ГЕОМОРФОЛОГИЯ, 2022, том 53, № 3, с. 96–106

СЕДИМЕНТОЛОГИЯ, ПАЛЕОГЕОКРИОЛОГИЯ, ПАЛЕОГИДРОЛОГИЯ

УДК 551.89:552.52 (470.4)

ЛИТОЛОГО-МИНЕРАЛОГИЧЕСКАЯ ХАРАКТЕРИСТИКА НИЖНЕХВАЛЫНСКИХ ШОКОЛАДНЫХ ГЛИН НИЖНЕЙ ВОЛГИ (НА ПРИМЕРЕ РАЗРЕЗОВ РАЙГОРОД И СРЕДНЯЯ АХТУБА)

Р. Э. Мусаэлян[1,*], М. П. Лебедева[1], Ю. В. Ростовцева[2], Е. Б. Варламов[1]

[1] *Почвенный институт имени В.В. Докучаева, Москва, Россия*

[2] *Московский государственный университет имени М.В. Ломоносова, геологический факультет, Москва, Россия*

**E-mail: romaniero1@gmail.com*

Поступила в редакцию 30.03.2022 г.
После доработки 10.04.2022 г.
Принята к публикации 15.04.2022 г.

Шоколадные глины – полифациальные морские отложения дискуссионного генезиса, широко распространенные в Нижнем Поволжье. Представлены результаты детального анализа особенностей микростроения, гранулометрических (42 образца) и минералогических (24 образца) составов разных слоев в толще нижнехвалынских шоколадных глин разрезов Средняя Ахтуба и Райгород. Разрезы расположены на противоположных сторонах Волго-Ахтубинской поймы. На основе данных, полученных с помощью лазерного дифрактометра, были рассчитаны литологические коэффициенты. Это позволило выделить семь общих для двух разрезов литотипов, каждый из которых также обладает особыми минералогическими и микроморфологическими характеристиками. Минералогические структурные особенности минералов во фракции <1 мкм в каждом литотипе и количественные соотношения глинистых минералов были определены методом рентгеновской дифрактометрии. Выявлено, что наиболее глинистые литотипы характеризуются преобладанием триоктаэдрического иллита над смектитом. Обратная ситуация наблюдается в алевритовых литотипах, где смектит преобладал над диоктаэдрическим иллитом. Набухающие компоненты были представлены высокозарядным бейделлитом в разрезе Средняя Ахтуба и высокозарядным монтмориллонитом в разрезе Райгород. Такие различия в соотношении и структуре глинистых минералов могут быть обусловлены разными источниками сноса или их различными синседиментационными или диагенетическими преобразованиями. Микроморфологические данные позволили установить биогенные текстуры в глинистых литотипах нижнехвалынских шоколадных глин. В алевритовых литотипах определены косая слоистость и углистое органическое вещество, что позволяет предполагать близость зоны их седиментации к береговой линии. Полученные материалы позволили показать сложный состав отдельных слоев толщи шоколадных глин и определить новые направления в изучении их генетических особенностей. Исследования отдельных литотипов нижнехвалынских шоколадных глин с детальной привязкой к глубинам проведены впервые.

Ключевые слова: литотипы, глинистая минералогия, литология, количественный анализ, микроморфология

DOI: 10.31857/S0435428122030105

1. INTRODUCTION

Polyfacial Lower Khvalynian marine Chocolate clays (ChC) are one of the most interesting geological objects within the Lower Volga region of Russia (Svitoch et. al, 2017). The ChC often underlain by Lower Khvalyn sands, sometimes by Atelian subaerial deposits and can be overlain by modern soils. Such soils contain ChC intraclasts (formed by syndepositional erosion of sediments) and ChC fragments (transported by aeolian processes). The age of Lower Khvalynian ChC is estimated between 17 and 13.4 kyr BP, based on the latest optically-stimulated luminescence data (OSL) (c). This interval corresponds to the most significant transgression of the Caspian Sea in the Late Quaternary. The water level rose sharply by 40–50 m above the current average global sea level, which meant a local sea level rise of more than 100 m (Svitoch, 2007; Rychagov, 2014) and according to some data by 160–170 m (Lokhin, Maev, 1990). This transgression is thought by some articles to have been caused by the inflow of meltwater from the Fennoscandian Ice Sheet into the upper reaches of the Volga River during the Last Glacial Maximum (Kvasov, 1975; Toropov, Morozova, 2011; Varushchenko et al., 1987). However, in the last decades it was found that the inflow of glacial melt waters in river Volga was relatively small and it had ceased before the beginning of the Khvalynian highstand (Panin, 2020, 2021). On the other hand, transgression may have been caused by an increase the flow in the Volga basin. According to some data, it exceeded the modern one by two times and reached 550 km^3/year (Sidorchuk et al, 2009). The history of research on ChC spans around 150 years, with many important studies on their genesis, sedimentation, paleogeography and stratigraphy being conducted over the last two decades. However, there are only very few general reports on the mineralogy of ChC (Arbuzova, 1970; Lavrushin et al., 2014; Svitoch, Makshaev, 2015; Makshaev, 2019), without any detailed or highly differentiated investigations on this topic.

The formation of ChC is a subject of discussion, but is somehow or other connected with the Khvalyn transgression. The hypothesis of the clay material being supplied by rivers in the periglacial period was put forward in the 1960s by A.I. Moskvitin (Moskvitin, 1962) and G.I. Goretsky (Goretskiy, 1966) The opinion on the formation of ChC in depressions of the relief, including lagoons, as a result of a series of staged sea level depressions is held by E.N. Badiukova (2000). At the moment, the hypothesis related to the accumulation of clay material during the maximum stage of the Early Khvalynian transgression in deep water conditions is being developed (Svitoch, Makshaev, 2015; Pravoslavlev, 1908; Priklonsky et. al, 1956; Svitoch, Yanina, 1997).

Over recent decades the compilation of a comprehensive paleogeographic scheme of the Lower Volga region has been an important research task, which can only be completed based on detailed studies of sedimentary sections within that region. The present study contributes to that research by providing more comprehensive characteristics of mineralogical composition, particle size distribution and micromorphological features of Lower Khvalynian sediments of the Srednyaya Akhtuba and Raygorod sections, which have been previously studied in lesser detail.

The presence of ChC fragments in the soil-forming sediments of the Caspian lowland by micro features allows us to clarify their genesis (Lebedeva, 2021), and the identification of their differences in soils from the original properties of individual layers of ChC allow us to diagnose the modern processes and conditions of their transformation (Lebedeva et al., 2018).

2. AIM AND OBJECTIVES OF THE STUDY

The aim of the study is to establish the main textural and mineralogical characteristics of the complex polyfacial sequence of chocolate clays of the Early Khvalynian age in the Raygorod and Srednyaya Akhtuba outcrops of the Lower Volga region.

The study objectives of the research were to: 1) study the variability within specific macrolayers of chocolate clays in granulometric, mineralogical, and crystallochemical parameters; 2) identify lithotypes (Lokhin, Maev, 1990) on the basis of granulometric characteristics; 3) study their microtexture and further mineralogical and textural comparison within and between the sections; 4) study the of micromorphological features to determine sedimentation conditions.

