sensitivity of these landscapes to past and present climatic changes. Understanding the dynamics of soil carbonates is one of the key aspects for reconstruction of regional soils and lanscapes response to climate variability in Baikal region.

The soil profile examinations were conducted within two areas. On the west from Lake Baikal it is forest-steppe landscapes of the Upper Angara region and on the east it is steppe landscapes of the central part of Selenga middle mountains and Onon-Argun’ interfluve (Fig. 1). General information about the sampling sites is shown in Table 1.

Forest-steppes of the Fore-Baikal region are characterized by a relatively large amount of mean annual precipitation (350–420 mm) compared with the steppe landscapes of the Transbaikalia (200–270 mm). The mean annual temperature is everywhere negative and amounts to −2.2 °C in the Fore-Baikal forest-steppe and the central part of the Selenga middle mountains and −3.2 °C in the Onon-Argun’ steppes. From west to east, the degree of climate continentality increases. Summer temperatures increase, winter temperatures decrease. The main parent material of soils of the Fore-Baikal region is relatively thin aeolian and colluvial loess-like calcareous loams of the Pleistocene. The predominant soil parent material of studied sites in Transbaikalia are beds of fine earth (colluvium of hard rocks) containing unweathered gravels and stones.

Despite the differences presented, there are few similar features in soil forming conditions in a cold extra continental climate (Buzlukova, 1974; Scientific and Applied Handbook…, 1989; Scientific and Applied Handbook…, 1991; Kolesnichenko, 2003; Kozlova and Makarova, 2012). First, the duration of periods with subzero air temperatures significantly exceeds periods with above-zero temperatures. Second, there is a pronounced contrast between dry and wet seasons of the warm period. About 80% of annual precipitation falls in the late July and August. From May to mid-July dry and warm conditions prevail on the territory. This contributes to the strong desiccation of soils in the first half of the warm period. The maximum humidity of the second half of summer coincides with a high moisture consumption for physical and biological evaporation (up to 130–140 mm per month), which prevents percolation of water into subsoil. The periodically-percolative type of water regime is established in the studied soils. The moisture circulation mainly covers the upper meter of the soil, and the most intensive circulation occurs the upper half meter. The underlying layers, due to their late thawing and low temperatures, are characterized by an almost complete absence of moisture circulation. Third, due to the low thickness of the snow cover, the soils are frozen to a considerable depth (2–2.5 m). Soils are in the frozen state for a long time and slowly thaw in the spring and summer. Thus, soil water regime is characterized by insufficient moisture with the presence of late seasonally frozen layer.

2.2. Field and laboratory research strategies and techniques

When conducting field studies, the main attention was paid to the morphogenetic description of soils, the morphological characteristics of carbonate pedofeatures, and the analysis of their distribution in profile. In the laboratory, soil samples were dried to an air-dry state, ground and sieved through a 1-mm sieve. The $CaCO_3$ content in fine-earth was determined by the breakdown of carbonates by an acid solution and back-titration of the remaining acid in the solution (Pansu and Gautheyrou, 2006). Total organic carbon (TOC) content was determined by dry combustion on a Vario Isotope analyzer (Elementar, Germany). The particle-size distribution was determined after removal of carbonates and dispersion of samples by sodium pyrophosphate pretreatment. Then, the coarse (1–0.25 mm) and fine (0.25–0.05 mm) sand fractions were isolated by wet sieving. Fractions of the coarse silt (0.05–0.01 mm), medium silt (0.01–0.005 mm), fine silt (0.005–0.001 mm) and clay (< 0.001 mm) were separated subsequently by sedimentation.

The age of soils and paleosols was determined by the radiocarbon method with scintillation measurement of ^{14}C activity from carbon of humic acids at St. Petersburg State University (Russia).

The carbonate coatings were collected together with the stone fragments they covered. Samples were then cut with a diamond saw perpendicularly to the predominant spread of the coating into sections 5–7 mm thick. The obtained sections of the carbonate pedofeatures were subjected to further investigations.

Material for isotopic measurements and radiocarbon dating was bored out with a goldsmith drill from the cross sections of coatings on stones, under stereoscopic microscope. In boring, special effort was made to follow the extension of individual laminae of coatings with the drill and, in case of the innermost (oldest) laminae, to avoid contact of the drill with the stone. The thicknesses of the sampled laminae were

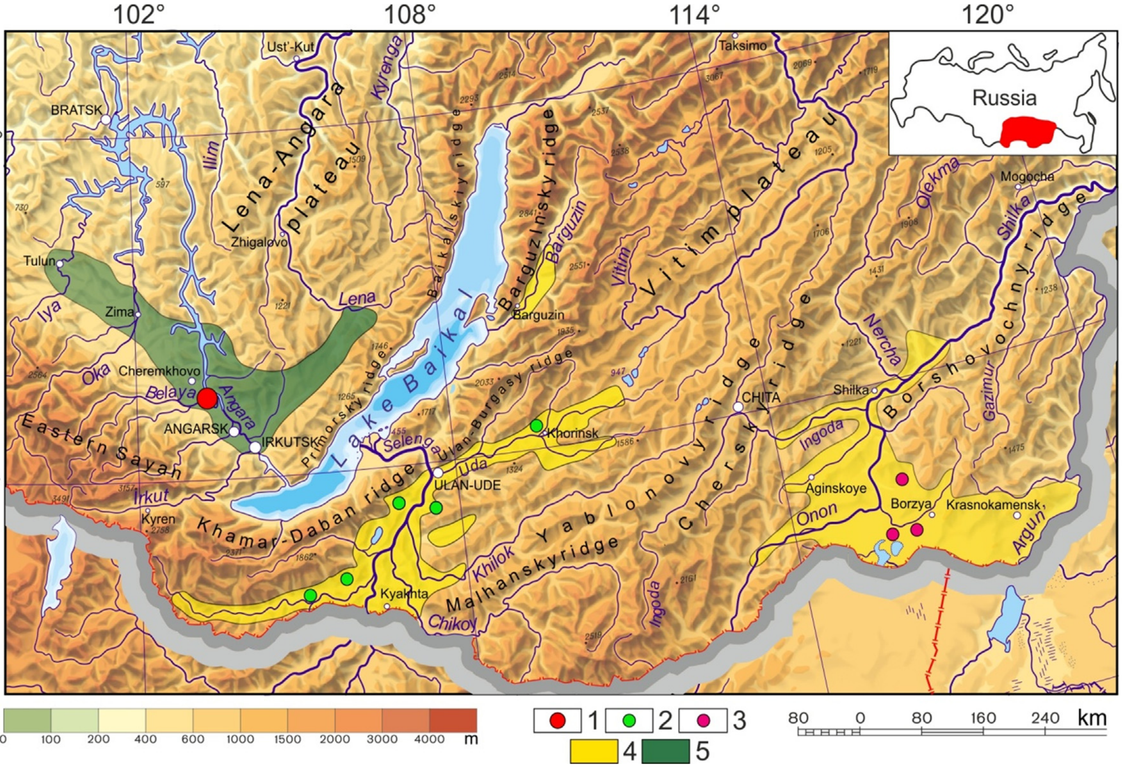

Fig. 1. Location of the main studied sites. Table of symbols: 1 – Fore-Baikal region, 2 – Selenga Middle mountains, 3 – Onon-Argun' steppes, 4 – distribution of steppe landscapes, 5 – distribution of forest-steppes.

0.2–0.3 mm.

Stable isotope analysis of carbonate material was performed at the Institute of Geosciences of the University of Tubingen, Germany, using a Finnigan MAT 252 gas source mass spectrometer combined with a Thermo Finnigan GasBench II/CTC Combi-Pal autosampler and at the V.S. Sobolev Institute of Geology and Mineralogy (Nowosibirsk, Russia) using Finnigan MAT 253 mass spectrometer combined with a Thermo Finnigan GasBench II.

Samples for $\delta^{13}C$ of soil organic carbon were rinsed (to remove detritus, rootlets, etc.), dried, and pretreated with 5% HCl to remove carbonates. The stable carbon isotope ratios were determined by mass spectrometry at the Center for Radiocarbon Dating and Electron Microscopy of the Institute of Geography, Russian Academy of Sciences (Moscow, Russia) using an Isoprime precisION IRMS mass spectrometer (Elementar, UK). The results of isotopic measurements in carbonates are reported as δ, ‰ = $(R_{sample}/R_{standard} - 1) * 1000$, where R is $^{13}C/^{12}C$ and PDB is the Pee Dee Belemnite standard. The precision of isotopic measurements was 0.1‰. $\delta^{18}O$ values of atmospheric precipitation are presented with respect to SMOW.

The carbonate material of the coatings was ground in an agate mortar to the powder state; the mineral composition of nonoriented samples was studied using X-ray diffractometry on a D8 Advance diffractometer (Bruker, AXS). The elemental composition was analyzed by X-ray fluorescence method using an S4 Pioneer spectrometer (Bruker, AXS).

Mesomorphological studies were performed in reflected light using a Micromed MS-2-ZOOM microscope. The micromorphological analysis of thin sections was performed on an AxioScope A1 Carl Zeiss microscope at the Institute of Physicochemical and Biological Problems of Soil Science (Puschino, Russia). Freshly fractured internal surfaces of coatings were examined with a JEOL JSM-6610LV scanning electron microscope (Japan) equipped with an energy-dispersive spectrometer (EDS) and elemental analyzer Oxford INCA Energy,Oxford INCA Wave. Samples were coated with Au before analysis. Microprobe analysis was performed at 15 kV.

^{14}C AMS dating of coatings layers marking different stages of pedogenesis was performed using the MICADAS system in the laboratory of Klaus Tschira Archäometrie Zentrum (Mannheim, Germany), as well as in the laboratory of accelerator mass spectrometry of the University of Arizona (Tucson, USA). Calibrated ^{14}C dates are given and used below in the text. Calibration performed using the INTCAL13 (Reimer et al., 2013).

3. Results

3.1. Characteristics and age of investigated soils

3.1.1. Forest-steppes of Fore-Baikal region

The studied sections (Fig. 2) are located on terraces of the Angara and Belaya rivers. Their structure is generally similar. Sections consist mainly of cover loess-like loams and sandy loams, overlapping sandy and pebble alluvial deposits. The sections are usually polygenetic and, in addition to modern ones, contain profiles of buried soils (with the exception of Osinovyi and Buret').

Such buried soils located at the depth of 1.5–2 m and formed mainly on alluvial deposits. Paleosols are intensively disturbed by cryogenic processes, namely cryoturbations. For this reason, soil horizons are often fragmented and presented as lenses. These soils formed during Karga thermochron (MIS-3) (Table 2). The age of such buried soil of the Tayturka-II section is determined on the basis of fossil remains of the Late Pleistocene fauna, which lie below in the profile. The best-preserved remains belong to the *Equus ferus*, *Bison priscus*, *Rangifer tarandus* and *Mammuthus primigenius*. All fauna is typical for the Late Pleistocene of the Baikal region. On the basis of the faunistic association, one can make an assumption about the Late Karga-Early Sartan age of the bone remains (MIS-2-MIS-3 border) (Klementiev, 2013).

The profiles of MIS-3 soils are overlapped by slope deposits on which surface soils are formed. Luvic Phaeozems (Nizhnyi Bulay-II, Osinovyi, Buret') form under the forest vegetation and Luvic Chernozems (Tayturka-I, Tayturka-II, Berezovyi) form under the

Table 1
General information of the sampling sites.

