

Lithochemistry of Upper Vendian–Lower Cambrian Clayey Rocks in the Central Part of the Moscow Syncline: General Features of Formation

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Received January 14, 2021; revised April 14, 2021; accepted April 16, 2021

Abstract—Approximately ~120 bulk chemical analyses of the Upper Vendian hereinafter Valdai Group and Lower Cambrian (Lezh and Galich formations) clayey rocks from the central part of the Moscow syncline (PRECSED data bank, IPGG RAS, St. Petersburg) were examined to reveal the main features of their formation (composition of source rocks, paleoclimate, etc.). It is shown that mudstones and mudstone-like clays of the above-mentioned lithostratigraphic units belong mainly to smectite clays with kaolinite, illite, and chlorite–smectite–illite admixture. The data set has a very homogeneous chemical composition. Their K_2O/Na_2O and SiO_2/Al_2O_3 ratios are typical of clayey rocks and indicate the absence of alteration by K-metasomatism and silicification. It was found that the studied rocks include both petrogenic (mudstones of the Ust-Pinega Formation) and lithogenic clayey rocks, which bear a significant contribution of sedimentary material evolved through more than one sedimentary cycle (mudstones and mudstone-like clays of the Pletenevka, Lyubim and Galich formations). The sources of fine aluminosiliciclastic for the Upper Vendian and Lower Cambrian clayey rocks from the axial zone of the Moscow syncline were the rocks of the crystalline basement of the East European Platform and underlying sedimentary and metasedimentary rocks eroded under relatively warm climatic conditions. Changes in climatic conditions on the catchment areas surrounding the Moscow syncline basin during the Late Vendian–Early Cambrian were not established. An analysis of the average values of paleoproductivity indicators for clayey rocks of different formations, such as the P_2O_5 content and $EF_{P_2O_5}$, suggests that the sedimentation areas that existed in the Upper Vendian–Lower Cambrian in the central and northern regions of the East European Platform were not characterized by noticeable bioproductivity. The average values of MgO , Na_2O , $(Na_2O + K_2O)$, as well as TiO_2/Al_2O_3 and K_2O/Al_2O_3 indicator ratios suggest that the mudstones and mudstone-like clays of the Upper Vendian, as well as the Lezh and Galich formations practically do not contain “camouflaged” pyroclastics.

Keywords: clay rocks, Upper Vendian, Lower Cambrian, Moscow syncline, lithochemistry

DOI: 10.1134/S0016702922010104

INTRODUCTION

In this paper, based on major-oxide composition of the Upper Vendian–Lower Cambrian clayey rocks of the Moscow syncline compiled in PRECSED database (IPGG RAS, St. Petersburg), the lithochemical features of clayey rocks of the Pletenevka, Ust-Pinega (Gavrilov Yam + Nepeitsino + Makar’ev), Lyubim, Lezh, and Galich formations are considered and an attempt was made to decipher the composition of source rocks, paleoclimate, and paleoproductivity of sedimentation basins within the transitional Precam-

brian–Phanerozoic interval, as well as to determine whether these rocks contain “camouflaged” pyroclastics¹.

The idea to create the PRECSED databank has arisen in early 1970s while studying several Proterozoic type sections of the East European and Siberian platforms under the leadership of A.V. Sochava (head of the Laboratory of Lithology and Biochronology of

¹ According to the concepts reported in (Kossovskaya, 1975), “camouflaged” pyroclastics is an ash material of volcanic explosions transformed into more stable mineral components. We use term “camouflaged” pyroclastics not only for ash, but also for coarser sized material.

† Deceased.

IPGG RAS). The databank was based on the analytical data on the bulk chemical composition of the Precambrian sedimentary and metasedimentary rocks from different regions of the USSR: Proterozoic Udokan Group, Siberia (A.V. Sochava, 1972–1975), Riphean and Vendian rocks of the Patom highland (A.N. Neelov and V.N. Podkovyrov, 1971–1975), Kola Peninsula and South Urals (A.V. Sochava and V.N. Podkovyrov, 1984–1985), Vendian rocks of Estonia and Podolian Dniester region (A.V. Sochava, 1984–1985). Methodical approach and a concept of specialized databank were developed by A.V. Sochava with participation of V.N. Podkovyrov, while its inner structure and methodical approach to data processing were implemented in the middle and late 1980 with active assistance of S.N. Felitsyn using computers at the Department of Data Processing (Computational Center) of the Central Laboratory of the Northwestern Geological Survey (Krasnoe Selo).

In the mid-1980s, A.V. Sochava proposed his colleagues and other geologists of the USSR to compile database on the chemical composition of Precambrian sedimentary and metasedimentary rocks from different regions around the country and developed its structure, which involved a detailed general and regional assignment, standardized list of major oxides, trace, and rare-earth elements, type of analysis, authors, references, and others. Many geologists responded to this proposal. In particular, large data set on the Riphean and Vendian clastic rocks of the South Urals (>1200 analyses) was given by E.Z. Gareev (Institute of Geology, Bashkirian Branch of the Soviet Academy of Sciences, Ufa). Data on the Proterozoic sequences of the Yenisei Range and western Siberian Platform were given by V.G. Petrov (Institute of Geology and Geochemistry, Siberian Branch of the Soviet Academy of Sciences, Novosibirsk), on Vendian and Cambrian rocks of the Baltic area, by E.A. Pirrus (Institute of Geology, Estonian Academy of Sciences, Tallinn), on the Vendian rocks of the Podolian Dniester region, by L.V. Korenchuk (Institute of Geological Sciences, Ukrainian Academy of Sciences, Kiev), Riphean and Paleozoic rocks of the North Urals, by A.E. Yudovich (Geological Institute of the Komi Branch of the Soviet Academy of Sciences, Syktyvkar), and many others. Thus, the PRECSED database has included data on the bulk chemical composition of the Proterozoic and Paleozoic–Mesozoic sedimentary and metasedimentary rocks of the East European and Siberian platforms and Middle Asia.

Ten years later, the database already has contained ~10400 chemical analyses partially supplemented by trace-element data (Ba, Sr, Rb, Cr, V, Ni, Co, Cu, Zn, Pb, Mo, Ga, Zr, Sn, Y, Be, and some others). However, unlike the bulk chemical composition of sedimentary rocks carried out in 1970s–beginning of 1990s mainly by conventional chemical technique in the certified laboratories of Mingeo of the Russian Federation and territorial geological surveys at high

control of quality and reproducibility of data, the geochemical data were mainly obtained by quantitative or semiquantitative spectral analysis and cannot be used for obtaining reliable conclusions. With the appearance of physical analytical methods (X-ray fluorescence, atomic absorption, ICP-MS) in 1990s, the PCECSED database was supplemented by geochemical data on the Riphean–Vendian deposits of the Srednii and Rybachii peninsulas and adjacent regions of Norway and data on clastic rocks recovered by boreholes in the central part of Moscow syncline, and other local objects. Database is sporadically supplemented at present in the course of accomplishment of RFBR projects and topical studies of IPGG RAS.

Analytical materials presented in the PCECSED database have been used in preparation of numerous publications, including abstracts, papers, and monographs (Sochava et al., 1992, 1994, 1996; Sochava and Podkovyrov, 1992, 1995; Grazhdankin et al., 2005; Maslov et al., 2006a, 2008a, 2008b, 2008c, 2013, 2014, 2015, 2016, 2018a; Nozhkin et al., 2009; Podkovyrov et al., 2011, 2017; Maslov and Podkovyrov, 2013, 2020; and others). These works were dedicated to the general tendencies in the formation of Upper Precambrian sedimentary successions, to the palaeoclimatic reconstructions, as well as comparison of lithochemical characteristics of synorogenic and syn-rift sandstones and clayey rocks, sediments of unfolded molasses, and many other urgent problems of the modern lithochemistry.