3. STUDY AREA AND SECTIONS

The Raygorod outcrop is located on the right bank of the Volga River and the Srednyaya Akhtuba outcrop is located on the left bank of the Akhtuba River (fig. 1). The daytime surfaces of the sections have the following absolute heights: 13.68 m for Raygorod (48°25′53.0″ N 44°58′02.1″ E) and 14.89 m for Srednyaya Akhtuba (48°42′1.47″ N 44°53′34.75″ E).

The Lower Khvalynian sediments in the Srednyaya Akhtuba and Raygorod sections are represented by alternation of silt, clay (chocolate-colored mono-clay) and fine sand, which are underlain by Atelian loess deposits (Kurbanov et al., 2021). The laminated ChC deposits can occasionally be overlain by modern soils. In these sections, the ChC lie close to the surface. In the studied sections, the polyfacial ChC were accumulated within a period from the end of the Last Glacial Maximum to the beginning of Younger Dryas.

4. METHODS

Sampling was performed in isolated and reliably distinguishable layers with contrasting features in granulometry, color, and density. Samples were taken from transition intervals between layers for a more detailed characterization of the layers. The material in the transition intervals is represented by fine-sand, fine-large silt interlayers.

Granulometric analysis was carried out on Microtrac Bluewave laser particle size analyzer. The fractions for mineralogical analysis were separated using the sedimentation method (Gorbunov, 1963). After that, the data were compared. The information obtained on the laser particle analyzer was applied to calculate lithological granulometric coefficients and for genetic diagrams. Sedimentation resulted in 4 fractions: <1 μm, 1–5 μm, 5–10 μm, >10 μm. All of them were subjected to XRD. Each fraction was analyzed in its air-dry state. The <1 μm fractions were solvated with ethylene glycol and heated at 550°C. Selected samples of the <1 μm fraction were additionally solvated with Li+ by R. Green-Kelly (1953) and K+ by C. Weaver (1958) in solutions of anhydrous lithium chloride and potassium chloride. Mineral phases in the <1 μm fraction were calculated by the Biscaye method (Biscaye, 1965). Microscopic investigations were carried out on an Olympus BX51 polarization microscope with an Olympus DP26 digital camera.

Fig. 1. Satellite image of the study area (Google Earth Pro). Section Srednyaya Akhtuba and Raygorod.
Рис. 1. Спутниковый снимок района исследования (Google Earth Pro). Разрезы Средняя Ахтуба и Райгород.

5. RESULTS

The detailed granulometric analysis of 42 samples in two outcrops allowed us to distinguish seven granulometric lithotypes according to the prevailing fractions (table 1): Cs1 (clay is a slightly silt), Cs2 (silt clay), CMS (coarse-medium silt), CMSfs (coarse-medium silt with fine-sandy admixture), FScms (fine-sandy material with coarse-medium silt), SC (silt with clay interlayers) and CS (clay with silt interlayers).

The depositional environment was verified using the CM diagram (after R. Passega (Passega, 1957). The CM diagram is based on two parameters, i.e., C – coarsest grain size and M – median grain size (Rukhin, 1969). In the CM diagram obtained (fig. 2), the studied clay material predominantly fits within the diagram area that characterizes sediments deposited by precipitation from suspensions (T). The coarser fractions occupy the region where S and R areas overlap.

Table 1. Granulometric lithotyping of the Lower Khvalynian deposits of the Raygorod and Srednyaya Akhtuba sections
Таблица 1. Гранулометрическая литотипизация нижнехвалынских отложений разрезов Райгород и Средняя Ахтуба

Granulometric typing				
Description in the field		Laser Diffractometry	Main fractions	Lithotype marking
Large layers (layers >1 mm)	Clay material	Clay is a slightly silt (Cs1)	1–5 µm 60%, 5–50 µm <35%	Cs1
		Silt clay (Cs2)	1–5 µm – 50–60%, 5–50 µm 37–45%	Cs2
	Solt-sandy material	Coarse-medium silt (CMS)	10–50 µm – 45–70%	CMS
		Coarse-medium silt with fine-sandy admixture (CMSfs)	10–50 µm – 40–60%, 50–100 µm – 20–35%	CMSfs
		Fine-sandy material with coarse-medium silts (FScms)	25–50 µm – 20–25%, 50–100 µm – 45–62%	FScms
Thin layer (layers <1 mm)	Interlacing	Clay with silt interlayers (CS)	1–5 µm – 45–70%, 5–50 µm 30–50%	CS
		Silt with silt interlayers (CS)	1–5 µm – 35–45%, 5–50 µm 45–55%	SC

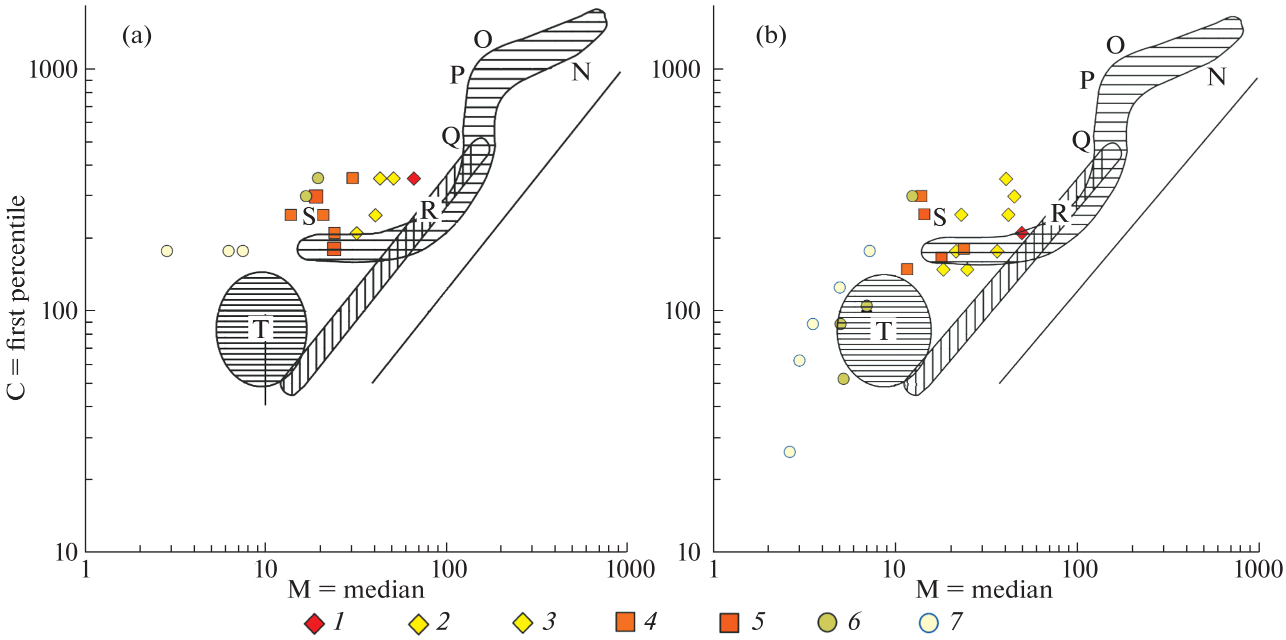

Fig. 2. Diagram of the median and maximum grain size (from Passega, 1957). (a) – section Srednyaya Akhtuba, (b) – section Raygorod. *1* – FScms (fine-sandy material with coarse-medium silt), *2* – CMSfs (coarse-medium silt with fine-sandy admixture), *3* – CMS (coarse-medium silt), *4* – SC (silt with clay interlayers), *5* – CS (clay with silt interlayers), *6* – Cs2 (silt clay), *7* – Cs1 (clay is a slightly silt). NO – Rolling, OP – Rolling with some grains transported in suspension, PQ – Graded suspension with some grains transported by rolling, QR – Graded suspension, RS – Uniform suspension, T – Pelagic suspension.