Section	Surface soil	Paleosols and their age	Parent material	Altitude, m	MAP, mm	MAT, °C	MT of January, °C	MT of July, °C
Upper Angara forest-steppes								
Tayturka-I	Luvic Chernozem	Karga thermochron (MIS3)	Loess-like loams	429	350–420	−2,2	–23.4	+17.7
Tayturka-II	Luvic Chernozem	Karga thermochron (MIS3)	Loess-like loams	436	350–420	−2,2	–23.4	+17.7
Berezovyi	Luvic Phaeozem	Karga thermochron (MIS3)	Loess-like loams	417	350–420	−2,2	–23.4	+17.7
Osinovyi	Luvic Phaeozem	–	Loess-like loams	460	350–420	−2,2	–23.4	+17.7
Buret’	Luvic Phaeozem	–	Loess-like sandy loams	403	350–420	−2,2	–23.4	+17.7
Nizhnyi Bulay -II	Luvic Phaeozem	Karga thermochron (MIS3)	Loess-like loams	496	350–420	−2,2	–23.4	+17.7
Selenga middle mountains steppes								
Khorinsk	Cambic Leptic Calcisol	–	Loess-like sandy loams	715	200–250	−2,3	–26.0	+20.5
2-Z-2018	Skeletic Cambic Leptic Calcisol Turbic	Late Holocene	Light sandy loams	633	240–250	−2,2	–25.0	+18.8
5-Z-2018	Skeletic Cambic Leptic Calcisol Hypercalcic Yermic	–	Light loams	787	240–250	−2,2	–25.0	+18.8
9-Z-2018	Skeletic Cambic Leptic Calcisol	Late Holocene	Light loams	691	240–250	−2,2	–25.0	+18.8
11-Z-2018	Skeletic Cambic Leptic Calcisol Hypercalcic Yermic	Late Holocene	Light loams	861	240–250	−2,2	–25.0	+18.8
Onon-Argun’ steppes								
16-Z-2018	Luvic Chernozem	Karga thermochron (MIS3)	Loess-like loams	679	260–270	−3,2	−30.0	+18
17-Z-2018	Leptic Chernozem	Late Holocene	Limestones	723	260–270	−3,2	−30.0	+18
19-Z-2018	Leptic Chernozem	–	Limestones	650	260–270	−3,2	−30.0	+18

steppes. Some soils are covered by sediments of small thickness. In the Tayturka-I section, this is ground outfall from a quarry; in the Tayturka-II section, these are sediments washed away from the upper parts of the slopes when plowing. Organic matter at the bottom of the Ah horizon of Chernozem in the Tayturka-I section has a Late Holocene age (2.6 kyr BP) (Table 2).

In the soils of the Upper Angara region, δ^{13}C values of organic matter vary from −25.85 to −22.13‰. An enrichment of the stable carbon isotopic composition is observed with depth, reaching a maximum in the MIS-3 soils.

Carbonates are found in the greatest amount in profiles of modern soils. In alluvial deposits and MIS-3 soils formed on them, the carbonate content is much lower. The Bk horizons of surface soils are clearly pronounced and have a sharp upper boundary on 70–100 cm from the surface (Fig. 2). Carbonates are almost absent above, with the exception of the Taiturka-II section (Fig. 3) where their presence is associated with the addition of soil material from the upper parts of the slopes. On average, the thickness of the carbonate-rich horizon is 50 cm.

The closest to the surface carbonate peak probably associated with their leaching and subsequent accumulation during modern pedogenesis. The profile of carbonates below also has several smaller peaks (Fig. 3). Generally, they are confined to the middle-profile horizons of buried soils. Such a distribution of carbonates is probably associated with their redistribution during the Late Pleistocene and Holocene stages of soil formation. The highest content of carbonates in soils is characteristic when carbonate-bearing rocks occur close to the soil surface (for example, Buret’ section) (Figs. 2 and 3).

3.1.2. *Micromorphology of soils in Fore-Baikal region*

In the B horizons of the surface soils, there are obvious signs of bioturbation, i.e., mesofauna casts with plant residues in voids and crushing of micromass (Fig. 4a). A lot of undifferentiated charcoal fragments with irregular shapes and indistinct patterns of plant tissues are also visible here. As a whole, the micromass has stipple-speckled b-fabric partly masked by humus impregnation; voids and micromass do not contain oriented clay coatings. The elongated and rounded grains of lithogenic carbonates are scattered in groundmass and partly masked by thin disperse substance (Fig. 4b, arrows).

The micromass of the Ahb (Fig. 4c) and Bt (Fig. 4d) horizons of buried soils is anisotropic and has granostriated and striated b-fabric. There are elongated grains of lithogenic carbonates (Fig. 4c, d, arrows) and separate sparite crystals in micromass (Fig. 4c, sp). In the Taiturka-I site, the granular (‘ooid-like’) microstructure is very characteristic (Fig. 4e, od), the fine material has concentric-striated, granostriated and porostriated b-fabric. There are isolated fragments of Fe-clay coatings (‘papules’) (Fig. 4f, ct) in micromass. In individual voids and on the surface of some mineral grains and ooids (‘granules’), the clay cappings are observed (Fig. 4e, f, cp). Carbonate pedofeatures are in certain voids as phytomorphic calcite connected with amorphous and crashed plant residues (Fig. 4g, h); sometimes the fragments of those pedofeatures are embed in micromass and locate close to the voids.

3.1.3. *Steppes of Transbaikalia*

In the Selenga middle mountains studied soil profiles are mainly located on piedmont plains composed by colluvial sediments in the valleys of the Uda (Khorinsk), Selenga (2-Z-2018) and Dzhida (5-Z-2018, 9-Z-2018, 11-Z-2018) rivers. Soils are formed on relatively thin (up to 1.5 m) sandy loams and light loams, containing a lot of unweathered gravels and stones. Some of the studied soils are polygenetic. For example, the upper part of section 11-Z-2018 is an alternation of the thin Ahb horizons buried periodically by colluvial deposits. In sections 2-Z-2018 and 9-Z-2018 upper part of Ah in surface soils with relatively low content of TOC are formed above the darker colored, and richer in organic buried humus horizons suggesting more humid soil forming conditions in the past. The age of the organic matter of such organic-rich horizons (3.3–3 kyr BP) (Table 2) allows us to correlate

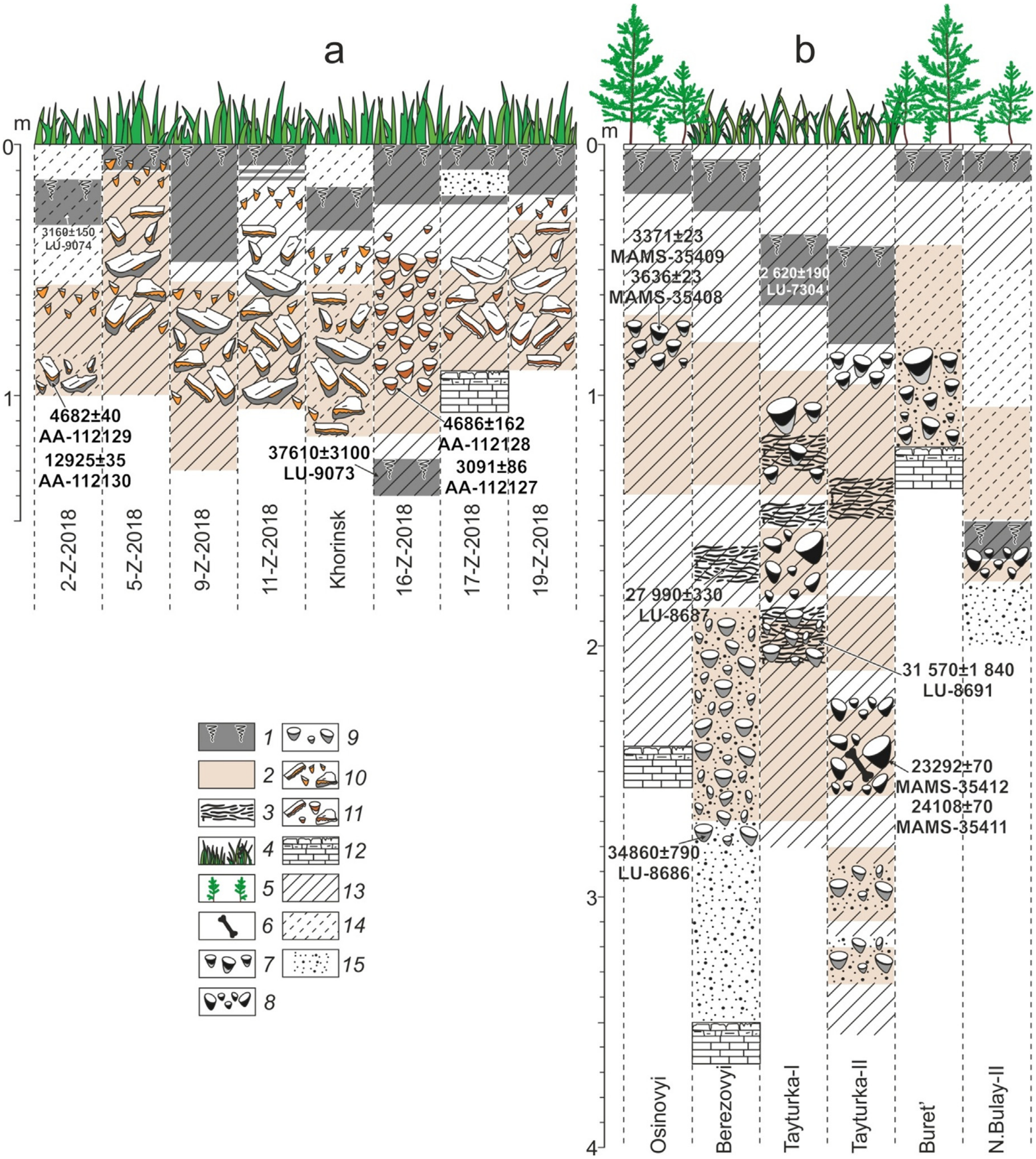

Fig. 2. Studied soil profiles in steppes of Transbaikalia (a) and forest-steppes of Fore-Baikal region (b). The studied carbonate accumulations were divided into five groups. Three of them (I-III) are formed in the forest-steppe soils of the Fore-Baikal region. The fourth and fifth group of coatings are located in steppe soils of the Selenga Middle mountains and Onon-Argun' interfluves, respectively. Table of symbols: 1 – Ah horizons, 2 – Bk horizons, 3 – Ahb horizons of buried MIS-3 soils, 4 – herbaceous vegetation, 5 - forest vegetation, 6 - fossil remains of the Late Pleistocene fauna, 7 – group I of coatings, 8 – group II of coatings, 9 – group III of coatings, 10 – group IV of coatings, 11 – group V of coatings, 12 – bedrock, 13 – loam, 14 – sandy loam, 15 – sand.

Table 2
Radiocarbon and calendar age of soils.

Section	Soil horizon	Depth, cm	Dating material	Lab number	Radiocarbon age	Calibrated age
Tayturka -I	Ah	55–60	Organic carbon	LU-7304	2560 ± 160	2620 ± 190
	3Ahb	195–205		LU-8691	26,950 ± 1570	31,570 ± 1840
Berezovyi	2Ahb	170–180		LU-8687	23,700 ± 370	27,900 ± 330
2-Z-2018	Ahb	13–23		LU- 9074	2990 ± 120	3160 ± 150
16-Z-2018	Ah	125–130		LU-9073	32,110 ± 2 410	37,610 ± 3 100