LITHOSTRATIGRAPHY OF THE UPPER VENDIAN–LOWER CAMBRIAN SEDIMENTS IN THE CENTRAL PART OF THE MOSCOW SYNECLISE

The Moscow syncline is the largest negative structure of the East European Platform (*Vendian...*, 1985; Garetsky and Nagornyi, 2006). It is in contact with the Voronezh anticline in the south and with Timan Range in the north. Its western flanks join the Baltic shield and Belarusian–Lithuanian salient, while the eastern flanks join the Volga–Kama massif (Fig. 1). The depths of the upper Vendian hereinafter also referred to as Valdai Group and Lower Cambrian sediments in the near-axial part of the syncline reach 1.5–2 km. The most complete Upper Vendian sections occur in this area, nearby the Lyubim, Reshma, Gavrilov Yam, Galich, and Kotlas. According to the classical monograph (*Vendian...*, 1985) edited by B.S. Sokolov and M.A. Fedonkin, the Valdai Group includes (from bottom upward) the Pletenevka, Ust-Pinega, Lyubim, and Reshma formations. Since the Gavrilov Yam 1–5, Orekhovo 3, Danilovskaya 11, Krasavino 2, and other deep holes were sampled by A.V. Sochava and V.N. Podkovyrov in 1989 and 1992–1994, the recovered Upper Vendian sediments were subdivided in compliance with concepts reported in (*Vendian...*, 1985).

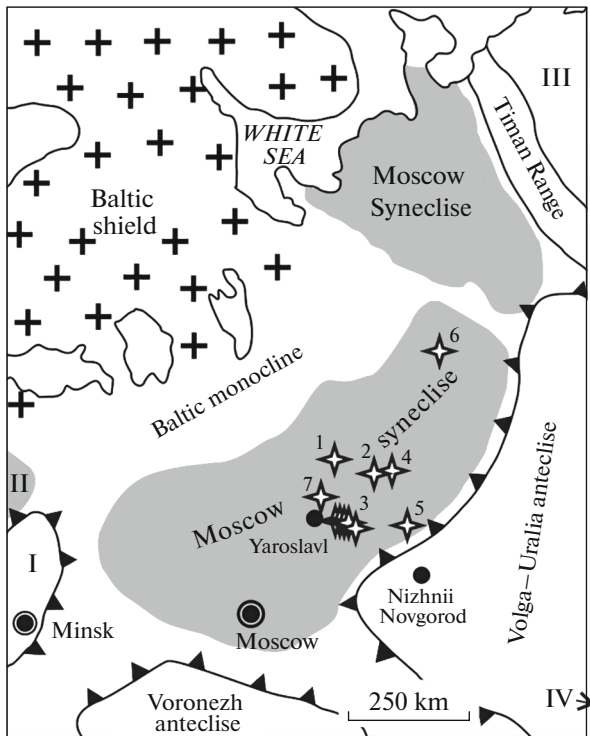


Fig. 1. Main tectonic elements of the East European platform (modified after (Biske, 2019; Chistyakova et al., 2020) and position of deep holes (asterisks) that recovered the Upper Vendian and Lower Cambrian sequences in the axial part of the Moscow syncline. (I) Belorussian anteflexure; (II) Baltic syncline; (III) Timan–Pechora plate; (IV) Shkapovo–Shikhany basin. Deep holes: (1) Danilovskaya 11; (2) Orekhovo 3; (3) Gavrilov Yam 1, 2, 3, 4 and 5; (4) Galichskaya; (5) Medvedevskaya 1; (6) Krasavino 2; (7) Mari'ino 1.

The Pletenevka Formation (thickness up to 50 m and more) is made up of gravelstones, coarse- and fine-grained sandstones, siltstones, as well as dark gray or almost black mudstones. It rests unconformably on the crystalline rocks of the East European platform basement and Riphean deposits of aulacogens. Some researchers (Kheraskova et al., 2005a; Grazhdankin, 2012) believe that the Pletenevka Formation has no clear stratigraphic assignment and, therefore, it is inappropriate to distinguish it.

The Ust-Pinega Formation (300–400 m) is represented by dark greenish gray and gray, as well as chocolate brown mudstones, which include thin interbeds and packages of siltstones and sandstones. According to (Solontsov and Aksenov, 1970), this formation is subdivided into three subformations: Lyamitsa, Teksa, and Kizhmol. Such stratigraphy has been preserved in the monograph (Vendian..., 1985). The Lyamitsa subformation consists mainly of mudstones and includes the first volcanoclastic-sedimentary horizon. The Teksa Subformation consists of sandstones, siltstones, and clayey rocks; its upper part comprises the second volcanoclastic-sedimentary horizon (tuffaceous mud-

stones, vitric tuffs, and smectite clays). The Kizhmol Subformation is represented by clayey rocks and siltstones; it is mainly developed in the northern part of the Moscow Syncline (Vendian..., 1985). The Ust-Pinega Formation transgressively overlies the basement crystalline rocks, Riphean rocks, and different units of the Pletenevka Formation.

The Lyubim Formation (up to 480 m thick) comprises units of sandstones and siltstones, gravelstones and conglomerates, as well as mudstones of greenish gray, dark gray, and variegated coloration. According to the concepts reported in (Solontsov and Aksenov, 1970), the sediments of the Lyubim Formation are subdivided into four subformations. In the central part of the Moscow Syncline, the formation lies conformably on the rocks of the Ust-Pinega Formation, truncates them to its walls, and grades to the rocks of the crystalline basement (Vendian..., 1985).

The Reshma Formation (>230 m) is made up of red and varicolored sandstones, siltstones, mudstones, and mudstone-like clays. It unconformably overlies diverse subformations of the Lyubim Formation (Vendian..., 1985). The studied data set of clayey rocks contains no samples of the Reshma Formation.

The sediments of the Reshma Formation are unconformably overlain by the rocks of the Nekrasovo Formation (10...20–100 m), which is ascribed to the Rovno horizon of the Baltic Group. It consists of two subformations. The lower parts consisting of varicolored and red sandstones, also with glauconite, grade to the alternation units of siltstones and clayey rocks (State..., 2016). Sometimes, it contains tuffaceous pelites (Kheraskova et al., 2005a).

For almost half a century since publications of above mentioned works, the stratigraphic scheme of the Upper Vendian deposits of the Moscow syncline has been modified. In particular, as reported in the explanatory note to the Vendian stratigraphic scheme of the Moscow syncline (Kuzmenko and Burzin, 1996), the Pletenevka, Lyubim, Reshma, and Nekrasovo formations have remained practically unchanged, as in monograph (Vendian..., 1985), whereas the Ust-Pinega Formation was subdivided into three formations (Gavrilov Yam, Nepeitsino, and Makar'ev) related by gradual transitions. Thereby, lower subformation of the Lyubim Formation was included in the Makar'ev Formation.

The Gavrilov Yam Formation (>140 m) is made up of inequigranular sandstones and dark and greenish gray, as well as brownish brown clayey rocks intercalated with siltstones and tuffs in the lower part and mudstones with intercalations of siltstones and sandstones in the upper part.