Рис. 2. Диаграмма медианного и максимального размера зерна (по Passega, 1957). (a) – разрез Средняя Ахтуба, (b) – Райгород. *1* – FScms (мелкопесчаный материал с крупносреднезернистым алевритом), *2* – CMSfs (крупносреднезернистый алеврит с мелкопесчаной примесью), *3* – CMS (крупносреднезернистый алеврит), *4* – SC (алеврит с прослоями глины), *5* – CS (глина с прослоями алеврита), *6* – Cs2 (глина аливритовая), *7* – Cs1 (глина алевритистая). NO – качение, OP – донная суспензия, PQ – градационная суспензия с некоторым количеством материала качения, QR – градационная суспензия, RS – однородная суспензия, T – пелагическая суспензия.

According to Passega (Passega, 1957), that part of the diagram corresponds to uniform suspension sediments deposited by slow currents.

The subsequent comprehensive mineralogical X-Ray analysis of each of the four fractions from 24 samples gave us the possibility to determine similarities and differences between lithotypes (lithological types) within each section as well as between the sections. The mineralogical composition of particles >1 μm, including several fractions of silt and sand, is chemically and texturally homogenous in all studied layers and includes the following minerals in decreasing concentration order: quartz, mica, potassium feldspars, plagioclases, chlorite and very few amphiboles, glauconite and kaolinite. The mineralogical composition of the clay (<1 μm) fraction is more diverse, as shown below (table 2).

In the clay lithotypes Cs1 and Cs2 (fig. 3), the following ratio of clay minerals is observed. For the Srednyaya Akhtuba section: smectite 30–46%, illite 43–57%, chlorite 5–6%, kaolinite 5–7%. In the Raygorod section, the proportion of illite over smectite is higher: smectite 18–43%, illite 46–65%, chlorite 5–9%, kaolinite 6–9%. Thus, in the clayey lithotypes (Cs1, Cs2) of the two sections, the content of illite prevails over smectite, and illite has a trioctahedral filling structure. The character of the octahedral filling in the crystal structures was calculated from the ratio of the first and second orders of illite.

The ratio of smectite to illite in the silt lithotypes (CMS, CMSfs, and FScms) of both sections is the same or shifted toward the swelling phase (fig. 4). The illite here has a dioctahedral structure. The ratio of clay minerals in the Srednyaya Akhtuba section is as follows: smectite is 23–54%, illite 37–61%, chlorite 4–8%, kaolinite 4–8%. The ratio in the Raygorod section: smectite is 30–50%, illite is 44–55%, chlorite is 5–7%, kaolinite is 5–8%.

The SC and CS granulometric lithotypes have the following ratio of clay minerals. For the Srednyaya Akhtuba section: smectite 32%, illite 54%, chlorite 6%, kaolinite 8%. For the Raygorod section: smectite 31–54%, illite 37–54%, chlorite 4–7%, kaolinite 5–8%. The studied thin (<1 mm) lenses of ChC consisted of both clay and silt material. Therefore, as a result of sample preparation we obtained homogeneous mixtures that represented either approximately clay or approximately silt-sand lithotypes.

Table 2. Mineral content of the <1μm fraction
Таблица 2. Содержание минералов во фракции <1 мкм

Raygorod section (RG-20)

Concentration of minerals in the <1 μm fraction, RG-20

Sample	Lithotypes	Sampling depth, cm	Fraction percentage, %	Ratio of main mineral phases, %				Content in the native sample, %			
				SM	I	Ch	Kl	SM	I	Ch	Kl
2	Cs1	80	65	43	46	5	6	28	30	3	4
5		130	77	22	60	9	9	17	46	7	7
12	Cs2	225	51	18	65	8	9	9	33	4	5
13	SMSfs	235	18	44	46	5	5	8	8	1	1
14		237	8	30	55	7	8	2	4	1	1
15		260	10	46	44	5	5	5	4	1	1
7	FScms	165	9	50	41	5	5	4	4	0	0
4		107	57	31	54	7	8	18	30	4	5
9	CS	175	42	47	44	5	5	19	18	2	2
10	SC	190	51	54	37	4	5	27	19	2	3

SM – Smectite, I – Illite, Ch – Chlorite, Kl – Kaolinite

Srednyaya Akhtuba section (SA19)

Concentration of minerals in the <1 μm fraction, SA-19

Sample	Lithotypes	Sampling depth, cm	Fraction percentage, %	Ratio of main mineral phases, %				Content in the native sample, %			
				SM	I	SM	I	SM	I	SM	Kl
9	Cs1	212	61	36	51	6	7	22	31	4	4
18		239	65	37	52	5	6	24	33	3	4
21		260	52	34	53	6	7	18	27	3	4
23		328	59	30	57	6	6	18	34	4	4
3	Cs2	108	41	45	46	5	5	18	19	2	2
7		164	48	46	43	5	6	22	21	2	3
13		220	66	43	47	4	6	28	31	3	4
20		250	48	43	47	5	5	21	22	2	2
10	CMS	213	14	54	37	4	5	7	5	1	1
22		321	16	23	61	8	8	4	10	1	1
17	SMSfs	237	19	52	40	4	4	10	8	1	1
19		241	14	51	39	5	5	7	5	1	1
5	FScms	130	15	50	40	5	5	8	6	1	1
11	SC	214	35	32	54	6	8	11	19	2	3

SM – Smectite, I – Illite, Ch – Chlorite, Kl – Kaolinite

Following the lithium-saturation treatment of the clay fraction, the smectite group was divided into beidellite and montmorillonite minerals. The K-saturation showed that high-charge layers were predominant in the smectite group. Differences between smectite minerals from the two studied sections were as follows: high-charge montmorillonite prevailed in samples from the Raygorod section and high-charge beidellite – in Srednyaya Akhtuba (fig. 5).

The micromorphological data allowed us to visualize the features of the distribution of silty and clayey particles among themselves in the identified lithotypes. At the microlevel, the silty lithotypes (CMS, CMSfs, FScms) revealed oblique-cut textures, which again indicates the presence of wave action or the influence of subsea-fluvial (flow) processes (fig. 6). Clay lithotypes (Cs1, Cs2), have a massive, optically oriented mass, but with rare very fine lenses of silty