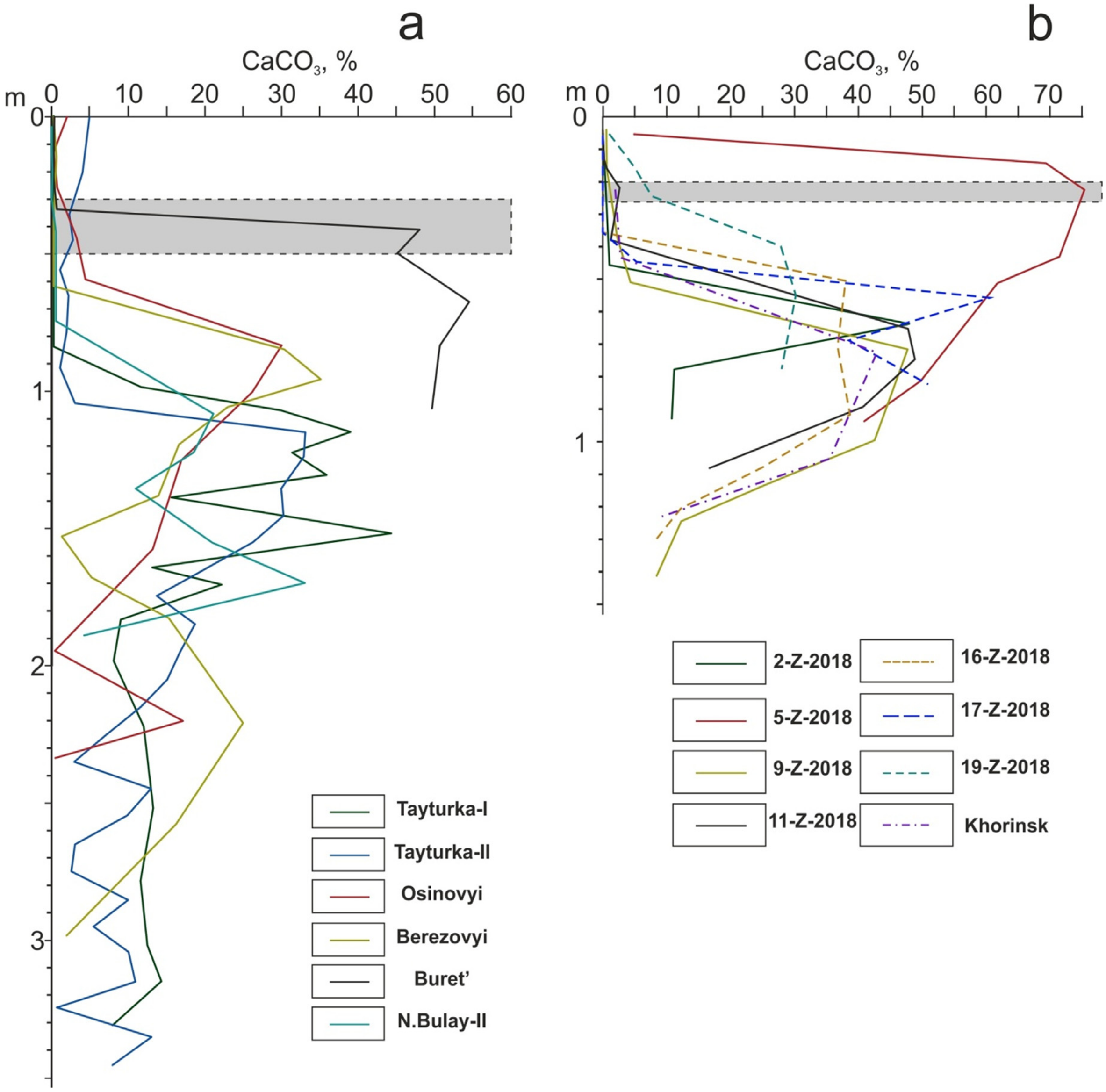

Fig. 3. $CaCO_3$ distribution patterns in forest-steppe soils of Fore-Baikal region (a) and steppe soils of Transbaikalia (b). Gray shading indicates the theoretical depth of the Bk-horizons at the current mean annual precipitation.

this stage of pedogenesis with the final stages of the Middle Holocene.

Chernozems formed on the terraces of the Turga river (16-Z-2018) as well as northeast of Lakes Zun-Torey and Barun-Torey (17-Z-2018, 19-Z-2018) were studied in Onon-Argun' steppes. Chernozem (16-Z-2018) was formed on loess-like loams containing a lot of inclusions of gravel and pebbles. There is a profile of the fossil soil in the lower part of this section (Fig. 2), which formed during the Karga thermochron (MIS-3) (Table 2). Chernozems in the 17-Z-2018 and 19-Z-2018 section were formed on loess-like loams and are underlain by bedrock at a depth of about 90 cm.

The main difference between the carbonate profiles of steppe soils of the Transbaikalia and forest-steppe soils of Fore-Baikal region is a shallower depth of carbonates in steppe soils, which varies from 40 to 60 cm (Figs. 2 and 3). This is correlates well with the lower annual precipitation in Transbaikalia. A shallower depth of the Bk horizon is noted for section 19-Z-2018, which may be due to poor drainage conditions due to the close occurrence of bedrock. The Bk horizons of studied steppe soils are clearly pronounced and have a adrupt upper boundary. Carbonates are almost absent above this border. The thickness of the Bk horizons coincides with that in the Fore-Baikal region (about 50 cm). The total carbonate content in steppe soils is noticeably higher, and in all cases fulfills quantitative criteria of Calcic horizon. $\delta^{13}C$ values of studied soil organic matter in Transbaikalia are on average −24‰.

3.2. Distribution, morphology and composition of carbonate coatings

The studied carbonate accumulations were divided into five groups as based on their morphology and composition (Table 3, Fig. 5). Three of them (I-III) are formed in the forest-steppe soils of the Fore-Baikal region. The fourth and fifth groups of coatings are related to steppe soils of the Selenga Middle mountains and Onon-Argun' interfluves, respectively.

Despite the different environmental conditions, certain common features are characteristic of the studied coatings.

1. In all cases, they are located on the lower surfaces of non-carbonate pebble and clast inclusions, which testifies to their formation at the leaching of carbonates from the layers above in course of pedogenesis.

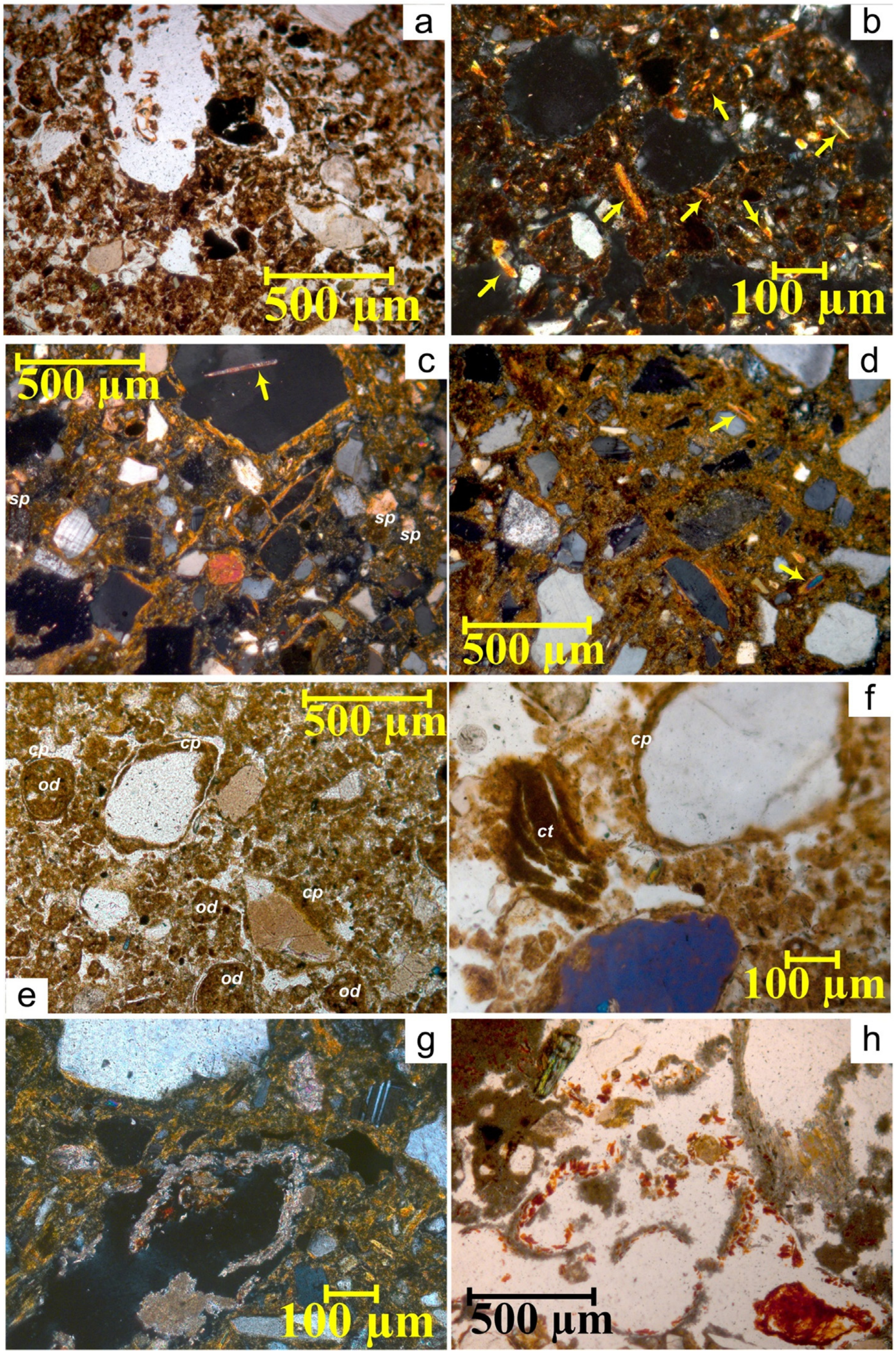

Fig. 4. Micromorphology of surface and buried soils of Fore-Baikal region. a, b – B horizons of surface soils; c, e – Ahb horizons of MIS-3 soils; d, f, g, h – Bt horizons of MIS-3 soils. See explanations in text.

2. Pebbles of the groups I, IV and V are located within the Bk horizons of surface soils. Coatings of groups II and III corresponding to the MIS-3 buried soils.
3. The study pendants are characterized by differentiation into inner and outer layers that are heterogeneous in morphology and composition, reflecting a change in pedogenesis conditions. The exception is the third group, which is quite homogeneous under binocular investigations. The character of borders between different layers of coatings in most cases is abrupt and wavy, runs roughly parallel to the clast surface on which they formed. The contact of coatings with the clasts in all cases is sharp.
4. The inner layers are enriched with organic matter and iron, which indicates the illuviation of these components in the carbonate-rich horizon during the formation of the described layers of coatings. This is especially pronounced in the coatings of the second and third groups. In the carbonate material of the outer layers of pendants these impurities are not observed (with an exception of third group).
5. The outer layers are similar in morphology and most likely represent the host soil mass cemented by carbonates, which later became the outer layer of pendants. Such accretionary origin of the outer layers of carbonate accumulations is confirmed by their composition. There is an increased content of Al_2O_3, Fe_2O_3, MgO and SiO_2 (Table 3) in outer layers of coatings. While the inner layers of the pendants are almost completely composed of calcite with traces (less

Table 3
Morphology and composition of carbonate coatings in soils of Baikal region.

Occurrence depth, cm; (group)	Inner layers				Outer layers			
	Morphology and thickness of layers	Density	Mineralogy	Main elemental compounds	Morphology and thickness of layers	Density	Mineralogy	Main elemental compounds
Forest-steppes of Fore-Baikal region								
70–130; (1)	Three main layers: (1) inner 10YR 8.5/2; 0,4–0,75 mm (2) middle 5YR 5/4; 0,25–0,5 mm (3) outer 10YR 8.5/1; 0,2–0,7 mm	Dense	Low-Mg calcite (3,01 Å), traces of quartz	CaO (59,1%) SiO_2 (3,6%) Fe_2O_3 (1,3%) Al_2O_3 (0,7%) MgO (1,7%)	Unstratified brownish-gray (2.5 Y 6/2) material with root channels; 0,7–2,1 mm	Porous, dense	Low-Mg calcite (3,01 Å), with quartz and feldspars	CaO (66,5%) SiO_2 (23,9%) Fe_2O_3 (2,6%) Al_2O_3 (4,3%) MgO (1,8%)
150–260; (2)	Microstratified pigmented brown (7.5YR 4/4 to 7.5YR 6/4) material with cavities on pebble contact; whole layer up to 0,9 cm, microlaminae up to 0,2 mm	Very dense	Calcite (3,02 Å)	CaO (54,1%) SiO_2 (2,7%) Fe_2O_3 (1,4%) Al_2O_3 (0,5%) MgO (1,4%)	Unstratified white (10 YR 9,5/2) material; 0,6–1,5 mm	Porous, dense	Calcite (3,02 Å) with quartz, feldspars and amphiboles	CaO (46,1%) SiO_2 (18,3%) Fe_2O_3 (1,4%) Al_2O_3 (2,8%) MgO (1,1%)
190–330; (3)	Microstratified pigmented pale-brown (10YR 7/3) to dark brown (7.5YR 4/6) material; whole layer up to 1 cm, microlaminae up to 0,2 mm	Hard	Calcite (3,02 Å) with quartz and feldspars	CaO (51,2%) SiO_2 (9,4%) Fe_2O_3 (2,6%) Al_2O_3 (1,5%) MgO (1,0%)	Microstratified pigmented yellowish-red (5YR 5/4) material; whole layer up to 8 mm, microlaminae up to 0,2 mm	Hard	Calcite (3,02 Å) with quartz and feldspars	CaO (53,8%) SiO_2 (17,6%) Fe_2O_3 (2,3%) Al_2O_3 (1,9%) MgO (1,2%)
Selenga middle mountain steppes								
30–110; (4)	Microstratified pigmented yellowish and brownish (2.5 Y 5/6, 7.5 YR 5/6 and 5 YR 4/6) material; whole layer up to 2 mm, microlaminae up to 0,25 mm	Dense	Low-Mg calcite (3,01 Å), traces of quartz and feldspars	CaO (49,1%) SiO_2 (3,7%) Fe_2O_3 (1,1%) Al_2O_3 (1,2%) MgO (0,9%)	Unstratified white (2,5 Y 9.5/1 to 2,5 Y 9/1) material with root channels; 1–4 mm	Porous, relatively soft	Calcite (3,02 Å) with quartz, feldspars and amphiboles	CaO (55,7%) SiO_2 (15,3%) Fe_2O_3 (2,7%) Al_2O_3 (4,9%) MgO (2,2%)
Onon-Argun' steppes								
35–100; (5)	Two main layers: (1) inner 10YR 5/8 with cavities on pebble contact; up to 3 mm (2) outer 10YR 5/3 to 10YR 5/6; fragmented up to 2 mm	Very dense	Calcite (3,02 Å), traces of quartz	CaO (50,8%) SiO_2 (4,8%) Fe_2O_3 (0,6%) Al_2O_3 (1,3%) MgO (2,8%)	Unstratified white (2,5 Y 9,5/1) material with root channels and reniform surface; up to 5–7 mm	Porous, relatively soft	Calcite (3,02 Å)	CaO (60,1%) SiO_2 (3,9%) Fe_2O_3 (0,8%) Al_2O_3 (1,1%) MgO (3,3%)