The Nepeitsino Formation (up to 90–95 m) (from bottom to top) comprises grayish green sandstones with intercalations of dark gray mudstones upward grading into grayish green and dark gray mudstones with thin siltstone and sandstone intercalations. The

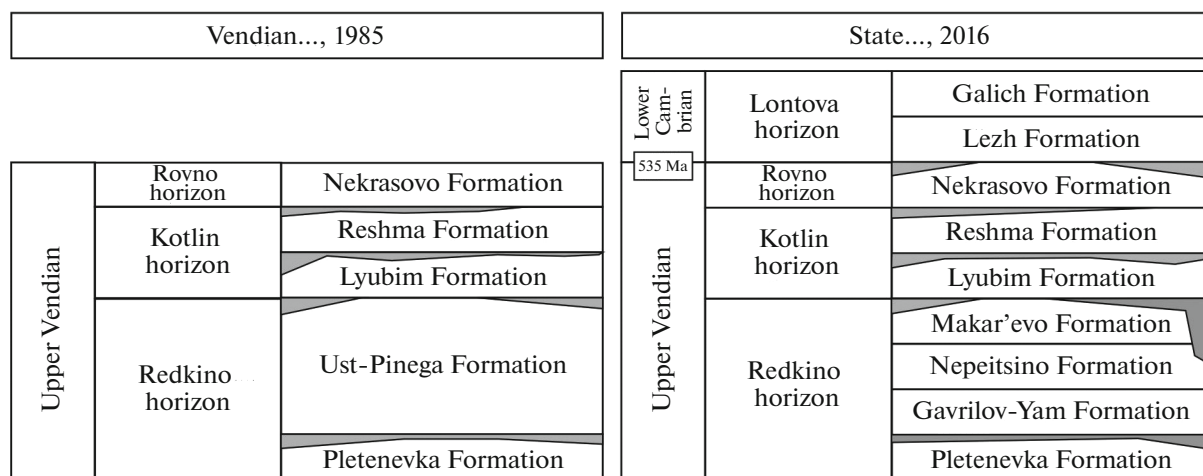


Fig. 2. Stratigraphic scheme of the Upper Vendian and Lower Cambrian sequences in the central parts of the Moscow syncline according to (Vendian..., 1985; State..., 2016). Gray background shows erosions and gaps.

upper part of the formation is dominated by greenish-gray sandstones, as well as dark and greenish-gray mudstones.

The Makar'ev Formation (70–145 m) is subdivided into two subformations, which contain dark and greenish gray sandstones and siltstones intercalated with mudstones in the lower part and mainly dark gray clayey rocks with scarce sandstone intercalations in the upper parts.

According to the explanatory note to the State Geological Map on a Scale 1 : 1000000 (third generation), sheet O-37—Yaroslavl (State..., 2016), the Upper Vendian includes the Pletenevka, Nepeitsino, and Makar'ev formations ascribed to the Redkino Group/horizon, as well as the Lyubim and Reshma formations that belong to the Kotlin Group/Horizon. Upsection, they give way to the Nekrasovo Formation of the Upper Vendian Rovno Horizon, as well as the Lezh and Galich formations of the Lower Cambrian Lontova horizon (Fig. 2).

The Lezh Formation (from 40 to > 100 m thick) lies conformably on the Upper Vendian rocks and is represented by greenish–bluish and dark gray, locally red colored clayey rocks, which are intercalated with siltstones and sandstones (including glauconite-bearing) in the lower part.

The Galich Formation (20–100 m and more) unites greenish- and bluish-gray mudstones and dense clays. Clayey rocks in the lower part of the formation contain interbeds of glauconite-bearing siltstones and sandstones. The rocks of the Galich Formation lie conformably on the sediments of the Lezh Formation.

MATERIALS AND METHODS

The lithochemical studies were based on the bulk chemical composition of clayey rocks of the Upper

Vendian, Lower Cambrian Lezh and Galich formations, as well as volcanic tuffs occurring among sediments of the Ust-Pinega Formation (PRECESED database, IPGG RAS, St. Petersburg, in total, ~120 samples). The major oxides (Table 1) were determined by “the conventional chemical technique at the Central Laboratory of the Northwestern Geological Survey (town of Krasnoe Selo).

All data were plotted in the classification and discriminant diagrams², which provided insight into the composition of clayey rocks, sources of fine aluminosiliciclastics, paleoclimatic settings, the possible presence of “camouflaged” pyroclastics, and some other features of sedimentation in the transitional Vendian–Cambrian epoch.

According to (Aksenov and Volkova, 1969; Kuzmenko et al., 1994; Kheraskova et al., 2005a), the mudstones of the Redkino level consist of kaolinite, mixed-layer illite–smectite, and chlorite. The sequences of the Lyubim and Reshma formations are dominated by illite clays, with subordinate epidote-bearing illite–smectite ash tuffs (Kheraskova et al., 2005a). The mudstones of the Nekrasovo Formation are also made up mainly of illite. According to (Gorokhov et al., 2005), sources for most part of fine aluminosiliciclastics from Vendian sequences of the Moscow syncline were Riphean sediments. The mudstones of the Lezh and Galich formations also have mainly illite composition with some admixture of smectite component (Kheraskova et al., 2005b, 2006).

According to (Pirrus, 1980), the main components of the Upper Vendian and Lower Cambrian clayey rocks of the Moscow syncline were illite and chlorites, kaolinite, and mixed-layer phases (illite–smectite).

² These diagrams were considered in detail in (Maslov et al., 2018b, 2020), and are not characterized in this paper.

Table 1. Average, minimum, and maximum contents of major rock-forming oxides in the Upper Vendian and Lower Cambrian clay rocks in the central parts of the Moscow syncline, wt %.