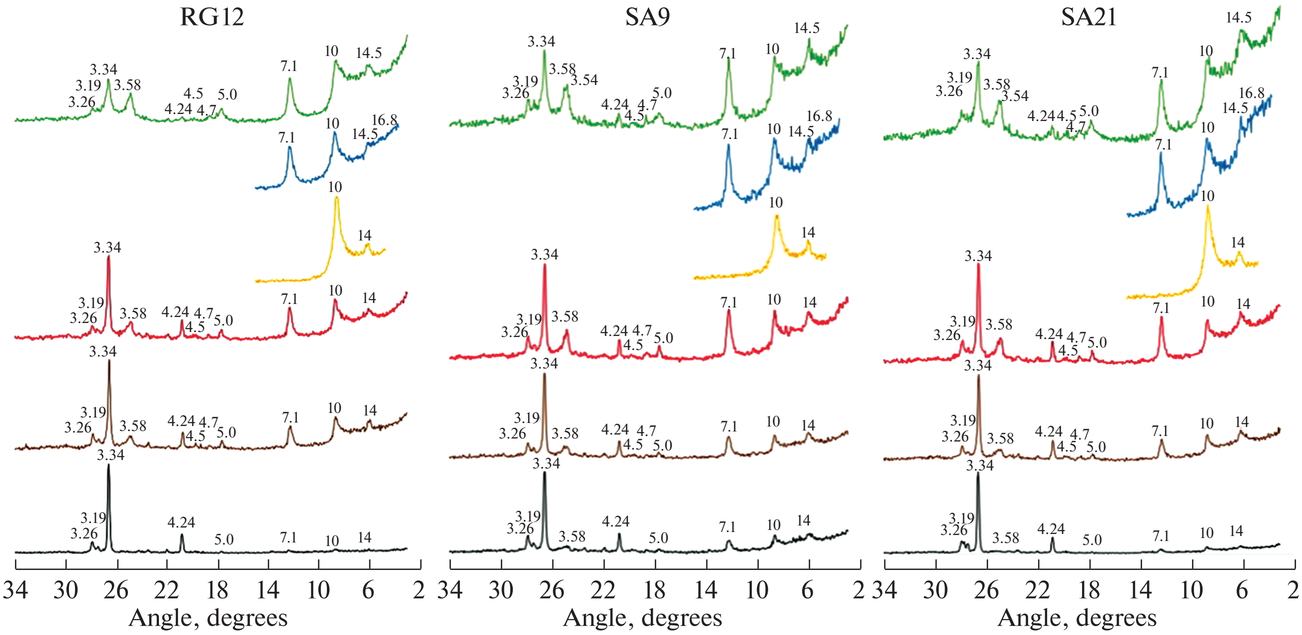

Fig. 3. Diffractograms of samples No. 12 of Raygorod and No. 9, 21 of Srednyaya Akhtuba (from left to right). Graphs: green – air-dry silt; blue – silt saturated with ethylene glycol; yellow – silt calcined at 550°C; red – fine dust (1–5 μm); brown – medium dust (5–10 μm); black – residue (>10 μm). Values are given in angstrom.

Рис. 3. Дифрактограммы образцов № 12 из разреза Райгород и № 9, 21 из Средней Ахтубы (слева направо). Графики: зеленый – воздушно-сухой ил; синий – ил, насыщенный этиленгликолем; желтый – ил, прокаленный при 550°С; красный – мелкая пыль (1–5 мкм); коричневый – средняя пыль (5–10 мкм); черный – остаток (>10 мкм). Значения приведены в ангстремах.

material (fig. 7). Also noted are vestigial, cloud-like textures accentuated by higher concentrations, presumably of ferrous compounds, forming sinuous, irregularly shaped detachments. Their genesis is currently unclear; we suggest that these textures can be attributed to formations of biogenic origin. Lithotypes SC (silt with clay interlayers) and CS (clay with interlayers of silt) are represented by interlayers and lenses of siltstone in the clay material (fig. 8). Dark bands similar in optical properties to "cloud-like" dark textures in clay lithotypes, along layers with a silty dense infilling (arrow in the fig. 8).

6. DISCUSSION

The identification of lithotypes is the basis for any lithologic-genetic research task. In the present study, the lithological types were identified by comparison of the particle-size distribution data and the X-ray patterns obtained. The particle-size distribution data allowed for a suggestion that the depositional environments changed during the accumulation of the Lower Khvalynian sediments. Deposition from slow currents, which typically resulted in the accumulation of fine sediments, was followed by deposition under more dynamic conditions. The alternation of thin interlayers of clay and silt materials reflects, most probably, the seasonal cycles of sedimentation. A similar suggestion has previously been published by other authors (Arkhipov, 1958; Moskvitin, 1962), who found similarities between deposition rhythms of Chocolate clays and varved clays. The most clayey strata could accumulate either within lagoon systems or within topographic depressions of the sea floor.

Based on the comparison of the mineralogical composition of the lithotypes, it was noted that they differed by the structural types of smectite and illite. In terms of genesis, it was difficult to attribute the crystallochemical varieties of smectite (i.e., montmorillonite and beidellite) and illite to certain depositional environments. In both studied sections, mica had identical crystal textures in clay lithotypes (Cs1, Cs2), which were different from those in silt lithotypes (CMS, CMSfs, FScms). The lithotypes also differed by the proportions of mineral phases, i.e., smectite was predominant in the silt lithotypes and illite – in the clay lithotypes.

Potassium reduction revealed that smectite has a high layer charge localized in the tetrahedrons. This suggests its origin from mica material. Its new formation occurred by the degradation transformation of layered silicates. The possibility of such synthesis of montmorillonite (smectite) was pointed out by Millot (1968). Thus, originally mica material could have been transformed in the process of mobilization as a result