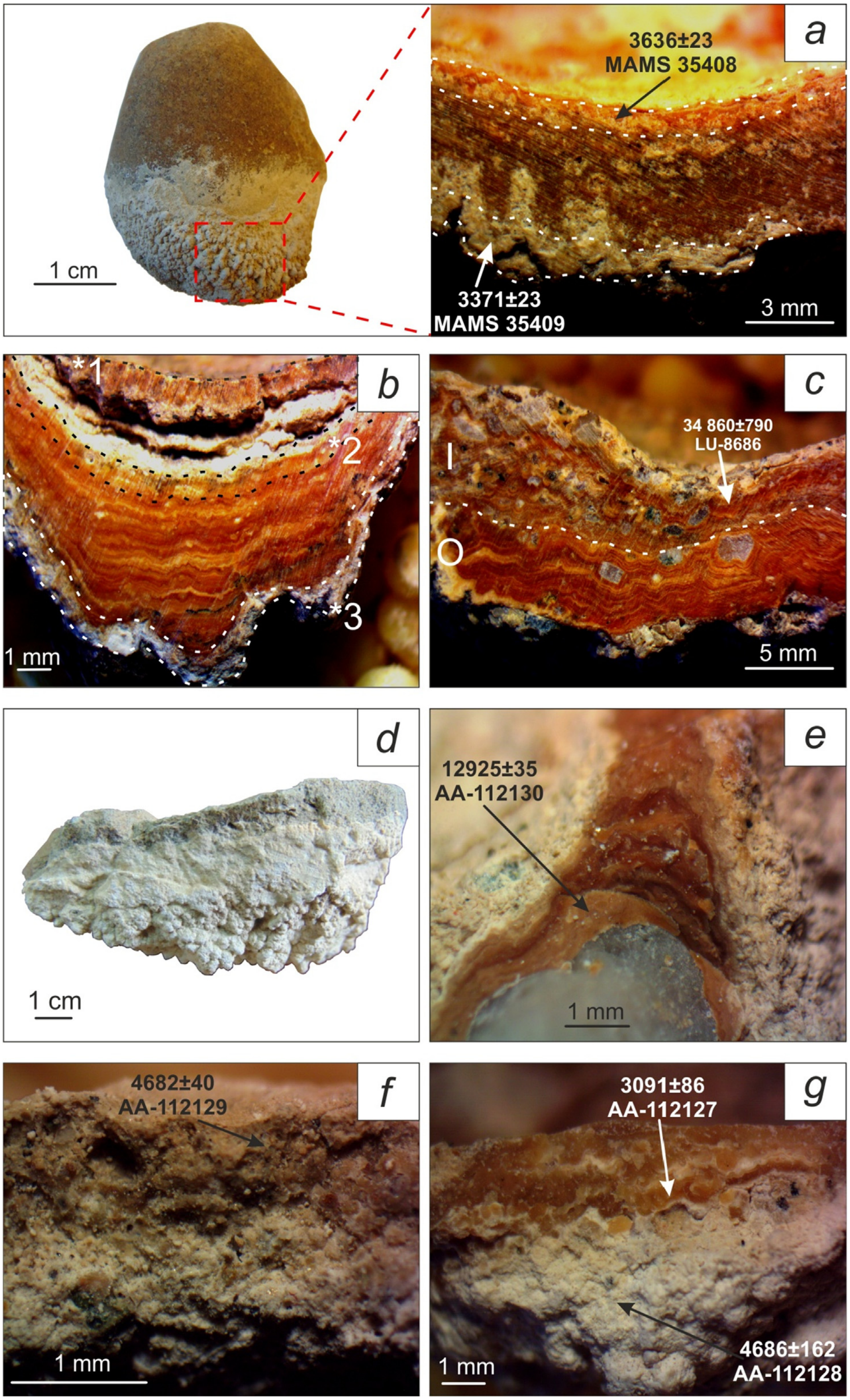

Fig. 5. Morphology of the carbonate coatings and ages of different layers. a – group I of coatings, b – group II of coatings (^{14}C-AMS dates: *1 – 23 189 ± 70 (MAMS-35410), *2 – 24 108 ± 70 (MAMS-35411), *3 – 23 292 ± 70 (MAMS-35412)), c – group III of coatings, the dashed line indicates the boundary between the outer and inner layers, d, e, f – localization on clast, inner and outer layers of coatings of the IV group, respectively, g – group V of coatings.

than 5%) of silicate inclusions, the outer layers have a significant number of inclusions of quartz (10%), feldspars (20%) and amphiboles (10%) embedded from host sediments.

3.3. Micro- and submicromorphology of carbonate coatings

The micromorphological study of coatings reveals that most of coatings are presented by an alternation of cryptocrystalline and micrite-microsparite micromass of calcite having several lamination layers

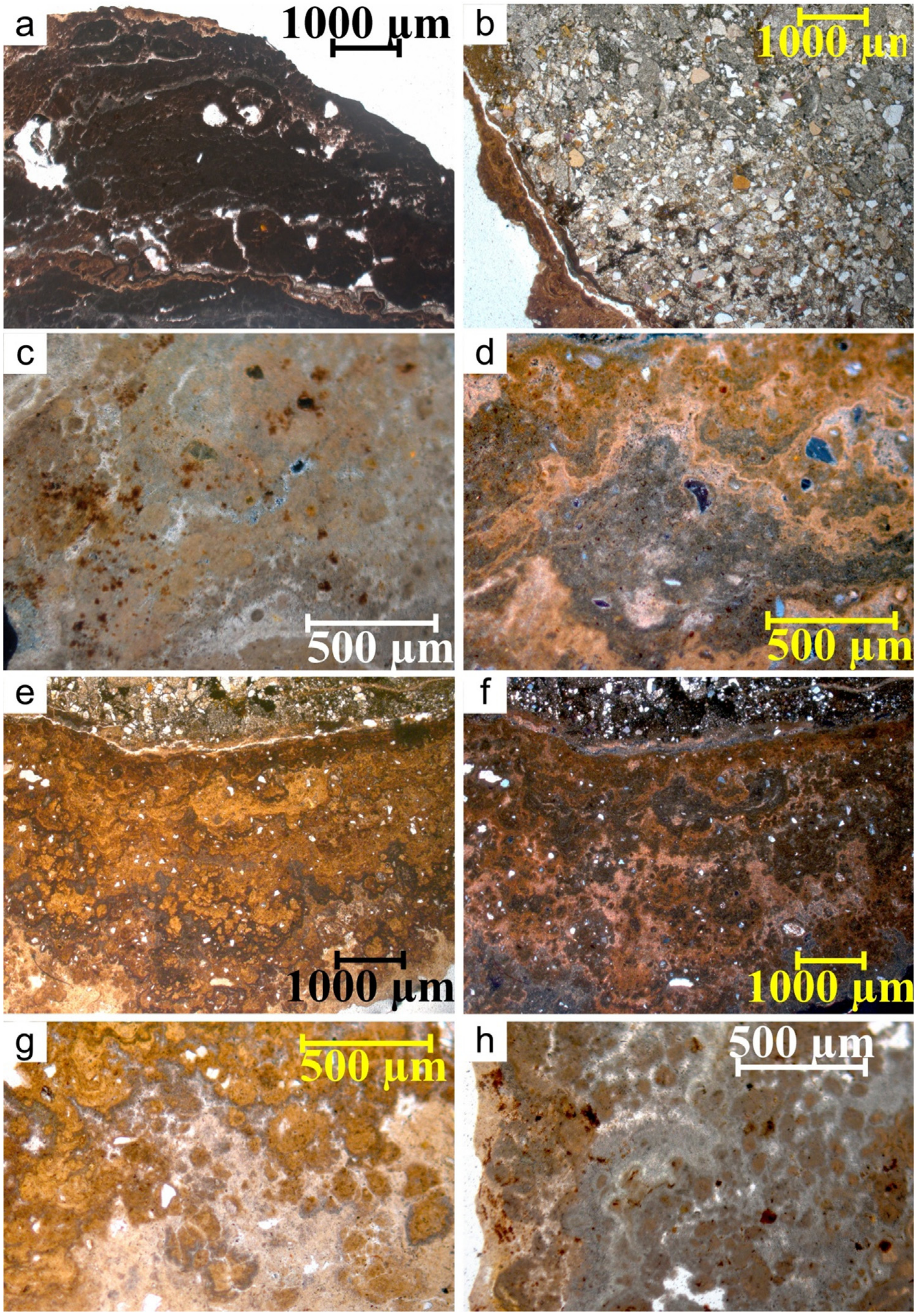

Fig. 6. Micromorphology of carbonate coatings. a, c, h – coatings from forest-steppe soils of Fore-Baikal region; b, d, e, f, g – carbonate coatings from steppe soils of Transbaikalia. a, b, e, g, h - PPL; c, d, f - XPL. See explanations in text.

(Fig. 6a, b). As a rule, mass of cryptocrystalline carbonates has brown or dark brown color provided by iron oxides and organic carbon admixtures (Fig. 6b-d). Mass of carbonates with visible crystals has light gray-blue color; films of iron oxides or organic carbon are practically absent inside this mass. It seems that initially, all the carbonate substance in carbonate coatings on stones had an admixture of iron oxides and organic carbon, and the microareas inside the coatings made of micrite-microsparite mass of carbonates appeared as a result of dissolution and recrystallization of carbonates *in situ*, i.e., inside the coatings.

The layers inside a coating are very different by thickness and color, the quantity of layers is also different at the same coating. On the same stone, the coating may be, for example, three- or two-layered in one part and thin, single-layered, as if it were pressed, into another. The processes of dissolution and recrystallization of a carbonate substance in an already formed coating are also irregular; the location of the "recrystallization spots" inside the coating has no regular occurrence (Fig. 6e, f).