Components, ratios	Formation						
	Pletenevka	Ust-Pinega			Lyubim	Lezh [#]	Galich
		Mudstones	Sample 939/11 (tuffs)	Sample 939/56 (tuffs)			
SiO ₂	$\frac{54.90 \pm 2.56}{51.36-59.26}$	$\frac{57.82 \pm 3.39}{50.80-66.48}$	72.37	75.05	$\frac{60.31 \pm 3.60}{53.14-66.32}$	62.89	$\frac{60.65 \pm 2.66}{56.19-63.42}$
TiO ₂	$\frac{0.94 \pm 0.14}{0.80-1.22}$	$\frac{0.83 \pm 0.13}{0.58-1.19}$	0.68	0.48	$\frac{0.90 \pm 0.08}{0.71-1.05}$	0.94	$\frac{0.87 \pm 0.14}{0.68-1.02}$
Al ₂ O ₃	$\frac{20.95 \pm 2.09}{17.92-22.91}$	$\frac{18.77 \pm 1.55}{15.73-23.96}$	13.64	11.22	$\frac{17.92 \pm 1.26}{15.42-21.14}$	16.54	$\frac{17.54 \pm 1.10}{16.25-18.89}$
Fe ₂ O ₃ *	$\frac{9.56 \pm 2.40}{7.04-14.00}$	$\frac{8.44 \pm 1.97}{4.50-18.17}$	3.05	2.55	$\frac{8.89 \pm 2.59}{5.08-14.17}$	8.00	$\frac{8.13 \pm 1.06}{6.66-10.13}$
MnO	$\frac{0.05 \pm 0.02}{0.03-0.10}$	$\frac{0.19 \pm 0.34}{0.01-2.28}$	0.05	0.15	$\frac{0.05 \pm 0.04}{0.01-0.24}$	0.05	$\frac{0.04 \pm 0.03}{0.01-0.10}$
MgO	$\frac{2.28 \pm 0.21}{1.99-2.58}$	$\frac{2.24 \pm 0.46}{1.25-3.61}$	1.95	1.76	$\frac{2.17 \pm 0.57}{1.05-3.29}$	2.60	$\frac{2.50 \pm 0.21}{2.22-2.85}$
CaO	$\frac{0.41 \pm 0.21}{0.28-0.86}$	$\frac{0.59 \pm 0.49}{0.17-3.74}$	0.56	1.68	$\frac{0.36 \pm 0.23}{0.17-1.39}$	0.31	$\frac{0.34 \pm 0.22}{0.21-0.88}$
Na ₂ O	$\frac{1.10 \pm 0.24}{0.89-1.60}$	$\frac{1.26 \pm 0.40}{0.24-2.70}$	2.28	1.22	$\frac{1.24 \pm 0.20}{0.89-1.68}$	0.59	$\frac{0.70 \pm 0.09}{0.56-0.80}$
K ₂ O	$\frac{3.35 \pm 0.75}{2.40-4.47}$	$\frac{3.83 \pm 0.48}{2.59-5.59}$	2.88	2.38	$\frac{3.75 \pm 0.31}{3.24-4.40}$	3.60	$\frac{4.76 \pm 0.22}{4.51-5.16}$
P ₂ O ₅	$\frac{0.14 \pm 0.14}{0.06-0.44}$	$\frac{0.09 \pm 0.11}{0.02-0.73}$	0.08	0.12	$\frac{0.08 \pm 0.13}{0.02-0.70}$	0.09	$\frac{0.04 \pm 0.02}{0.02-0.08}$
L.O.I.	$\frac{6.70 \pm 2.31}{3.77-9.53}$	$\frac{6.29 \pm 1.77}{3.18-9.63}$	2.25	3.11	$\frac{4.63 \pm 1.13}{3.05-8.79}$	4.64	$\frac{4.69 \pm 0.42}{4.07-5.31}$
HM	$\frac{0.58 \pm 0.05}{0.49-0.64}$	$\frac{0.49 \pm 0.08}{0.34-0.79}$	0.34	0.29	$\frac{0.46 \pm 0.08}{0.35-0.64}$	0.41	$\frac{0.44 \pm 0.05}{0.38-0.53}$
CIA	$\frac{77 \pm 4}{72-81}$	$\frac{72 \pm 4}{55-77}$	63	59	$\frac{73 \pm 2}{67-77}$	75	$\frac{72 \pm 1}{70-73}$
K ₂ O/Na ₂ O	$\frac{3.15 \pm 0.80}{1.50-3.96}$	$\frac{3.64 \pm 3.20}{1.09-23.29}$	1.26	1.95	$\frac{3.11 \pm 0.65}{2.10-4.94}$	7.39	$\frac{6.89 \pm 0.82}{5.84-8.05}$
SiO ₂ /Al ₂ O ₃	$\frac{2.65 \pm 0.35}{2.29-3.11}$	$\frac{3.11 \pm 0.40}{2.12-4.14}$	5.31	6.69	$\frac{3.39 \pm 0.40}{2.68-4.30}$	3.81	$\frac{3.48 \pm 0.36}{2.97-3.86}$
K ₂ O/Al ₂ O ₃	$\frac{0.16 \pm 0.04}{0.13-0.21}$	$\frac{0.20 \pm 0.02}{0.16-0.27}$	0.21	0.21	$\frac{0.21 \pm 0.02}{0.17-0.24}$	0.22	$\frac{0.27 \pm 0.01}{0.25-0.29}$
TiO ₂ /Al ₂ O ₃	$\frac{0.045 \pm 0.005}{0.039-0.054}$	$\frac{0.044 \pm 0.007}{0.031-0.060}$	0.050	0.043	$\frac{0.050 \pm 0.005}{0.041-0.059}$	0.056	$\frac{0.049 \pm 0.007}{0.039-0.059}$
Na ₂ O + K ₂ O	$\frac{4.44 \pm 0.74}{3.78-5.60}$	$\frac{5.09 \pm 0.57}{4.05-6.46}$	5.16	3.60	$\frac{5.00 \pm 0.30}{4.29-5.58}$	4.19	$\frac{5.46 \pm 0.27}{5.07-5.96}$
EF _{P2O5}	$\frac{0.47 \pm 0.15}{0.36-0.76}$	$\frac{0.50 \pm 0.38}{0.12-1.73}$	0.69	1.26	$\frac{0.37 \pm 0.29}{0.11-1.09}$	0.60	$\frac{0.27 \pm 0.16}{0.12-0.51}$
Fe ₂ O ₃ */Al ₂ O ₃	$\frac{0.47 \pm 0.17}{0.32-0.78}$	$\frac{0.45 \pm 0.10}{0.23-0.85}$	0.74	0.90	$\frac{0.50 \pm 0.14}{0.29-0.75}$	0.48	$\frac{0.46 \pm 0.05}{0.40-0.54}$
<i>n</i>	7	70	1	1	27	2	8

Numerals in numerator are mean arithmetic and standard deviation; numerals in denominator are minimum and maximum contents. (L.O.I.) loss on ignition, *n* is the number of analyzed samples, [#]—mean arithmetic.

The latter are mainly developed in the lower levels of the Upper Vendian. The basal levels of the Kotlin horizon contain significant amount of kaolinite, which is likely related to the pervasive humid weathering in the source areas during attenuation of volcanic activity. The analysis of the average contents of clay minerals “in some sections” allowed E.A. Pirrus to trace the main pathways of their influx in the basin of the Moscow syncline. In particular, it was established that at the beginning of Late Vendian chlorite was supplied from the northeast and southeast, while kaolinite, from the west. These sources have been preserved later. In the Rovnian time, kaolinite was transferred from the west and northwest, while chlorite-group minerals, from the southeast; the northeastern source of chlorite disappears. Insignificant changes occurred during the Lontova time. Data presented in (Pirrus, 1980) suggest that in the Late Vendian and Early Cambrian a spacious weakly rugged continent has existed west of the Moscow syncline and experienced chemical weathering under humid climate. This land was a main source of a “frontal flow” of kaolinite. To the east of the Moscow syncline, sources of clayey material varied and likely involved Riphean sedimentary sequences.

FACTUAL MATERIAL AND DISCUSSION

In the diagram $(K_2O + Na_2O)/Al_2O_3$ – $(Fe_2O_3^* + MgO)/SiO_2$ (Yudovich and Ketris, 2000), the majority of data points of all available samples of the Upper Vendian and Lower Cambrian clayey rocks in the central part of the Moscow syncline plot in fields II (mainly smectite clays with kaolinite and illite admixture) and V (standard three-component chlorite + smectite + illite system) (Fig. 3a). This suggests that the considered data set is homogenous in terms of $(K_2O + Na_2O)/Al_2O_3$ and $(Fe_2O_3^* + MgO)/SiO_2$ relations.

Field V also includes data points of volcanic tuffs. However they have $(Fe_2O_3^* + MgO)/SiO_2 < 0.01$, which differ them from the most part of the Upper Vendian and Lower Cambrian “common” clayey rocks. The reference point of the average Post-Archean Australian Shale, PAAS (Taylor and McLennan, 1985) in the considered diagram falls in the overlap zone of fields II and V.

In the K/Al – Mg/Al diagram (Turgeon and Brum-sack, 2006), data points of the Upper Vendian and Lower Cambrian mudstones and mudstone-like clays also define a compact cluster, indicating that they are made up mainly of illite, with subordinate kaolinite and smectite (Fig. 3b). This is consistent with previous conclusions on the mineral composition of the considered rocks.