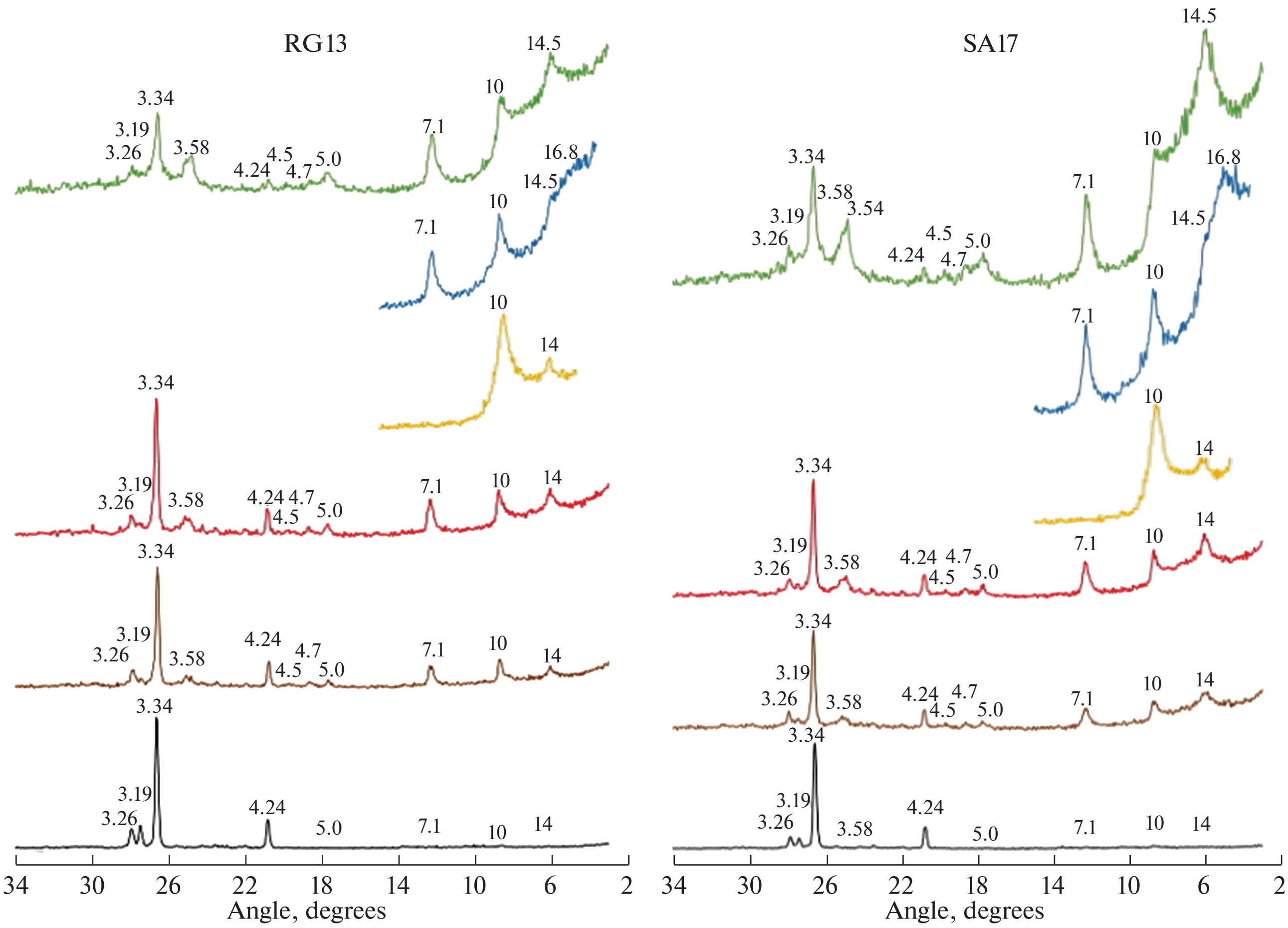

Fig. 4. Diffractograms of samples No. 13 Raygorod, No. 17 Srednyaya Akhtuba (from left to right). See fig. 3.

Рис. 4. Дифрактограммы образцов № 13 Райгород, № 17 Средняя Ахтуба (слева направо). Усл. обозначения см. рис. 3.

of changes in water characteristics. This question requires additional research. The revealed changes in the clay components within the studied strata reflect mineral formation processes in different post-sedimentation environments.

We suggest that the results of micromorphological analysis can provide some clarification to the nature of sedimentation. As noted earlier, the Cs1 and Cs2 lithotypes may have been accumulated in calm, isolated parts of the basin. Their undulating dark brown textures (fig. 7) could indicate the influence of the biogenic factor. But the timing of their formation is not yet clear. It could have occurred at the time of sedimentation in isolated shallow water basin or it may have happened during short-term periodic drainage, if it took place. Therefore, the study of the genesis and composition of these textures and their occurrence in the chocolate clay layers should be continued.

The CMS, CMSfs, and FScms lithotypes, which originally had horizontal layering textures, are assumed to have been eroded to form oblique layering, although such textures may also be related to rippling of the wave. If this observation would be confirmed by further investigations, it'll be possible to determine the depth interval of lithotype accumulation. Thin carbon-like organic matter, diagnosed only in thin sections and located in the horizontal stratification, probably indicates the proximity to the accumulation zone of continental coastal sediment material.

The texture of the CS and SC lithotypes at the microlevel shows signs of gradational layering. The thin sections clearly show a smooth enlargement of the material towards the top, which may indicate a relatively gradual change of hydrodynamics in the sedimentation site. On the other hand, we can see the predomination of both clayey and fine-dust particles in the composition of these layers, which determines further study of their mineralogical composition.

Thus, the obtained materials allowed us to raise new questions and define new directions in the study of the genetic features of chocolate clays sedimentation sequences. It should be noted that micromorpho-

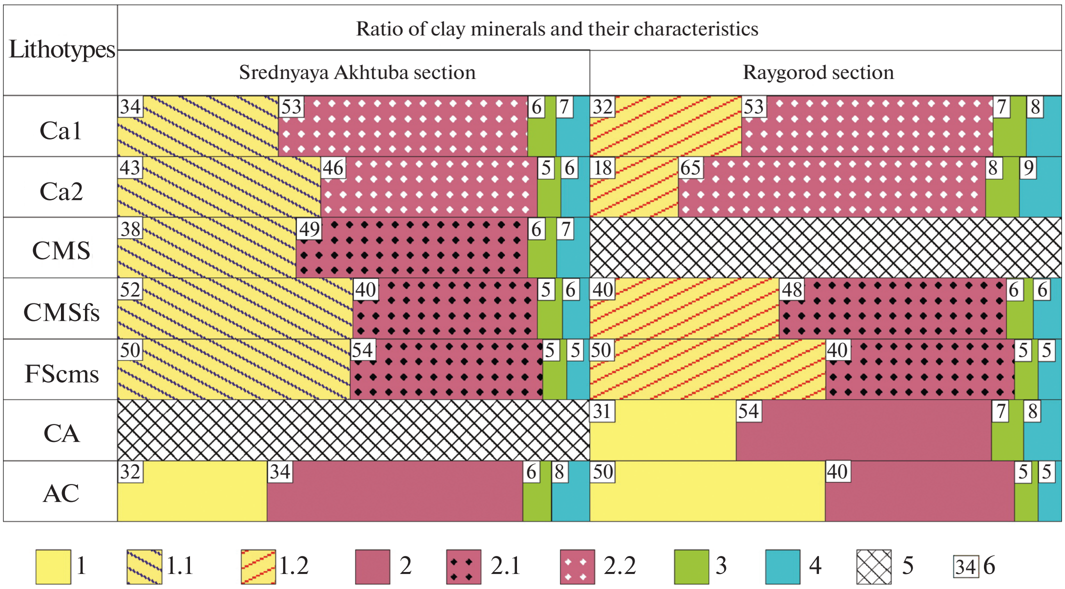

Fig. 5. Relationship of clay minerals in the Raygorod and Srednyaya Akhtuba sections and their crystallographic features. Cs1 – clay is a slightly silt, Cs2 – silt clay, CMS – coarse-medium silt, CMSfs – coarse-medium silt with fine-sandy admixture, FScms – fine-sandy material with coarse-medium silt, SC – silt with clay interlayers, CS – clay with silt interlayers. 1 – smectite, 1.1 – predominance of highly charged baidelite in the smectite group, 1.2 – predominance of highly charged montmorillonite in the smectite group, 2 – mica structures, 2.1 – predominance of dioctahedral structures in illite (hydromuscovite), 2.2 – predominance of trioctahedral structures in illite (hydrobiotite), 3 – magnesium-ferruginous chlorite, 4 – kaolinite, 5 – research were not conducted, 6 – percentage concentration.

Рис. 5. Соотношение глинистых минералов в разрезах Райгород и Средняя Ахтуба и их кристаллографические особенности. Cs1 – глина алевритистая, Cs2 – глина аливритовая, CMS – крупносреднезернистый алеврит, CMSfs – крупносреднезернистый алеврит с мелкопесчаной примесью, FScms – мелкопесчаный материал с крупносреднезернистым алевритом, SC – алеврит с прослоями глины, CS – глина с прослоями алеврита. 1 – смектит, 1.1 – преобладание высокозарядного байделита в смектитовой группе, 1.2 – преобладание высокозарядного монтмориллонита в смектитовой группе, 2 – иллит, 2.1 – иллит с преобладанием диоктаэдрических структур (гидромусковит), 2.2 – иллит с преобладанием триоктаэдрических структур (гидробиотит), 3 – магнезиально-железистый хлорит, 4 – каолинит, 5 – исследования не проводились, 6 – процентное содержание.