It is obvious, that the formation of the carbonate coatings is irregular and under disturbance due to the slightest changing of environmental conditions, as it is not visible carbonate substance having uniform thickness and extension along the whole boundary with a stone for all the studied sites. Examined individual microareas of coatings at high magnifications, it can be noted the ordered location of brown spots resembling colonies of microorganisms (Fig. 6g-h). Investigations of carbonate coatings on stones, made in other world regions, allowed

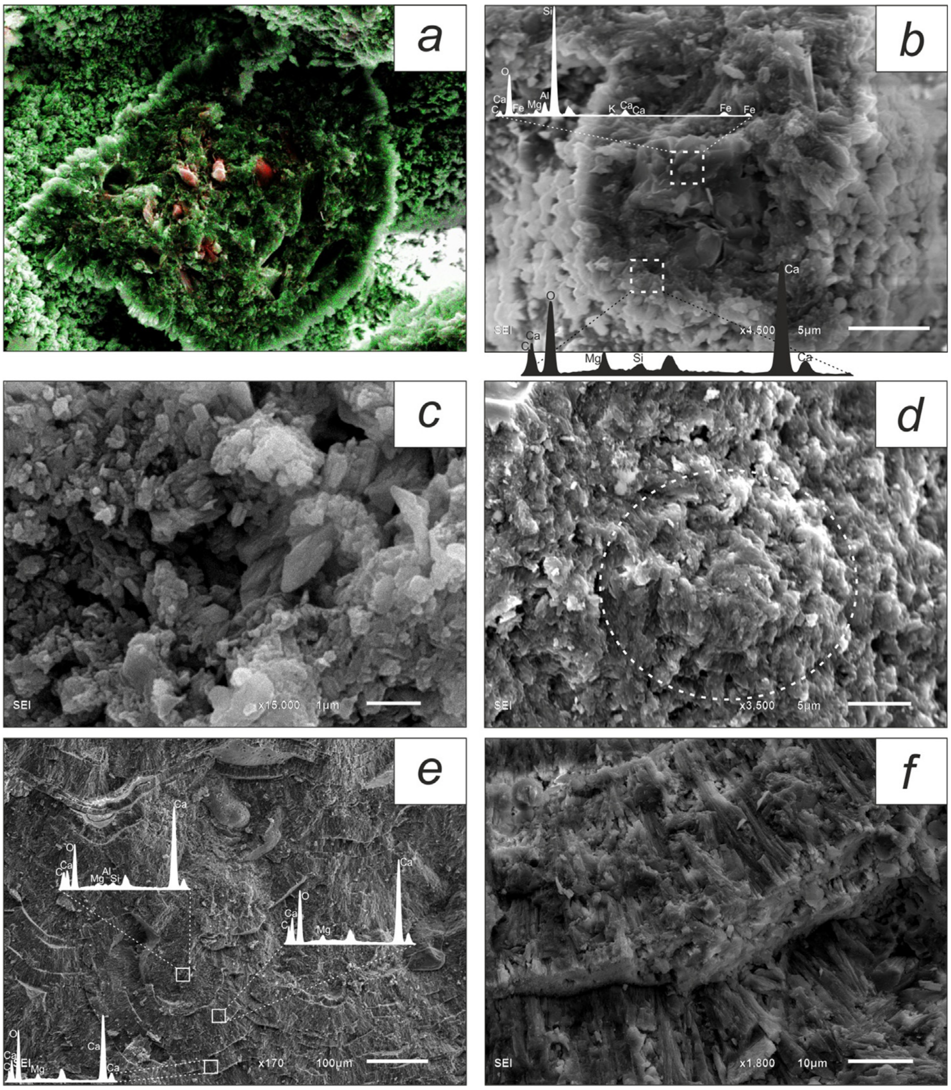

Fig. 7. Submicromorphology and composition (EDS) of the carbonate pendants from forest-steppes of Fore-Baikal region. a - spherulite nuclei (quartz grains) in pendants of the first group. Green – Ca, red - Si; b - carbonate spherulites in the outer layers of the pendants of the first group; c - disordered orientation of calcite crystals in the outer layers of coatings of the first and second groups; d - spherulites smoothed by colloform cryptocrystalline calcite in the inner layers of the cutans of the second group; e - densely packed spherulites composing the layers of cutans of the third group; f - micro-layers of spherulites, consisting of radially oriented columnar crystals of calcite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

researchers (Zamanian et al., 2016; Durand et al., 2018) to suggest that coatings may have formed through mediation of organisms (microorganisms can participate either in the formation or subsequent *in situ* recrystallization of the carbonate substance inside a coating). Therefore, such phenomenon also attracted our attention.

Under a binocular microscope, the layers of the coatings of the first group are different (Fig. 5a). However, there are some similarities in their morphology at the submicroscopic level. The inner brown layers are composed of tightly packed radial-fibrous micrite-microsparite calcite crystals organized in spherulitic aggregates. The diameter of such spherulites reaches 100 µm. Their cores are grains of quartz and feldspars (Fig. 7a). Dissolution caverns with a cellular texture and calcite platy crystals degraded to filiform separates are found. Spherulites in the outer layers of coatings are characterized by much smaller sizes (up to 10–15 µm) (Fig. 7 b), the signs of etching and dissolution of crystals are much rare.

Etching zones are characteristic of the inner layers of group II coatings, where rhombohedral calcite crystals recrystallize to filiform separates, and the crystal orientations become disordered (Fig. 7c). The described layers are composed of densely packed spherulites; however, radial-fibrous aggregates are smoothed from the surface by cryptocrystalline colloform calcite (Fig. 7d). The packing of crystals in the outer layers of the coatings is loose. They are composed of randomly oriented platy or tabular micritic crystals.

The morphology of the coatings of the second and third groups is similar under binocular microscope (Fig. 5b, c). However, submicroscopic study show differences. The loose packing of micritic crystals is also noted for the outer layers of III coatings group. At the same time, the inner microstratified layers of coatings of the third group are composed of fan-like structures with very dense packing (Fig. 7e). Each of these fans consists of numerous thin (up to 10 µm) layers of radially oriented microsparite crystals (Fig. 7f).

The inner layers of the coatings of IV group are composed of radially oriented and elongated rhombohedral microsparite crystals with well-defined faces organized into spherulitic aggregates with a diameter of 30–100 µm (Fig. 8a). Crystal surfaces have no signs of etching. The packing of spherulites is rather dense, but cavities are noted in places on the contacts of the aggregates. There is similarity of crystal morphology in the outer and inner layers. At the same time there are signs of intense dissolution of the crystals in the outer layers, when initially the sharp crystal edges break up into filamentary parts and in maximum manifestations acquire a smoothed appearance (Fig. 8 b). This is especially pronounced in the cavities at the contacts of the spherulites.

There are two types of structure for the outer layers of the coatings in sections 9-Z-2018 and 2-Z-2018 (IV group). The first is typical for areas with a small amount of mineral inclusions from the soil mass. Such sites are composed of randomly oriented elongated rhombohedral microsparite crystals without signs of etching. The surfaces of many crystals show signs of growth in the form of isometric micritic calcite crystals (Fig. 8c). The second structural type is observed for areas with a

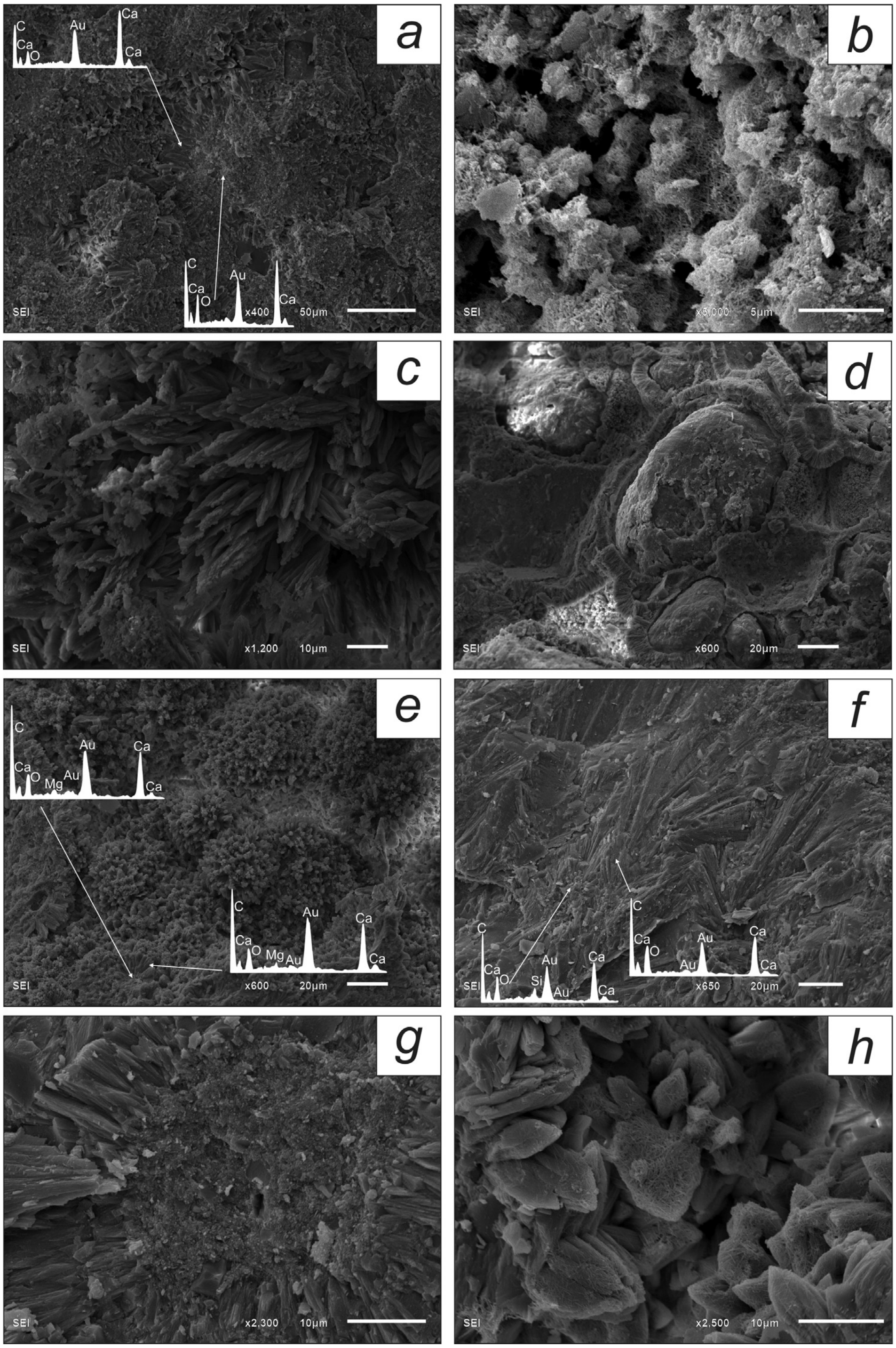

Fig. 8. Submicromorphology and composition (EDS) of the carbonate coatings from steppe soils of Transbaikalia. a - radially oriented and elongated rhombohedral microsparite crystals organized into spherulitic aggregates in the inner layers of the coatings of the IV group, b - signs of dissolution of the crystals in the outer layers of the coatings of the IV group, c - signs of growth in the form of isometric micritic calcite crystals on the crystal surfaces in the coatings of the IV group, d - radial orientation of carbonate minerals around mineral inclusions from the host soil mass in the coatings of the IV group, e - numerous loose packed carbonate spherulites organized around small mineral inclusions in the coatings of the IV group, f - composition of inner layers of the cutans of the V group, g - spherulites in middle layers of the coatings of the V group, h - composition of outer layers of the cutans of the V group.

large number of inclusions from the host soil mass. Here, carbonate minerals grow on top of such inclusions and acquire a radial orientation (Fig. 8d). With a large number of small inclusions of dust particles, carbonate minerals are organized into numerous loose packed carbonate spherulites with a diameter of 20–50 μm (Fig. 8e). The described coating layers of sections 9-Z-2018 and 2-Z-2018 are a soil mass cemented by carbonates, which later became the outer layer of coatings. In this case, the minerals of the host soil mass are basis for organizing the carbonate matter of the outer layers of pendants.

At the submicroscopic level, the inner layers of the group V coatings are composed of tightly packed radially oriented columnar sparite crystals (Fig. 8f). Upon transition to the middle parts of coatings, the crystal sizes noticeably decrease to microsparite with a similar morphology and organization. The central part of the coatings have a spherulitic organization, similar to group IV coatings. However, elongated rhombohedral and prismatic microsparite crystals in this case are oriented around the aggregates of cryptocrystalline calcite, cementing numerous small grains of quartz and other minerals (Fig. 8g). Spherulites are densely packed. The outer white layers have almost no inclusions. They are composed of micrite-microsparite isometric rhombohedral and tabular crystals with numerous areas of dissolution and recrystallization (Fig. 8h).

3.4. Radiocarbon age of carbonate coatings

Coatings of the first group were formed in the Middle Holocene

Table 4
Radiocarbon and calendar age of pedogenic carbonate coatings.