³ $Fe_2O_3^*$ is a total iron as Fe_2O_3 .

⁴ In the Russian publications, this diagram is traditionally named as the NAM–FM diagram.

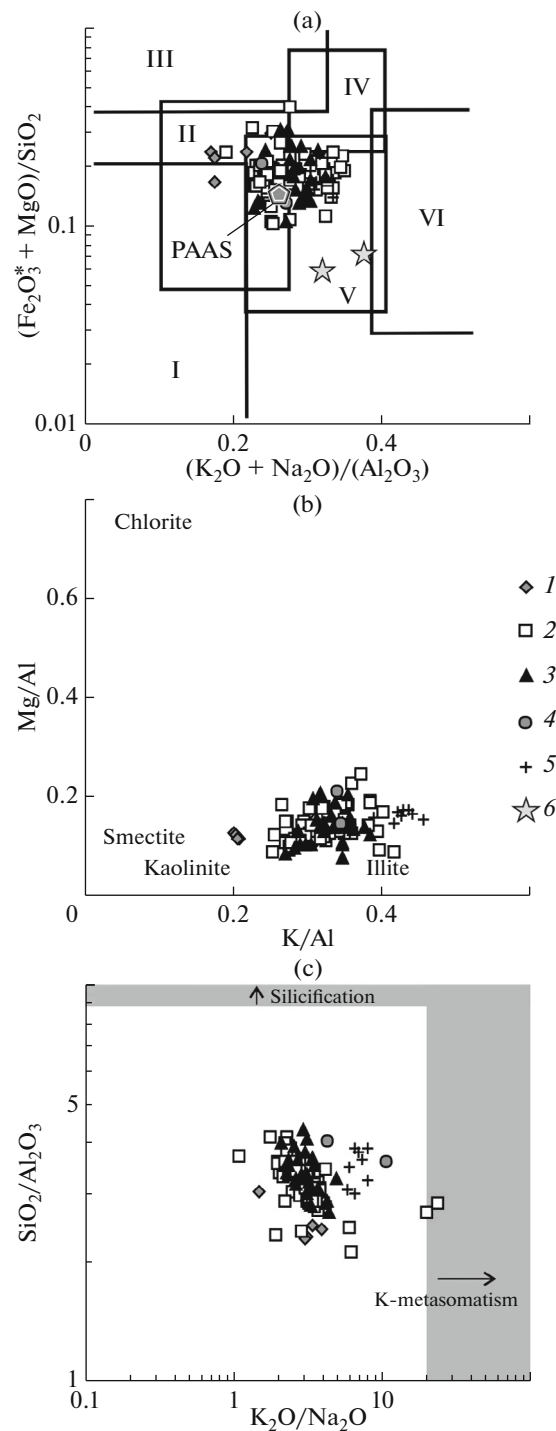


Fig. 3. Position of data points of clay rocks from different stratigraphic units of the Upper Vendian and Lower Cambrian sequences in the diagrams $(K_2O + Na_2O)/Al_2O_3$ – $(Fe_2O_3^* + MgO)/SiO_2$ (a), K/Al – Mg/Al (b), and K_2O/Na_2O – SiO_2/Al_2O_3 (c). Formations: (1) Pletenevka; (2) Ust-Pinega; (3) Lyubim; (4) Lezh; (5) Galich; (6) volcanic tuffs. (a): Compositional fields of clays: (I) mainly kaolinite; (II) mainly smectite with admixture of kaolinite and illite; (III) mainly chlorite with admixture of Fe-illite; (IV) chlorite–illite; (V) chlorite–smectite–illite; (VI) illite with significant admixture of dispersed feldspars.

The position of clayey rocks of the studied data set in the $K_2O/Na_2O-SiO_2/Al_2O_3$ diagram (Bolnar et al., 2005) gives grounds to suggest that they were not subjected to K-metasomatism and silicification (Fig. 3c). This is an important conclusion for further genetic considerations.

It is important to determine the type of aluminosiliciclastics in clayey and clastic rocks: petrogenic type, which passed through a single sedimentary cycle and, respectively retained most characteristics of its formation, or lithogenic type that evolved through more than one sedimentary cycle and lost many primary “signals”. This problem can be solved with approach proposed in (Yudovich and Ketris, 2000, 2015, and others) based on major oxide contents in the clayey rocks. According to this approach, a positive correlation between TM^5 and IM and a negative correlation between NAM and HM modules suggest affiliation to petrogenic rocks.

Analysis of relations in the clayey rocks of the Pletenevka and Lyubim formations shows that the aforementioned modules are linked by a negative correlation ($r_{TM-IM} = -0.09$ and -0.11 , $r_{NAM-HM} = -0.60$ and -0.21)⁶ and, hence, clayey rocks of the given Upper Vendian levels contain significant admixture of lithogenic material. In contrast, the mudstones of the Ust-Pinega Formation are characterized by a positive correlation between TM and IM modules ($r = 0.20$) and a negative correlation between NAM and HM modules ($r = -0.38$). Hence, they are made up mainly of petrogenic material weakly transformed during sedimentogenesis. The clayey rocks of the Galich Formation demonstrate a negative correlation between modules ($r_{TM-IM} = -0.06$, $r_{NAM-HM} = -0.56$) and are mainly made up of lithogenic material. This indicates that the clayey rocks of the Ust-Pinega (Gavrilov Yam + Nepeitsino + Makar’ev) Formation passed through a single cycle of “weathering \Rightarrow transfer \Rightarrow sedimentation \Rightarrow diagenesis \Rightarrow catagenesis” and their lithochemical features could be used for different genetic reconstructions. The rocks of all other formations considered in this work are lithogenic, i.e., passed through several cycles of transfer and redeposition, or contain significant admixture of lithogenic material.

Compared to PAAS, the clayey rocks of the Pletenevka Formation on average are slightly depleted

⁵ Hereinafter: (TM) titanium module TiO_2/Al_2O_3 , (IM) iron module $(Fe_2O_3^* + MnO)/(Al_2O_3 + TiO_2)$, (NAM) normalized alkalinity module, $(Na_2O + K_2O)/Al_2O_3$, and (HM) hydrolyzate module $(Al_2O_3 + TiO_2 + Fe_2O_3^* + MnO)/SiO_2$, (FM) femic module $(Fe_2O_3^* + MgO)/SiO_2$, (AM) alkaline module Na_2O/K_2O , (SM) sodium module Na_2O/Al_2O_3 , PM potassium module K_2O/Al_2O_3 , (AM) alumina-silica module Al_2O_3/SiO_2 (Yudovich and Ketris, 2000).

⁶ r – correlation coefficient.

in silica and phosphorus oxides (0.87 ± 0.04 and 0.85 ± 0.85 PAAS, respectively). The average content of calcium oxide in them accounts for 0.31 ± 0.16 PAAS (Fig. 4a). The average content of total iron as FeO is 1.34 ± 0.34 PAAS. The contents of other oxides approximately correspond to those in the average Post-Archean Australian Shale.