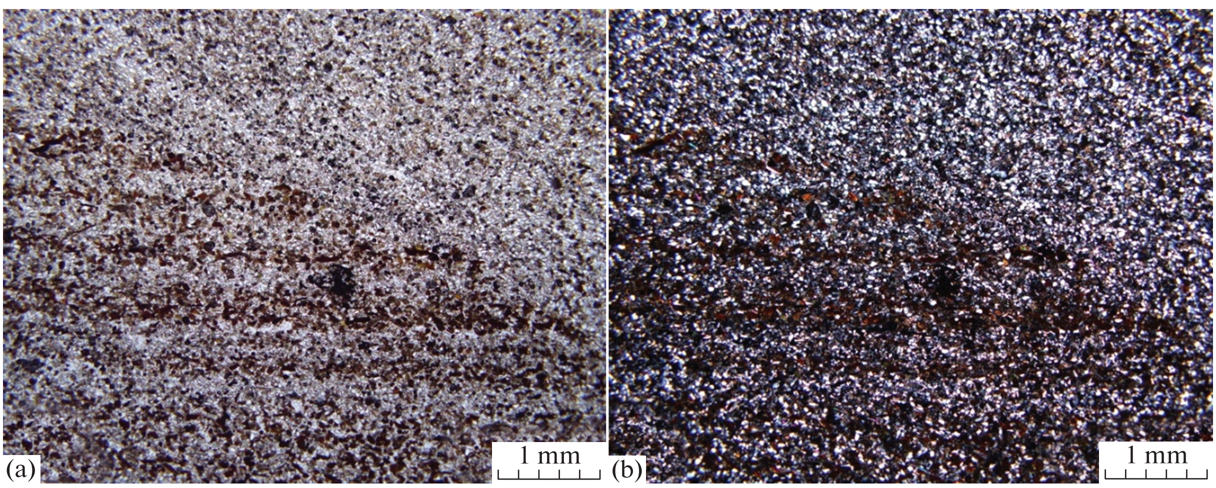

Fig. 6. Thin section SA19 – 242.1 cm. The oblique texture of the silty layers of the CMSfs lithotype. (a) – PPL, (b) – XPL.

Рис. 6. Шлиф SA19 – 242.1 см. Косая текстура алевритовых слоев в литотипе CMSfs. (a) – PPL, (b) – XPL.

logical studies of the Lower Khvalynian Chocolate clays with a detailed reference to depths were carried out for the first time.

The complex and site-specific depositional environments for ChC in each studied section are likely to be due to the hydrodynamic variability (i.e., impacts of bottom currents and avalanche-like depositions of materials), which is illustrated in the CM diagram, and the cycles of marine transgressions and regression (Lavrushin et al., 2014).

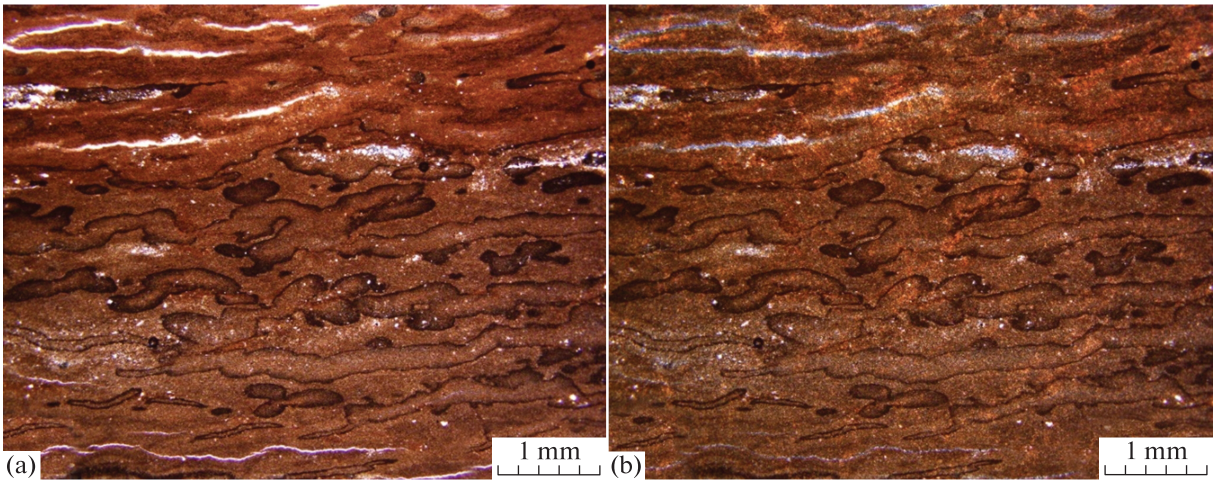

Fig. 7. Thin section SA23 – 386.2 cm. Layered distribution of biogenic textures in the clayey material of the Cs1 lithotype. (a) – PPL, (b) – XPL.

Рис. 7. Шлиф SA23 – 386.2 см. Послойное распределение биогенных текстур в глинистом материале литотипа Cs1. (a) – PPL, (b) – XPL.

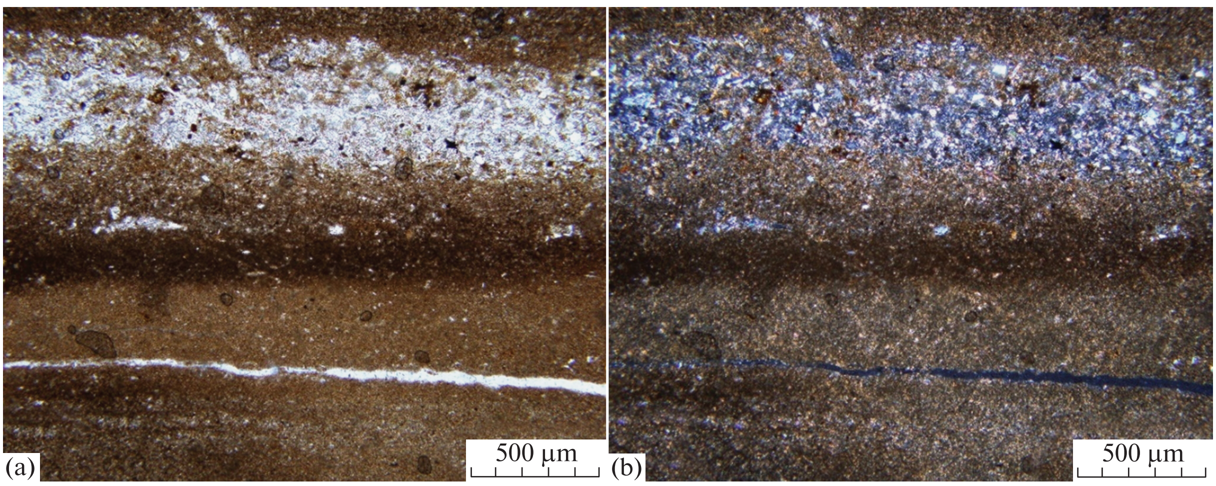

Fig. 8. Thin section SA16 – 235.9 cm. Microlayered interbedding of silty and clayey material of different thicknesses in the CS lithotype. (a) – PPL, (b) – XPL.