Section	Soil horizon	Depth, cm	Dating material	Layer	Lab number	Radiocarbon age	Calibrated age
Group I							
Osinovyi	Bk	80–90	Carbonate carbon	inner	MAMS-35408	4861 ± 23	3695–3636
				outer	MAMS-35409	4678 ± 23	3476–3370
Group II							
Tayturka -II	Ck	240–250	Carbonate carbon	inner	MAMS-35410	21,000 ± 70	23,618–23,190
				middle	MAMS-35411	22,070 ± 70	24,579–24,109
				outer	MAMS-35412	21,110 ± 70	23,716–23,291
Group III							
Berezovyi	2Ck	195–205	Carbonate carbon	inner	LU-8686	30,690 ± 780	34,860 ± 790
Group IV							
2-Z-2018	Bk	85–95	Carbonate carbon	inner	AA-112130	11,061 ± 35	13,045–12,805
				outer	AA-112129	4145 ± 40	4827–4538
Group V							
16-Z-2018	Bk	55–65	Carbonate carbon	inner	AA-112127	2950 ± 24	3177–3005
				outer	AA-112128	4167 ± 67	4848–4525

(3600–3300 cal yr BP) (Table 4). Accumulations of the second and third groups appeared in the second half of MIS-3 (24,100–23,300 and ~34,000–35,000 cal yr BP, respectively). The time frames of group IV coatings formation is quite wide (12,925–4682 cal yr BP) (Table 4). Abovementioned groups of coatings are characterized by the decreasing of age from the inner to the outer layers with a regularity dealing with the sequential nature of the accumulation of carbonate material of pendants. However, in the most ancient coatings of the second and third groups, cavities partially filled with carbonate material were sometimes observed at the contact with the pebble. Its dating showed an inversion of radiocarbon age (Table 4, Fig. 5b), which was previously described (Brock and Buck, 2005).

A similar inversion of radiocarbon age is also observed for the group V coatings. A more ancient date (4686 cal yr BP) was obtained for the outer layer. It is almost identical to the age of the outer layers of the group IV coatings (Table 4, Fig. 5f, g). Given the rather uniform, undisturbed structure of these layers it seems reliable. At the same time, the inner layers have an age of 3091 cal yr BP. Carbonate material of the inner layers was collected near the cavity. Apparently, in this case, as well as for group II of pendants, the inversion of radiocarbon age is associated with a partial dissolution of the oldest layers of pendants and re-crystallization of fresh carbonates in the cavities formed. This phenomenon is probably widespread and indicates the openness of carbonate coatings to external processes.

It should be stressed that the ^{14}C data obtained are measured ages, which do not necessarily correspond to true chronology of carbonate accumulation

3.5. δ^{13}C and δ^{18}O of pedogenic carbonate coatings

The δ^{13}C values for the pendants of the first group vary from −6.8 to −3.25‰, decreasing in the outer (younger) layers (Table 5, Fig. 9). The δ^{18}O values range from −16.33 to −10.95‰, increasing in the outer layers with respect to the inner ones. The composition of stable carbon isotopes of the second and third coating groups is close and slightly heavier in comparison with the cutans of the first group. The accumulations of the third group are characterized by δ^{13}C values from −4.2 to −2.05‰, decreasing in the outer layers.

The coatings of the second group display δ^{13}C values in the range from −4.11 to −2.5‰, which also decrease in the outer layers with respect to the inner ones. Significant differences are noted in the oxygen isotopic composition of carbonate accumulations. If the pendants of the third group are characterized by δ^{18}O values - from −12.63 to −11.99‰, which slightly (by 0.5–0.6‰) decrease in the outer layers, then for the coatings of the second group this range is much wider (from −14.03 to −10.24‰). In this case, the δ^{18}O values significantly (by 3–3.5‰) increase in the outer layers.

Table 5
Stable carbon and oxygen isotopic composition of carbonate coatings.

Coating number	δ^{13}C, ‰		δ^{18}O, ‰	
	Inner layer	Outer layer	Inner layer	Outer layer
Group I				
Tayturka-I				
1	−3,25	−4,73	−16,33	−13,58
2	−3,68	−5,04	−15,05	−11,2
3	−4,34	−5,41	−13,74	−10,95
Tayturka -II				
4	−4,51	−5,78	−13,41	−13,01
5	−4,12	−6,8	−15,91	−13,83
6	−3,86	−6,3	−14,83	−11,99
Group II				
Tayturka -I				
7	−3,3	−4,05	−13,68	−10,25
Tayturka -II				
8	−2,6	−3,2	−13,74	−10,24
9	−2,83	−3,7	−13,61	−10,89
10	−3,4	−4,11	−14,03	−11,01
Nizhnyi Bulay-II				
11	−2,5	−3,41	−13,89	−10,2
Group III				
Berezovyi				
12	−2,3	−4,2	−12,18	−12,57
13	−2,11	−3,96	−12,07	−12,61
Tayturka -I				
14	−2,05	−3,14	−12,04	−12,52
15	−2,23	−4,1	−11,99	−12,63
Group IV				
2-Z-2018				
16	−3,9	−4,9	−10,8	−10,5
5-Z-2018				
17	−3,2	−4,6	−9,3	−8,3
9-Z-2018				
18	−3,8	−5,1	−8,6	−7,9
11-Z-2018				
19	−3,7	−4,8	−9,0	−8,4
Group V				
16-Z-2018				
20	−4,6	−6,2	−9,3	−8,1
17-Z-2018				
21	−3,9	−6,7	−9,7	−9,2
19-Z-2018				
22	−4,1	−6,05	−8,9	−8,3

In the inner layers of coatings forming in the soils of the Selenga Middle mountains (group IV), δ^{13}C values vary from −3.9 to −3.2‰,

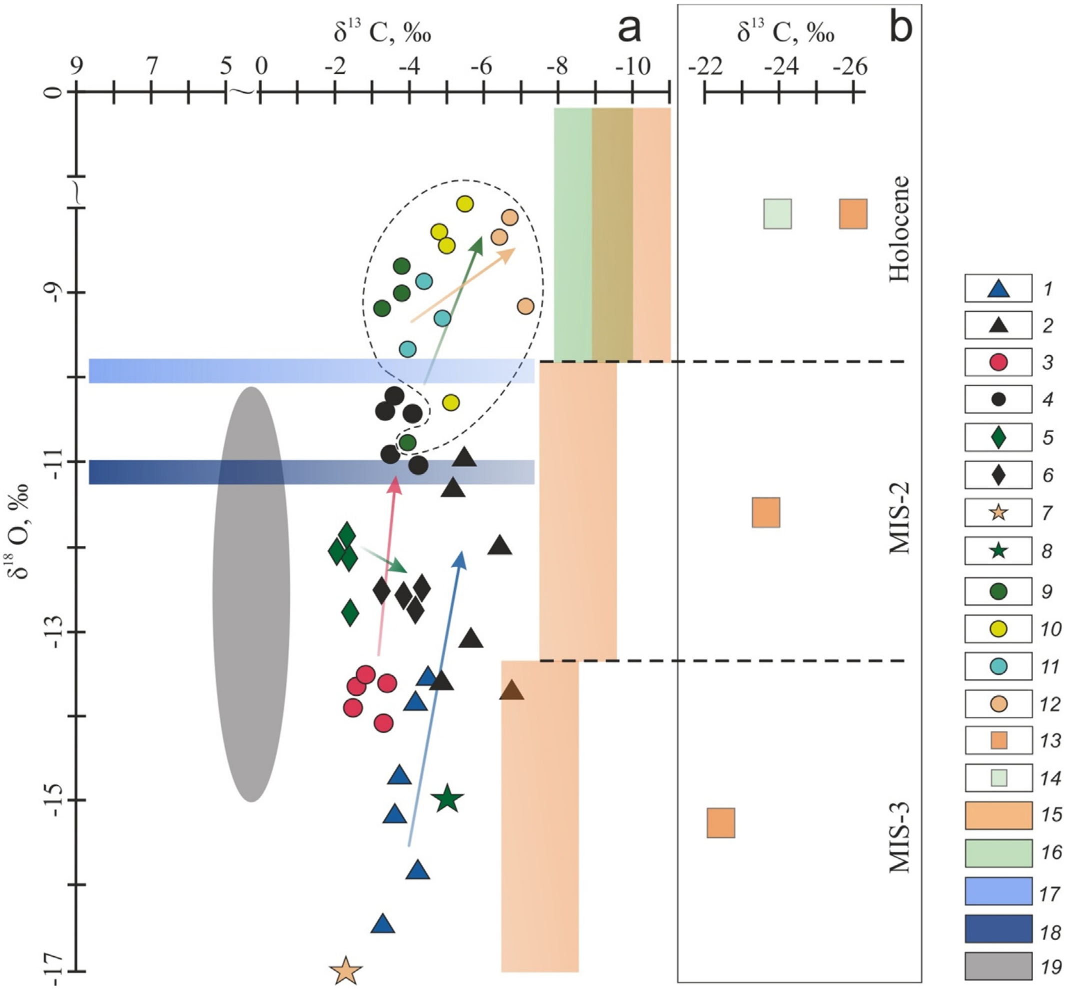

Fig. 9. Stable carbon and oxygen isotopic composition of coatings (a) and stable carbon isotopic composition of host soils (b). Dashed line indicate the δ^{13}C and δ^{18}O values of carbonate coating from soils of Transbaikalia. The arrows indicate changes in the isotopic composition from the inner to the outer layers of various groups of coatings. Table of symbols: 1 – inner layers of coatings of the I group, 2 - outer layers of coatings of the I group, 3 - inner layers of coatings of the II group, 4 - outer layers of coatings of the II group, 5 - inner layers of coatings of the III group, 6 - outer layers of coatings of the III group, 7 - average stable carbon and oxygen isotopic composition of coating in soils of North-Eastern Asia (Pustovoytov, 1998), 8 - average stable carbon and oxygen isotopic composition of carbonates in soils of Alaska (Marion et al., 1991), 9 - inner layers of coatings of the IV group, 10 - outer layers of coatings of the IV group, 11 - inner layers of coatings of the V group, 12 – outer layers of coatings of the V group, 13 – stable carbon isotopic composition of surface and buried soils of Fore-Baikal region, 14 - stable carbon isotopic composition of surface soils of Transbaikalia, 15 – area of isotopic equilibrium with soil-respired CO_2 for soils of Fore-Baikal region, 16 - area of isotopic equilibrium with soil-respired CO_2 for soils of Transbaikalia, 17 – stable oxygen isotopic composition of meteoric water for Transbaikalia, 18 - stable oxygen isotopic composition of meteoric water for Fore-Baikal region, 19 - stable isotopic composition of carbon and oxygen in pedogenic carbonates formed under cold periglacial conditions (Cerling, 1984).

decreasing in the outer layers by more than 1‰ (Table 5, Fig. 9). Their range varies from −5.1 to −4.6‰ in the outer layers. δ^{18}O values of inner layers of coatings range from −10.8 to −8.6‰, increasing in the outer layers to −10.5 - (−7.9)‰.

In the inner layers of the V group of coatings (Onon-Argun' steppes), the range of δ^{13}C is from −4.6 to −3.9‰. The carbon isotopic composition is depleted by ^{13}C in the outer layers of the accumulations by more than 1.5‰, varying from −6.7 to −6.1‰. The δ^{18}O values in the inner layers of the coatings vary from −9.7 to −8.9‰, increasing in the outer layers by 0.5–1.2 ‰. Here they range from −9.2 to −8.1‰.

4. Discussion

4.1. Carbonate profile of forest-steppe and steppe soils of Baikal region

The studied soil profiles are characterized by a significant $CaCO_3$ content (Fig. 3). In the forest-steppe soils of the Fore-Baikal region average $CaCO_3$ content is 20–30%, while in the steppe soils of Transbaikalia it is even higher (35–45% in average).

The most carbonate-rich soils are formed in Transbaikalia on foothill plains. Previous studies (Nogina, 1964; Volkovintser, 1978) have not confirmed the interrelation between carbonate content in parent material and rates of carbonate accumulation in soils. Thus, the main point of view on the origin of such a high $CaCO_3$ content in the soils of Transbaikalia is not their formation *in situ*, but the addition of weathering products from the surrounding mountain ranges to the basins (Nogina, 1964; Volkovintser, 1978).

We argues for a key role of lithological factor in a ratio of $CaCO_3$ accumulation in the forest-steppe soils of the Fore-Baikal region (Golubtsov et al., 2019). Soils in most of the territory are formed on the weathering products of Jurassic non-carbonate rocks. Carbonates in these soils are almost absent. Well-defined carbonate accumulations and the highest carbonate content in the fine earth are observed only for the high river terraces. Here, a cover of loess-like deposits is developed, which are mainly slope deposits and accumulated from the weathering products of Cambrian carbonate-bearing rocks (limestone and dolomites) (Molodykh, 1958). Therefore, as in Transbaikalia, a huge amount of carbonates in the soils is formed not *in situ*, but as a result of the lithogenic influence.