Compared to PAAS, the mudstones of the Ust-Pinega level are characterized by lowered average contents of titanium, calcium, and phosphorus oxides (0.83 ± 0.13 , 0.45 ± 0.37 , and 0.59 ± 0.71 PAAS). The average content of divalent iron oxide in them, as in the clayey rocks of the Pletenevka Formation, is slightly higher than in PAAS (1.18 ± 0.28). Contents of other oxides are close to those of PAAS (Fig. 4b). Volcanic tuffs present among sediments of the Ust-Pinega Formation (samples 939/11 and 939/56, Table 1) are characterized by slightly higher average content of SiO_2 and (in one of two samples) Na_2O compared to PAAS. The contents of other oxides (except for CaO) are lower than in PAAS. In particular, the FeO^* content in the volcanic tuffs is $0.36-0.43$ PAAS, while K_2O , $0.64-0.78$ PAAS. The CaO is close to that of PAAS or significantly lower (thereby, volcanic tuff sample 939/12 with 21.39 wt % CaO was excluded from consideration).

The clayey rocks of the Lyubim Formation have nearby PAAS average concentrations of silica, titanium, aluminum, magnesium, sodium, and potassium oxides. The average concentrations of divalent iron in them is slightly higher than in PAAS, while the contents of calcium and phosphorus oxides are much lower (1.24 ± 0.36 , 0.27 ± 0.17 , and 0.50 ± 0.82 , respectively) (Fig. 4c).

The average contents of silicon, titanium, aluminum, and potassium oxides in the clayey rocks of the Lower Cambrian Lezh Formation are comparable to those of PAAS, whereas the average concentrations of iron and magnesium oxides in them are slightly higher, while calcium, sodium, and phosphorus oxides are much lower than in PAAS (Fig. 4d).

The mudstones and mudstone-like clays of the Galich Formation are close to PAAS in the average concentrations of silicon and aluminum oxides (0.97 ± 0.04 and 0.93 ± 0.06), while the average content of divalent oxide, magnesium, and potassium oxides in them are slightly higher than in PAAS; the calcium, sodium, and phosphorus oxides account for from a quarter to a half of their contents in the average Post-Archean Australian Shale (correspondingly, 0.26 ± 0.17 , 0.58 ± 0.08 , and 0.25 ± 0.15) (Fig. 4e). The content of titanium oxide in the clayey rocks of the given level of the section varies from 0.68 to 1.02 PAAS at average content of 0.87 ± 0.14 .

In general, the PAAS-normalized distribution patterns of main rock-forming oxides in the Upper Vendian and Lower Cambrian clayey rocks of the central Moscow syncline are similar to each other, except for

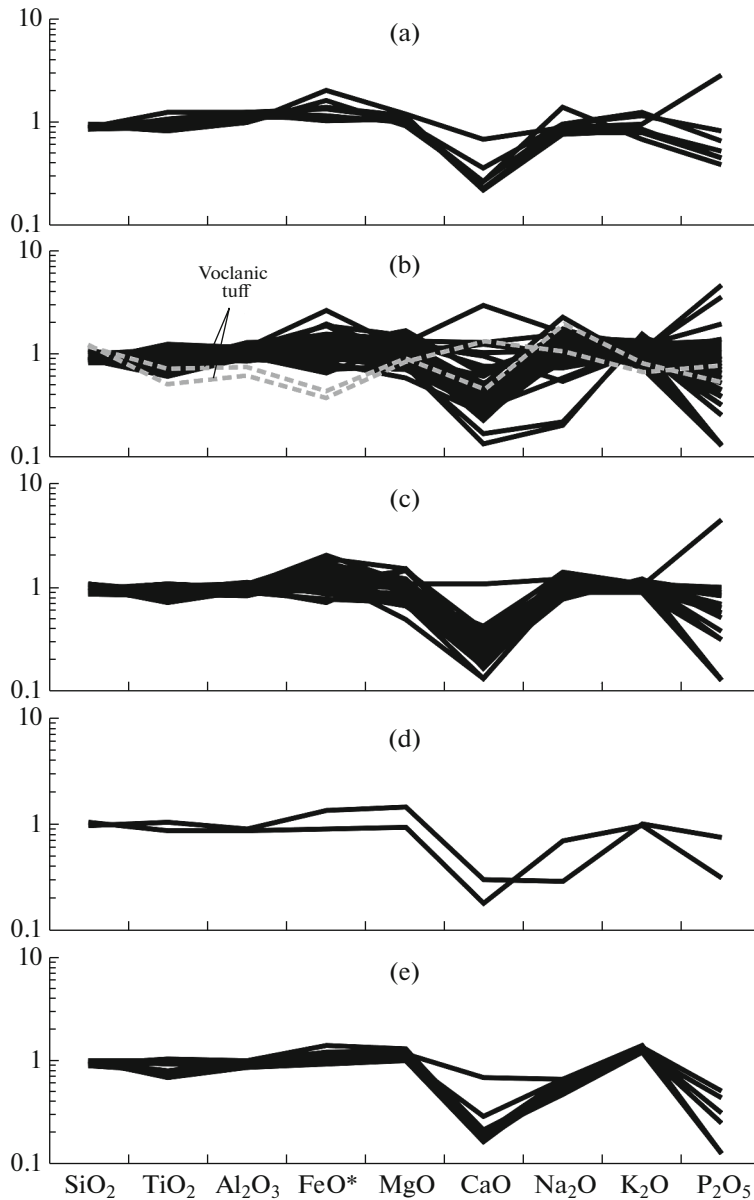


Fig. 4. PAAS-normalized contents of major rock-forming oxides in the Upper Vendian–Lower Cambrian clay rocks in the central areas of the Moscow syncline and volcanic tuffs from sediments of the Ust-Pinega Formation. Formations: (a) Pletenevka; (b) Ust-Pinega; (c) Lyubim; (d) Lezh; (e) Galich;

phosphorus oxide contents in the Upper Vendian clayey rocks, which markedly vary to the lower and higher values relative to PAAS contents. In the Lower Cambrian mudstones, the average P_2O_5 content is lower than in PAAS.

A general variation trend of the Upper Vendian–Lower Cambrian clayey rocks from central Moscow syncline can be described by variations of different indicator ratios of main rock-forming oxides. For this work, we selected two ratios: SiO_2/Al_2O_3 and K_2O/Na_2O (Fig. 5). Within errors, the clayey rocks of the Lyubim–Galich interval have statistically higher

values of the former ratio than the Pletenevka–Ust-Pinega mudstones. The values of the latter ratio in the Lower Cambrian clayey rocks are markedly higher than in the Upper Vendian mudstones. The K_2O/Na_2O ratios in the latter are statistically indistinguishable from that of PAAS, and are twice higher in the former. It is noteworthy that gaps separating the Pletenevka and Ust-Pinega, as well as Ust-Pinega and Lyubim formations did not affect significantly on both these parameters in clayey rocks. This was likely caused by their short duration and the absence of intense tectonic rearrangements in a source area.

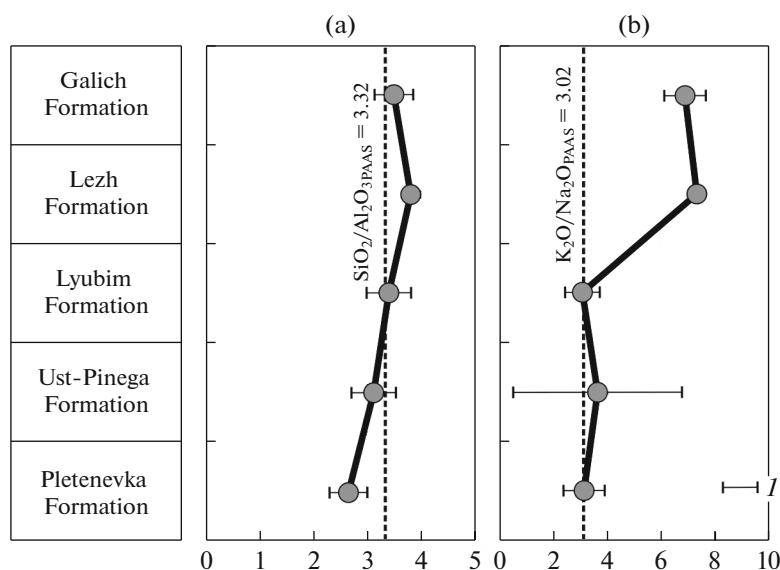


Fig. 5. Variations of average $\text{SiO}_2/\text{Al}_2\text{O}_3$ (a) and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ (b) values in the clay rocks from different Upper Vendian and Lower Cambrian stratigraphic units in the central part of the Moscow Syncline. (I) value \pm standard deviation.