Рис. 8. Шлиф SA16 – 235.9 см. Микрослоистое переслаивание алевритового и глинистого материала разной толщины в литотипе CS. (a) – PPL, (b) – XPL.

7. CONCLUSIONS

1. The multifaceted approach to the analysis of particle-size distribution in the Lower Khvalynian deposits within the studied sections allowed for the identification of seven grain-size lithotypes. Each lithotype was described in terms of mineralogy and structural-textural features confirmed by micromorphological analyses.

2. Clay mineralogy was analyzed and compared in the Srednyaya Akhtuba and Raygorod sections. The most clayey interlayers (clay is a slightly silt (Cs1), silt clay (Cs2)) were characterized by the predominance of trioctahedral illite over smectite. An opposite situation was observed in the silt interlayers (coarse-medium silt (CMS), coarse-medium silt with fine-sandy admixture (CMSfs), fine-sandy material with coarse-medium silt (FScms)), where the smectite phase prevailed over dioctahedral illite. The swelling components were represented by high-charge beidellite in the Srednyaya Akhtuba section and high-charged montmorillonite in the Raygorod section. Such differences in the proportions and structures of clay minerals may occur due to their origins from different localities or their sinsedimentary, diagenetical transformation.

3. Micromorphological studies of individual lithotypes of the Lower Khvalynian Chocolate clays

showed certain features of their texture, not visible at the macro level and allowed us to assume their genesis: 1) in massive interlayers biogenic textures were first shown, 2) in silty and fine sand interlayers oblique stratification as well as carbon-like organic matter were revealed, which suggests the neighborhood of sedimentation zone with the coastline, 3) in SC (silt with clay interlayers) and CS (clay with silt interlayers) lithotypes gradual gradational layering was shown. Further study of the composition and microorganization of Chocolate clays is required to clarify their genesis.

Lithological-Mineralogical Characteristics of the Lower Khvalynian Chocolate Clays of the Lower Volga Region (a Case Study of Raygorod and Srednyaya Akhtuba Sections)

R. E. Musaelyan[a,#], M. P. Lebedeva[a], Yu. V. Rostovtseva[b], and E. B. Varlamov[a]

[a] *Dokuchaev Soil Science Institute, Moscow, Russia*

[b] *Lomonosov Moscow State University, Faculty of Geology, Moscow, Russia*

[#] *E-mail: romaniero1@gmail.com*

Chocolate clays are polyfacial marine sediments of disputable genesis, widely distributed in the Lower Volga region. We present the results of detailed analysis of microstructure features, granulometric (42 samples) and mineralogical (24 samples) compositions of different layers in the thickness of the Lower Khvalynian chocolate clays of the Srednyaya Akhtuba and Raygorod sections. The sections are located on opposite sides of the Volga-Akhtuba floodplain. Based on the data obtained with a laser diffractometer, lithological coefficients were calculated. This allowed us to distinguish seven lithotypes common to the two sections, each of which also has specific mineralogical and micromorphological characteristics. The mineralogical structural features of minerals in the <1 μm fraction in each lithotype and the quantitative ratios of clay minerals were determined by X-ray diffractometry. It was revealed that the most clayey lithotypes are characterized by the predominance of trioctahedral illite over smectite. The opposite situation was observed in the silty lithotypes, where smectite predominated over dioctahedral illite. The swelling components were represented by highly charged beidellite in the Srednyaya Akhtuba section and highly charged montmorillonite in the Raygorod section. Such differences in the ratio and structure of clay minerals may be caused by different sources of drift or by their different synsedimentation or diagenetic transformations. Micromorphological data allowed us to establish biogenic textures in the clay lithotypes of the Lower Khvalynian Chocolate clays. In silty lithotypes, oblique layering and carbonaceous organic matter were determined, which suggests the proximity of their sedimentation zone to the coastline. The obtained materials made it possible to show the complex composition of individual layers of the chocolate clay sequence and determine new directions in the study of their genetic features. Studies of individual lithotypes of the Lower Khvalynian chocolate clays with a detailed reference to the depths were carried out for the first time.

Keywords: lithotypes, clay mineralogy, lithology, quantitative analysis, micromorphology

ACKNOWLEDGEMENTS

Authors would like to express their gratitude to Anna Viktorovna Yudina for help and consultation during granulometric sample preparation. Research was supported by the Russian Science Foundation, projects No. 21-74-20121.

REFERENCES

Arbuzova S.K. *Mineralogicheskie osobennosti khvalynskikh glin v basseine Nizhnei Volgi* (Mineralogical features of Khvalynsky clays in the Lower Volga basin). *Byull. Komissii po izucheniyu chetvertichnogo perioda*. 1970. No. 37. P. 41–46. (in Russ.)

Arkhipov S.A. *K litologo-facial'noi kharakteristike khvalynskikh shokoladnykh glin i usloviyam ikh obrazovaniya* (To litologo-facial characteristic of the Khvalynian chocolate clays and to conditions of their accumulation). *BCSQ*. 1958. No. 22. P. 63–72. (in Russ.)

Badyukova E.N. *Genezis khvalynskih (pleistotsen) shokoladnykh glin Severnogo Prikaspiya* (Genesis of Khvalynian (Pleistocene) chocolate clay of Northern Caspian). *Byull. MOIP. Otdel geologicheskii (Bull. MOIP Geology*). 2000. Vol. 75. P. 25–34. (in Russ.) https://doi.org/10.31857/S0435428120030025

Biscaye R.E. Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent Seas and Oceans. *Bull. Geol. Soc. Am*. 1965. Vol. 76. P. 803–832. https://doi.org/10.1130/0016-7606(1965)76[803:MASORD]2.0.CO;2

Gorbunov N.I. *Vysokodispersnye mineraly i metody ikh izucheniya* (Fine Minerals and Methods of Their Investigation). Moscow: Izdatel'stvo Akademii nauk SSSR (Publ.), 1963. 302 p. (in Russ.)

Goretskiy G.I. *Formirovanie doliny Volgi v rannem i srednem antropogene* (The Development of the Volga Valley During Early and Middle Anthropogene). Moscow: Nauka (Publ.), 1966. 412 p. (in Russ.)

Greene-Kelly R. Identification of montmorillonoids. *J. Soil. Sci*. 1953. Vol. 4. No. 2. P. 223–227. https://doi.org/10.1111/j.1365-2389.1953.tb00657.x

Kurbanov R., Murray A., Thompson W., Svistunov M., Taratunina N., and Yanina T. First reliable chronology for the early Khvalynian Caspian Sea transgression in the Lower Volga River valley. *Boreas*. 2021. Vol. 50.

P. 134–146.
https://doi.org/10.1111/bor.12478

Kvasov D.D. *Pozdnechetvertichnaya istoriya krupnykh ozer i vnutrennikh morei Vostochnoi Evropy* (Late Quaternary History of Large Lakes and Inland Seas in Eastern Europe), Leningrad: Nauka (Publ.), 1975. 279 p. (in Russ.)

Lavrushin Yu.A., Spiridonova E.A., Tudryn A., Chalié F., Antipov M.P., Kuralenko N.P., Kurina E.E. and Tucholka P. *Kaspii: gidrologicheskie sobytiya pozdnego kvartera* (The Caspian Sea: hydrological events of the Late Quaternary). *Byull. Komissii po izucheniyu chetvertichnogo perioda*. 2014. No. 73. P. 19–51. (in Russ.)