Further migration of carbonates, their leaching during pedogenesis formed the observed carbonate profile and secondary accumulations of study soils. When analyzing the carbonate profile of surface soils, it is worth paying attention to the ratio of the depth of carbonates to the amount of precipitation. The mean annual precipitation and its seasonal distribution determine the depth, to which carbonates are leached and, accordingly, the depth of their accumulation in soils (Egli and Fitze, 2001; Royer, 1999; Retallack, 2005). Thus, in the forest-steppes of Fore-Baikal region with the mean annual precipitation of 350–400 mm, the depth of the Bk horizons should theoretically be 30–50 cm, while in fact this depth is 70–100 cm (Fig. 3 a), which corresponds to precipitation of 450–520 mm. This may attest to more humid conditions in the past, so that the leaching of carbonates to a greater depth was possible. The same pattern is observed in steppe soils of Transbaikalia, where the depth of carbonates is 40–60 cm (Fig. 3b), which theoretically corresponds to the mean annual precipitation of 370–400 mm, although at the current level of atmospheric precipitation (200–300 mm/yr) carbonates should have accumulated in the upper 20–25 cm of the soil profile.

Based on these assumptions, we believe that the carbonate profile of surface soils of the studied territories has a relict nature. It is likely that it was formed as a result of the downward migration and accumulation of carbonates under more humid conditions of the previous Holocene periods and does not undergo significant changes under modern climatic conditions.

In particular the nowadays stability of the carbonate profile is due to the periodically-percolative type of water regime of the studied soils. The moisture circulation mainly covers the upper meter of the soil, and the most intensive circulation occurs the upper half meter. The underlying layers are characterized by an almost complete absence of moisture circulation due to their late thawing and low temperatures. The relict nature of the carbonate profile of surface soils is also confirmed by the ages of carbonate coatings. The age of the youngest layers of I, IV, and V groups of coatings is estimated as mid-Holocene (from 4.6 thousand years for pendants of groups IV and V, and 3.3 thousand years in cutans of group I).

The relict nature and stability of the carbonate profile of studied soils are important for the interpretation of the obtained radiocarbon dates, because suggests the absence of decreasing of age of the secondary carbonates during dissolution, re-crystallization and the introduction of young CO_2.

4.2. Radiocarbon age of carbonate coatings and soil organic matter. Growth rates of coatings

At this stage of the study, we are able to compare the ages of surface soils and carbonate cutans for two sections. In Fore-Baikal region it is Tayturka-I and in Transbaikalia it is 2-Z-2018. Although radiocarbon age of the coatings of the I group is unknown yet for the Tayturka-I section, based on the similarity of occurrence conditions and morphology, we can assume their synchronous formation with I group accumulations of Osinovyi section.

The age of the organic matter of the 2-Z-2018 section (3.3–3 kyr BP, Table 2) is younger than the age of the youngest layers of cutans forming here (group IV, 4.6 kyr BP). The same regularity is noted for the group I coatings from the Chernozems of the Tayturka-I section. The age of carbonate coatings of the first group (3600–3300 cal yr BP, Table 4) older than age of humic acids from the deeper part of the surface humus horizon of Tayturka-I (2600 cal yr BP). Coatings of the third group (Berezovyi section) also show an older age than the organic matter of soils in which they are formed (Tables 2 and 4).

At the moment, we see two main explanations for this age discrepancy. Introduction of ancient carbon by incorporating lithogenic carbonate particles into the secondary carbonates, which can lead to increasing of the age (Deutz et al., 2002) on the one hand. Soil organic matter can become younger during active carbon exchange due to biological turnover, on the other hand. Humus age decreasing can reach 20% or even more (Aleksandrovskiy and Chichagova, 1998). We consider radiocarbon dates of carbonates to be more reliable for the following reasons. First, our micromorphological studies have shown the absence of lithogenic carbonate inclusions in coatings (Fig. 6). At the same time, such inclusions are abundant in the enclosing sediments (Fig. 4). Second, the successive accumulation of coating material resulting in the covering of the older layers by the new carbonates reduces their contact with the environment. This, in turn, reduces the probability of the dissolution and reprecipitation of coating material, which can decrease the potential fluctuations in the radiocarbon age of the coatings. The validity of the obtained ^{14}C ages is also supported by the fact that, for most coatings, decreasing of age is observed from the inner to the outer layers, which is consistent with successive accumulation of coating material.

The duration of the formation of the coatings of the first group is estimated at 300 years as based on difference of ^{14}C ages of inner and outer layers. The rates of their formation (considering the average thickness of the pendants of this group is 6 mm) is 2 mm per 100 years. It is still problematic to determine the rates of formation of a group IV of coatings at this stage. The question remains open about the continuity of the formation of these accumulations for such a long time (12.9–4.6 thousand years). Most likely, the pendants in the soils of the 2-Z-2018 section went through long stages of absence of growth, followed by active accumulation of carbonate material in their development.

The Late Karga (final stages of MIS-3) coatings of the second group correlates well with the Late Karga-Early Sartan (MIS-3-MIS-2 border) age of faunal remains from the Tayturka-II section. The duration of the formation of the coatings of the second group is estimated at 800 years at a rate of carbonate material accumulation of 0.6 mm per 100 years. For coatings of the third group, only the age of the inner layers is known. Therefore, it is not possible to determine the duration of their formation and the rate of accumulation of carbonate material at this stage. This also applies to coatings of group V, for which only the age of the outer layers (4.6 thousand years) can be considered as correct at this stage of investigation.

The approximate growth rates of the coatings appear to be unusually high for a soil system (Pustovoytov, 2003). However, we consider them rather credible, taking in account significant carbonate content in the soil fine earth (Fig. 3). Holocene coatings are characterized by maximum growth rates, which correlates with the highest carbonate content in the sediments where they are found. Coatings were formed as a result of leaching of carbonates from slope deposits, weathering products of carbonate-rich rocks. At the same time, MIS-3 coatings formed mainly on significantly less carbonate-rich alluvial deposits, which apparently affected their lower growth rates.

4.3. Carbonate coatings formation environment indicated by C and O isotopes

Variations in the ratios of stable isotopes $^{12}C/^{13}C$ and $^{16}O/^{18}O$ in pedogenic carbonates reflect the conditions of their formation (Cerling, 1984; Quade et al., 1989; Marion et al., 1991; Pustovoytov et al., 2007; Monger et al., 2009; Breecker et al., 2009; Peters et al., 2013; Barta et al., 2018).

The observed $\delta^{13}C$ values of carbonate coatings are heavier than the equilibrium $\delta^{13}C$ values of soil organic matter in almost all cases (Fig. 9), which may indicate a significant influence of atmospheric CO_2 on the formation of the studied coatings. Such values indicate the absence of isotopic equilibrium of carbonates with soil-respired CO_2, when $\delta^{13}C$ values of carbonates are 14–16‰ heavier than the carbon isotopic composition of soil organic matter (Cerling, 1984). This phenomenon was previously noted for carbonates forming in cold conditions (Cerling, 1984; Quade et al., 1989; Marion et al., 1991; Courty et al., 1994; Vogt et al., 2018).

Relatively cold climatic conditions may be associated with the enrichment of the isotopic composition of coatings by the ^{13}C. Under dry and cold conditions, due to the low density of the vegetation cover and the low soil respiration rates, atmospheric CO_2 diffuse actively into soil and has a significant effect on the isotopic composition of the secondary carbonates (Cerling, 1984). In this case, $\delta^{13}C$ values of pedogenic carbonates at any soil depth is almost invariably not a direct indicator of the isotopic composition of the biological source of CO_2 (and plant community composition), but is instead a soil CO_2 barometer, reflecting differing soil respiration rates and soil CO_2 concentrations (Quade et al., 1989; Breecker et al., 2009; Oerter and Amundson, 2016). Based on this point of view, the heavy carbon isotopic composition of coatings and the absence of equilibrium with soil CO_2 can be explained by the significant effect of atmospheric CO_2 on their isotopic composition under conditions of relatively low soil respiration rates. The latter is probably due to the low density of the vegetation cover, which could be caused by environmental conditions unfavorable for plants development, in particular, low temperatures.

The pedogenic coatings of Transbaikalia have a slightly lighter carbon isotopic composition and are slightly closer to the soil CO_2 isotopic equilibrium area. This may indicate a higher soil respiration rate during their formation and, possibly, different seasonality of the formation of the coatings in steppe soils of Transbaikalia and forest-steppe soils of Fore-Baikal region. This point of view can be verified by analyzing the stable oxygen isotopic composition of coatings.

In Fore-Baikal region $\delta^{18}O$ values of precipitations are in average –11.13‰ (with respect to SMOW) (Statistical treatment…, 1992). For the territory of Transbaikalia, the $\delta^{18}O$ values are –10.0 (SMOW) (Kurita et al., 2003). The stable oxygen isotopic composition of most of the coatings in steppe soils of Transbaikalia is heavier than the isotopic composition of oxygen in precipitation here (Fig. 9). At the same time, the stable oxygen isotopic composition in most of the pendants of forest-steppe soils of the Fore-Baikal region is noticeably depleted, compared with the oxygen isotopic composition of atmospheric precipitation.

Distinct $\delta^{18}O$ and $\delta^{13}C$ values suggest that the coatings of Transbaikalia and Fore-Baikal region have been formed under contrast environmental conditions. The isotopic composition of oxygen in soil water almost does not change during transpiration. However, evaporation causes a significant enrichment of residual water with heavy ^{18}O, and freezing leads to an enrichment with light ^{16}O (Marion et al., 1991; Cerling and Quade, 1993). The Transbaikalia coatings, which have more enriched $\delta^{18}O$ values should be formed in a relatively more evaporative condition. On the other hand, carbonate material of forest-steppe coatings of Fore-Baikal region precipitated upon freezing of the soil solution. Isotopic composition of oxygen is controlled by atmospheric precipitation and oxygen fractionation during freezing in this case. This lead to depletion of their oxygen isotopic composition in relation to atmospheric precipitation.

Given the above and the environmental conditions of the study area, we can assume that the formation of pedogenic carbonates in the steppe soils of the Transbaikalia is mainly confined to the summer season, when the soil is most warmed up, and the plants actively consume water and emit a large amount of CO_2. This agrees well with the slightly higher temperatures of the warm season and the greater aridity of the Transbaikal region.

In turn, carbonate precipitation in forest-steppe soils of Fore-Baikal region occurred during the degassing of soil solutions in the course of periodic freezing and thawing, dynamic increase and decrease in soil biological activity, alternation of phases of snowmelt and rainwater infiltration into the soil and its subsequent freezing, which can be observed in the region in spring and autumn. Snowmelt/rainwater dissolves the primary carbonates contained in sediments, which then crystallize as calcite during freezing. Under these conditions, atmospheric CO_2 had the main effect on the isotopic composition of carbon; isotopic composition of oxygen of carbonates was controlled by isotopic fractionation during freezing of soil solutions. A significant influence of periodical freezing-thawing on soil formation (especially MIS-3 soils) follows from micromorphological data (see Section 3.1.2.). Striated b-fabrics, in particular poro- and granostriated (Fig. 4) have been commonly documented in present or past frost-affected soils and associated with alternating freeze-thaw (Van Vliet-Lanoë and Fox, 2018). Such soil microstructure can serve as one of the confirmation of the formation of coatings during periodic freezing and thawing of soils.

4.4. Carbonate coatings as palaeoclimatic proxy

On the basis of the morphology of accumulations of the first group, two main stages in their development may be recognized. At the first stage, the inner layers were formed. The increased content of organic matter and iron in them testifies to active humus illuviation into the carbonate-accumulative horizon and to the development of the Al–Fe–humus process under cold humid conditions. The age of the described layers of coatings (3600 cal yr BP) corresponds to the humid cold phase in the development of pedogenic coatings (3700 cal yr BP) in cryoarid soils of Tuva (Bronnikova et al., 2017). Wang et al. (2004) (cit. in Klinge and Sauer, 2019) reconstructed several cool and wet periods for northern Mongolia during late Holocene indicated by low magnetic susceptibility. One of them was occurred 4.0–3.5 kyr BP.