Sources of fine aluminosiliciclastics that compose the clayey rocks of the Upper Vendian, as well as the Lezh and Galich formations were determined using $(\text{CaO} + \text{MgO})\text{--SiO}_2/10\text{--}(\text{Na}_2\text{O} + \text{K}_2\text{O})$ (Bavinton, 1981) and F1–F2⁷ (Roser and Korsch, 1988) diagrams. In the former diagram, all data points of the Upper Vendian and Lower Cambrian clayey rocks define a compact cluster in the region of sedimentary rocks (field II) and beyond it, approximately at $(\text{CaO} + \text{MgO})$ values typical of felsic magmatic rocks (field I) (Fig. 6a). This gives grounds to suggest that fine aluminosiliciclastics for the considered interval of the sedimentary infill of the Moscow syncline was derived from rocks of the East European crystalline basement and Riphean (?) sedimentary rocks (?). The distribution of data points in the F1–F2 plot also indicates the contribution of both sedimentary and magmatic rocks to the formation of the Upper Vendian and Lower Cambrian clay rocks (Fig. 7). Careful examination of arrangement of data points of different lithostratigraphic units shows that data points of the mudstones of the Pletenevka Formation are mainly confined to the fields of igneous mafic and intermediate rocks. Data points of the clayey rocks of the Ust-Pinega and Lyubim formations mainly fall in the fields of intermediate and felsic rocks, also partially occupying the field of quartz-rich sedimentary rocks. Data points of the Lezh and Galich formations are restricted either to the latter field or plot in the field of igneous felsic rocks. If this

is the case, the formation of the Upper Vendian–Lower Cambrian sedimentary sequences of the Moscow syncline was controlled by indistinct composition evolution of rocks that composed catchment areas.

The comparison of composition fields of the Upper Vendian and Lower Cambrian clay rocks from the axial zone of the Moscow syncline, Baltic monocline (Podkovyrov et al., 2017), northwestern Mezen syncline (Belomorian–Kuloi plateau) (Grazhdankin et al., 2005), and Shkapovo–Shikhany basin (Maslov et al., 2006b) in the $(\text{CaO} + \text{MgO})\text{--SiO}_2/10\text{--}(\text{Na}_2\text{O} + \text{K}_2\text{O})$ diagram indicates that all these rocks, except for the field of the Upper Vendian mudstones of the Baltic monocline, are characterized by almost 70–80% overlap (Fig. 6b), thus suggesting that fine aluminosiliciclastics for sedimentary basins existing at that time at the Eastern European platform was derived from paleocatchment areas of similar composition. Slightly greater role of high-Si source rocks for the Upper Vendian mudstones of the southern and southeastern periphery of the Baltic Shield could be caused by the closer position of this area to the regions of intense chemical weathering.

Indicators of *paleoclimate* during lithochemical studies are hydrolyzate module (HM) and several chemical indices, in particular, chemical index of alteration (CIA) (Nesbitt and Young, 1982), index of compositional variability, IVC (Cox et al., 1995), and others (Maslov, 2005; Maslov et al., 2016). We use only two of them, HM and CIA. The higher the value of each of the indicators, the higher/intenser the chemical weathering of rocks at the paleocatchments. The average HM values in the Upper Vendian–Lower Cambrian sequences of the Moscow syncline decrease from

⁷ F1 = $30.638\text{TiO}_2/\text{Al}_2\text{O}_3 - 12.541\text{Fe}_2\text{O}_3^*/\text{Al}_2\text{O}_3 + 7.329\text{MgO}/\text{Al}_2\text{O}_3 + 12.031\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 + 35.402\text{K}_2\text{O}/\text{Al}_2\text{O}_3 - 6.382$; F2 = $56.500\text{TiO}_2/\text{Al}_2\text{O}_3 - 10.879\text{Fe}_2\text{O}_3^*/\text{Al}_2\text{O}_3 + 30.875\text{MgO}/\text{Al}_2\text{O}_3 - 5.404\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 + 11.112\text{K}_2\text{O}/\text{Al}_2\text{O}_3 - 3.89$.

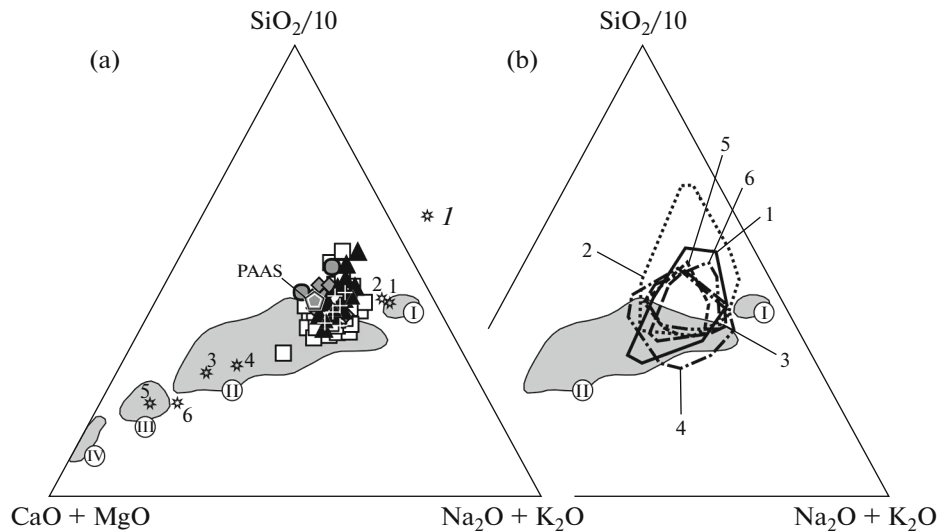


Fig. 6. Position of data points of mudstones and mudstone-like clays from different Upper Vendian and Lower Cambrian lithostratigraphic units in the axial part of the Moscow Syncline (a) and compositional fields of clay rocks of the same interval from different regions of the East European Platform (b) in the diagram $(\text{CaO} + \text{MgO})\text{--SiO}_2/10\text{--}(\text{Na}_2\text{O} + \text{K}_2\text{O})$. (a): (1) average types of different magmatic rocks (1) Archean granites, (2) Proterozoic granites, (3) Late Archean andesites, (4) Late Proterozoic andesites, (5) Late Archean calc-alkaline basalts; (6) Late Proterozoic calc-alkaline basalts), after (Condie, 1993). Roman numerals in circles are compositional fields after (Bavinton, 1981): (I) granites; (II) sedimentary rocks; (III) basalts; (IV) ultramafic rocks. (b): (1) Upper Vendian rocks from the axial zone of the Moscow syncline; (2) Upper Vendian rocks from the Baltic monocline; (3) Upper Vendian rocks from the Belomorian–Kuloi plateau; (4) upper Vendian rocks from the Shkapovo–Shikhany basin; (5) Lower Cambrian rocks from the central part of the Moscow syncline; (6) Lower Cambrian rocks from the Baltic monocline. Clay rocks from different regions of the East European platform. For other symbols, see Fig. 3.

the Pletenevka to the Lezh levels (0.58–0.41), and then slightly increase (–0.44 for the Galich Formation) (Fig. 8a). Within errors, the degree of “chemical maturity” of clayey rocks of the Galich Formation is slightly lower than that of the Pletenevka mudstones. The average CIA values in the Upper Vendian as well

as Lezh and Galich formations show no such contrasting variations upsection (Fig. 8b). All they fall in the interval of 72–77, i.e., sources of fine aluminosiliciclastics were eroded in relatively warm (but not hot) climate, and, with allowance for errors, the Vendian–Early Cambrian paleocatchment areas surrounding the Moscow syncline basin showed no any systematic changes in climatic settings.