Lebedeva M., Makeev A., Rusakov A., Romanis T., Yanina T., Kurbanov R., Kust P., and Varlamov E. Landscape Dynamics in the Caspian Lowlands since the Last Deglaciation reconstructed from the pedosedimentary sequence of Srednaya Akhtuba, Southern Russia. *Geosciences*. 2018. Vol. 8. P. 1–21.
https://doi.org/10.3390/geosciences8120492

Lebedeva M.P., Plotnikova O.O., Varlamov E.B., Churilin N.A., and Romanis T.V. *Vliyanie sostava i svoistv khvalynskikh otlozhenii na evolyutsiyu pochv i pochvennogo pokrova volgo-ural'skogo mezhdurech'ya (po rezul'tatam mineralogo-mikromorfologicheskikh issledovanii)* (Influence of the composition and properties of khvalynsk deposits on the evolution of soils and soil cover of the volga-ural interfluve (based on the results of mineralogical and micromorphological studies)). *Mat-ly 2 nauch. konf. puti evolyutsionnoi geografii.* Vol. 2. 2021. P. 527–530. (in Russ.)
https://doi.org/10.3390/geosciences8120492

Lokhin M.Yu. and Maev E.G. *Pozdnepleistotsenovye del'ty na shel'fe severnoi chasti Srednego Kaspiya* (Late Pleistocene Deltas on the Shelf of the Northern Part of the Middle Caspian). Vestn. *Mosk. un-ta. Ser. 3. Geografiya*, 1990. P. 37–45. (in Russ.)

Makshaev R.R. *Paleogeografiya Srednego i Nizhnego Povolzh'ya v epokhu rannekhvalynskoi transgressii Kaspiya* (Paleogeography of the Middle and Lower Volga Region in during the Caspian Early Khvalyn transgression). PhD Thesis. Moscow: MSU (Publ.), 2019. 160 p. (in Russ.)

Millot G. Geology of Clays (weathering, sedimentology, geochemistry). Leningrad: Nedra (Publ.), 1968. 360 p.

Moskvitin A.I. *Pleistotsen Nizhnego Povolzh'ya* (Pleistocene of the Lower Volga region). *Trudy Geol. Inst.* Moscow: Nauka (Publ.), 1962. Vol. 64. 263 p. (in Russ.)

Panin A., Astakhov V., Komatsu G., Lotsari E., Lang J., and Winsemann J. Middle and Late Quaternary glacial lake-outburst floods, drainage diversions and reorganization of fluvial systems in northwestern Eurasia. *Earth-Sci. Rev*. 2020. Vol. 201. No. 103069.
https://doi.org/10.1016/j.earscirev.2019.103069

Panin A.V., Sidorchuk A.Yu., and Ukraintsev V.Yu. The Contribution of Glacial Melt Water to Annual Runoff of River Volga in the Last Glacial Epoch. *Water Resources*. 2021. Vol. 48. No. 6. P. 877–885.
https://doi.org/10.1134/S0097807821060142

Passega R. Texture as a characteristic of clastic deposition. *AAPG Bulletin*. 1957. Vol. 41. P. 1952–1984.
https://doi.org/10.1306/0BDA594E-16BD-11D7-8645000102C1865D

Pravoslavlev P.A. *Materialy k poznaniyu nizhnevolzhskikh kaspiiskikh otlozhenii* (Materials for the Knowledge of the Lower Volga Caspian Deposits). Warsaw: Univ. Press (Publ.), 1908. 467 p. (in Russ.)

Priklonsky V., Gorkova I., and Oknina N. *Inzhenerno-geologicheskie osobennosti khvalynskih glinistykh porod v svyazi s usloviyami ikh formirovaniya* (Engineeringgeological properties of Khvalynian clays in the context of environments of their deposition). *Trudy laboratorii gidrogeolicheskikh problem*. 1956. Vol. 13. P. 1–152. (in Russ.)

Rukhin L.B. *Osnovy litologii* (Basics of lithology). Leningrad: Nedra (Publ.), 1969. 703 p. (in Russ.)

Rychagov G.I. *Khvalynskii etap v istorii Kaspiiskogo morya* (Khvalynian epoch in the history of the Caspian Sea). *Vestn. Mosk. un-ta. Ser. 5. Geografiya*. 2014. No. 4. P. 3–9. (in Russ.).

Sidorchuk A., Panin A., and Borisova O. Morphology of river channels and surface runoff in the Volga River basin (East European Plain) during the Late Glacial period. *Geomorphology*. 2009. Vol. 113. P.137–157.
https://doi.org/10.1016/j.geomorph.2009.03.007

Svitoch A.A. *O prirode khvalynskoi transgressii Kaspiya* (About the nature of the Khvalynian transgression of the Caspian Sea). *Okeanologiya*. 2007. Vol. 47. No. 2. P. 304–311. (in Russ.).

Svitoch A.A. and Makshaev R.R. *"Shokoladnye" gliny Severnogo Prikaspiya: rasprostranenie, usloviya zaleganiya i stroenie* ("Chocolate" clays of the Northern Caspian: distribution, occurrence, and structure). *Geomorfologiya*. 2015. No. 1. P. 101–112. (in Russ.)
https://doi.org/10.15356/0435-4281-2015-1-101-112

Svitoch A.A., Makshaev R.R., Rostovtseva Ju.V., Klyuvitkina T.S., Berezner O.S., Tregub T.F., and Homchenko D.S. *Shokoladnye gliny Severnogo Prikaspiya* (Chocolate clay of the Northern Caspian region). Moscow: Geograficheskiy fakul'tet MSU (Publ.), 2017. 140 p. (in Russ.)

Svitoch A.A. and Yanina T.A. *Chetvertichnye otlozheniya poberezhii Kaspiiskogo morya* (Quaternary deposits of the Caspian sea coasts). Moscow: RASKhN (Publ.), 1997. 268 p. (in Russ.)

Toropov P.A. and Morozova P.A. *Otsenka kolebanii urovnya Kaspiiskogo morya v epokhu pozdnepleistotsenovogo kriokhrona po rezul'tatam chislennogo modelirovaniya klimata* (Evaluation of level variations of the Caspian Sea in the epoch of Late Pleistocene cryochrone by the results of numerical modeling of climate). *Vestn. Mosk. un-ta. Ser. 5. Geografiya*. 2011. No. 2. P. 55–61. (in Russ.)
https://doi.org/10.31857/S0321059621060134

Varushchenko S.I., Varushchenko A.N., and Klige R.K. *Izmenenie rezhima Kaspiiskogo morya i besstochnykh vodoemov v paleovremeni* (Changes in the Regime of the Caspian Sea and Drainless Water Bodies in Paleotime). Moscow: Nauka (Publ.), 1987. 239 p. (in Russ.)

Weaver C.E. The effects and geologic significance of potassium "fixation" by expandable clay minerals derived from muscovite, biotite, chlorite, and volcanic material. *American Mineralogist*. 1958. Vol. 43. No. 9–10. P. 839–861.
https://doi.org/10.1016/0016-7037(67)90060-9

Yapaskurt O.V. *Litologiya* (Lithology). Moscow: Akademiya (Publ.), 2008. 336 p. (in Russ.)