Generally, two types of environment are favorable for mobilization, migration and subsoil illuvial accumulation of humus compounds: First, humid climate, low pH (poor, sandy parent materials), Al-Fe-humus migration, and semi-arid climate. Second, mostly loamy and clayey parent materials, solonetzic process. Both scenarios, in theory, could be possible for the studied area, both are possible in warm and cold conditions. Key point allowing us to argue for the cold and humid environment as follows: morphological similarity of humus-iron-enriched coatings to those in Spodic materials, and their difference from coatings related to the solonetzic process.

Similar soils which contain compound coatings (calcium carbonate with microlaminae of illuvial humus, rarely in combination with iron) were earlier described under tundra-steppe environments in the North-East of Russia: continental part of Chukotka peninsula (Bystryakov, 1988; Chernyakhovskij, 1997; Pustovoytov, 1998). All the above-mentioned authors also considered illuvial origination of humus coatings (or microlaminae in calcareous coatings), analogous to coatings in Spodosols. In this region soils with such coatings (Sceletic Protocalcic Cambisoils) are combined in soil mantel with Entic Podzol which contains humus coatings but free of carbonates. Later similar coatings were studied in more details in South-East Altai (Tyva Republic) (Bronnikova et al., 2017). The combination within a single profile humus illuviation and accumulation of calcium carbonates seems to be rather contradictory. But even nowadays Ah horizons in such soils contain pretty much of easily soluble organic compounds and have pH 5–6, which is favorable for humus mobilization and migration; neutral or alkaline pH in Bk horizons and presence of carbonates allows accumulation of these compounds in Bk horizons. But in more humid periods the conditions for mobilization migration and accumulation of organic matter would have been even better.

Relatively cold climatic conditions of this time may be associated with the general enrichment of the isotopic composition of the inner layers of first group of coatings by the ^{13}C. Under dry and cold conditions, due to the low density of the vegetation cover and the low soil respiration rates, atmospheric CO_2 diffuse actively into soil and has a significant effect on the isotopic composition of the secondary carbonates (Cerling, 1984). In this case, $\delta^{13}C$ values of pedogenic carbonates at any soil depth is almost invariably not a direct indicator of the isotopic composition of the biological source of CO_2 (and plant community composition), but is instead a soil CO_2 barometer, reflecting differing soil respiration rates and soil CO_2 concentrations (Quade et al., 1989; Breecker et al., 2009; Oerter and Amundson, 2016). Based on this point of view, the heavy carbon isotopic composition of coatings of first group and the absence of equilibrium with soil CO_2 can be explained by the significant effect of atmospheric CO_2 on their isotopic composition under conditions of relatively low soil respiration rates. The latter is probably due to the low density of the vegetation cover, which could be caused by environmental conditions unfavorable for plants development, particularly by low temperatures.

The outer layers of coatings (the second stage) were formed during the secondary illuvial redistribution of carbonates under relatively dry climatic conditions. Their formation was finished 3300 cal. yr BP. The material of pendants was crystallized from strongly saturated carbonate solutions. This is evidenced by the small size of crystals in coatings and the absence of signs of their etching and dissolution. Increased (on average 5–10%) $CaCO_3$ content in outer layers could be a result of temperature rise, which caused a decrease in CO_2 solubility and an increase in its concentration in soil air due to the higher biological activity. Under such conditions, the formation rate of pedogenic carbonates significantly increases (Zamanian et al., 2016). An increase in biological activity and an increase of influence of soil-respired CO_2 on the formation of coatings at this stage are indirectly confirmed by the fact that the $\delta^{13}C$ values of the outer layers noticeably shift toward isotopic equilibrium (Fig. 9).

Climate aridization at this stage is also confirmed by changes in the composition of stable carbon and oxygen isotopes in the layers of coatings. The values of $\delta^{13}C$ decrease in the outer layers in comparison with the inner layers. Contrary to them, the values of $\delta^{18}O$ in the younger layers of coatings become higher, indicating a gradual enrichment of local precipitation with ^{18}O.

The interpretation of such isotopic changes as a reflection of aridization and temperature increase at this time is confirmed by materials from paleosoil studies (Vorobyova, 2010), a decrease in the content of diatoms in sediments of Lake Kotokel and the increase in their oxygen isotope composition (Kostrova et al., 2016), the dynamics of humidity in the Baikal region and adjacent areas (Wang and Feng, 2013). In the eastern Sayan Mountains, Mackay et al. (2012) investigated a sediment core of an alpine lake. Based on the biome reconstruction derived from pollen analysis, diatom and chironomid assemblages, they inferred cold climatic conditions and decline in July temperatures during the mid-Holocene that lasted until 3.5 ka. They reconstructed warm conditions after 3.5 ka, based on a change to light coniferous forests and occurrence of chironomids indicating high July temperatures. Herzschuh (2006) (cit. in Klinge and Sauer, 2019), in her review about moisture changes in central Asia, reported a trend towards drier climatic conditions about 3.5 ka ago. A similar direction of environmental changes is in good agreement with the formation conditions of the coatings of the first group.

The inner layers of coatings in the steppe soils of the Selenga Middle mountains (group IV) are almost identical in morphology and composition, which suggests a close date for the beginning of their formation. It occurred at a relatively short-term stage of climate warming during the Late Glacial period, which chronologically coincides with Bølling. It is well known that the climate of East Siberia during the last glacial was not only cold, but also dry (Velichko, 1999; Bezrukova et al., 2010). The lowland landscapes of Siberia during the last glacial period were dominated by the so-called "mammoth steppe" which was characterized by uniquely fertile calcium-rich soils (Guthrie, 2001). The almost twice increasing in precipitation at the beginning of the warm phases of the Bølling-Allerød led to intensive leaching of soluble components, in particular carbonates, from the soils of mammoth steppes, which, according to opinion of some authors (Chebykin et al., 2002), even affected the geochemistry of sediments delivered to the Lake Baikal. It is logical to assume that such a redistribution of carbonates in soils was the starting point for the formation of coatings in the soils of the Selenga Middle mountains. The carbon isotopic composition of coatings of IV group is similar to that for pendant of first group, which indicates a low soil respiration rates, probably associated with a low temperatures. The described layers of coatings are enriched with organic matter, which indicates the redistribution of not only carbonates, but also humus in the soil profile. This fact can confirm the relatively high moisture content of soils in the considered time period. Such a dark laminae of coatings may have formed through mediation of organisms. This is indicated by numerous spherulites, to which many authors attribute the biogenic origin (Verrecchia et al., 1995; Zhou and Chafetz, 2009).

The time of the end of the stage of formation of the inner layers and the change in the conditions of accumulation of carbonates remains unknown. However, it is known that the formation of coatings was completed about 4.6 thousand years ago. An interesting fact is the almost complete agreement of this date with the youngest carbonate material of coatings in the steppe soils of Onon-Argun' interfluves (group V) and Northeast Siberia (Pustovoytov, 1998). It is likely that the formation of pendants in steppe soils of Transbaikalia was completed at the stage of a rather sharp cooling and aridization, which is noted about 4.5 kyr BP in different regions of Eurasia (Velichko et al., 1997; Michelutti et al., 2006), including the Olkhon region (Danko, 2009), peat bogs in the Northern Baikal region (Bezrukova et al., 2006), sediments of Lake Baikal (Karabanov et al., 2000) and soil-sedimentary sequences of the Selenga Middle mountains (Golubtsov et al., 2017). Gradual climate aridization over the past 5 thousand years, recorded by pedological data, has been observed in Olkhon region (Danko, 2009), central (Lehmkuhl et al., 2011), and northern Mongolia (Lehmkuhl et al., 2012). Chen et al., 2008 noted a decrease in the level of the Mongolian lakes from about 4.5 thousand years. A decrease in climate humidity is reflected in the bottom sediments of Lake Arachley in the Central Transbaikalia (Reshetova et al., 2013).

It is likely that after this climatic phase, redistribution of carbonates in soils did not occur or occurred with a limited intensity. Most likely, this is due to the fact that the main carbonate reserves in the upper parts of the soil profiles were redistributed to the underlying horizons.

The formation of the second and third groups of coatings correlates chronologically with two regional stages of soil formation (the Lower and Upper Osinsk periods) (Vorobyova et al., 2015) and with an increase in the number of diatoms in the bottom sediments of Kotokel' Lake, when their oxygen isotope composition became heavier, 36,000–32,000 cal. yr BP and during MIS-2 (Kostrova et al., 2016). These stages correlate with short-term intervals in the Dansgaard–Oeschger oscillations (2 and 7), reflecting the rise in the mean air temperature in the Northern Hemisphere (Rasmussen et al., 2014).

Significantly lower growth rates of MIS-3 coatings are noted in comparison with Holocene pendants (0.6 mm per 100 years versus 2 mm per 100 years, respectively). Micromorphological data (see Section 3.1.2) and an analysis of the occurrence conditions of Karga and Holocene soils, presumably, indicate that MIS-3 soils were formed under cold and relatively humid conditions on low river terraces. Some researchers (Vorobyova et al., 2015) consider MIS-3 soils mainly as soils of forest environments formed in more humid climates compared with the modern climate of Fore-Baikal region. At the same time, the Holocene soils were formed already under the conditions of the predominant distribution of grasslands on cover slope deposits of higher terraces. Thus, we can assume a higher moisture content of the MIS-3 soils and, correspondingly, more humid climatic conditions of the Karga thermochron in the study area. This assumption is confirmed by the morphology and composition of coatings. The pendants of the second and third groups are more enriched with impurities of organic matter, which at that time, most likely, was more actively washed into the accumulative-carbonate horizons of soils.

The stable carbon and oxygen isotopes ratio in the coatings formed in the Middle Holocene and in the Late Karga time is quite close. Despite the fact that these coatings formed in soils under different landscapes, the carbon isotopic composition does not show any significant differences. Perhaps this phenomenon is related to significant effect of atmospheric CO_2 on carbon isotopic composition of coatings under conditions of relatively low soil respiration rates. Taking into account the main influence of the processes of periodic freezing-thawing of soils on the isotopic composition of coatings, this enables us to assume that the soil forming conditions in these periods were close in terms of relatively low temperatures and long-term seasonal freezing of soils.

5. Conclusions

The studied coatings were formed in carbonate-rich soils on river terraces and piedmont plains as a result of leaching of carbonates and their subsequent accumulation. Their formation was most intense in the second half of MIS-3 (24.1–23.3 and ~34–35 kyr BP), during the warm phases of the Late Glacial (starting from 12.9 kyr BP) and in the final stages of the Middle Holocene (3.6–3.3 kyr BP). Thus, pedogenic carbonate coatings in soils of the Baikal region are mainly relict feature of the previous epochs of pedogenesis and Middle Holocene stage of surface soil formation.

The seasonality of the formation of pedogenic carbonates in the steppe soils of Transbaikalia and forest-steppe soils of Fore-Baikal region seems to be significantly different. Based on the stable carbon and oxygen isotopic composition of coatings and given the environmental conditions of the study area, we can assume that the formation of pedogenic carbonates in the steppe soils of the Transbaikalia is mainly confined to the summer season, when the soil is most warmed up, and the plants actively consume water and emit a large amount of CO_2. This agrees well with the slightly higher temperatures of the warm season and the greater aridity of the Transbaikal region. In turn, carbonate precipitation in forest-steppe soils of Fore-Baikal region occurred during the degassing of soil solutions in the course of periodic freezing and thawing, dynamic increase and decrease in soil biological activity, alternation of phases of snowmelt and rainwater infiltration into the soil and its subsequent freezing, which can be observed in the region in spring and autumn.

A significant $CaCO_3$ content in the studied soils contributed to the high growth rates of pendants. Holocene coatings are characterized by maximum growth intensity, which correlates with the highest carbonate content in the slope sediments where they are found. At the same time, MIS-3 coatings formed mainly on significantly less carbonate-rich alluvial deposits, which apparently affected their lower growth intensity. Based on an analysis of the growth rates of coatings, comparison of the isotopic composition of different age groups of pendants and soil micromorphology the more humid climatic conditions of the Karga (MIS-3) thermochron is assumed in comparison with the Middle Holocene. The temperature conditions of pedogenesis may be similar. Both for the Middle Holocene and for the Karga time, relatively low temperatures of pedogenesis and long-term seasonal soil freezing are supposed.

Paleoecological conditions reconstructed for the identified stages of formation of carbonate coatings correlate well with the trend of climatic changes in the Baikal region and adjacent areas. They reflect the effect of temperature and moisture fluctuations on the dynamics of soil-forming processes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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