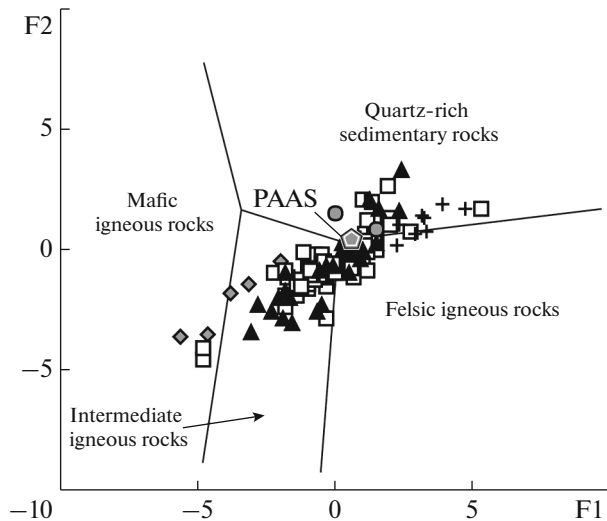


Fig. 7. Position of data points of the clay rocks from different Upper Vendian and Lower Cambrian lithostratigraphic units in the axial part of the Moscow syncline in the diagram $F1\text{--}F2$. For symbols, see Fig. 3.

It is pertinent to mention that the correlation between HM and CIA in the clayey rocks from different Upper Vendian and Lower Cambrian lithostratigraphic units reveal significant variations (Fig. 9). In particular, the correlation coefficients between mentioned parameters are 0.47 for mudstones of the Pletenevka Formation, and slightly lower (0.30) for mudstones of the Ust-Pinega Formation. The clayey rocks of the Lyubim Formation are characterized by $r_{\text{HM-CIA}} = 0.20$, while mudstones and mudstone-like clays of the Galich Formation demonstrate the absence of correlation between considered paleoclimatic indicators, which requires special consideration.

Some lithochemical characteristics of fine-grained sedimentary rocks make it possible to estimate also the *bioproductivity* of marine basins in the geological past. The high bioproductivity is usually inferred for paleo-basins, sediments of which are enriched in organic matter (OM) (Planavsky et al., 2010; Plewa et al., 2012; Yeasmin et al., 2017; and others), because marine OM, in addition to C, N, and P, contains such

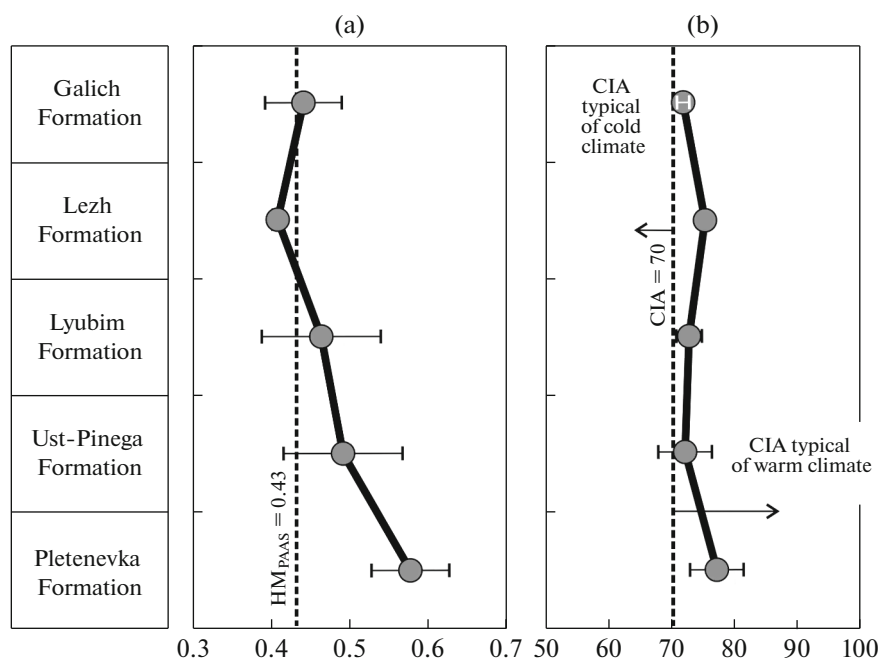


Fig. 8. Variations of the average values of HM (a) and CIA (b) in the clay rocks of different Vendian and Lower Cambrian formations in the central part of the Moscow syncline. For symbols, see Fig. 5.

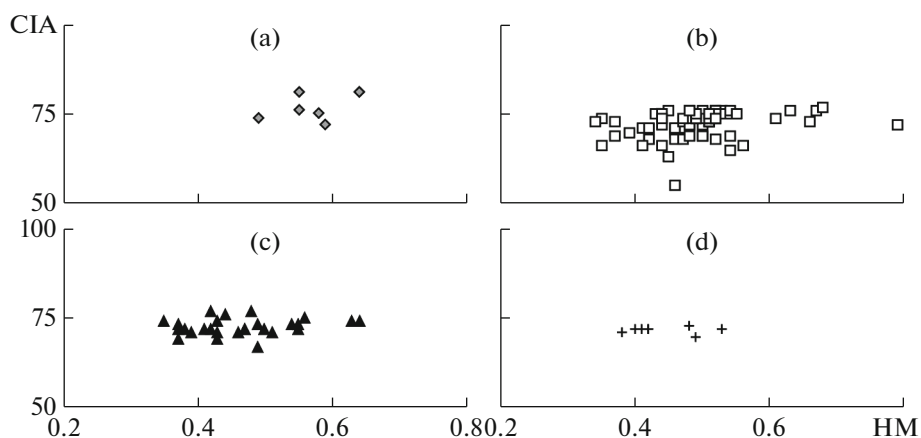


Fig. 9. Correlation of HM and CIA in the clay rocks of the Pletenevka (a), Ust-Pinega (b), Lyubim (c), and Galich (d) formations. For symbols, see Fig. 3.

key nutrients as K, Mg, Ca, Sr, Fe, Zn, Cu, Co, Cd, Mo, and others (Algeo and Ingall, 2007; Och, 2011; and others). The most known indicators of the paleobioproductivity are Ba and P. The P content in most sedimentary rocks is tightly related with amount of buried OM. Hence, it can be considered as a function of paleobasin bioproductivity. However, the application of such indicator has several constraints (Jarvis et al., 1994; Piper and Perkins, 2004). In some cases, even essentially elevated P content in sedimentary rocks cannot serve as heavy evidence for the high bioproductivity of paleobasin, since the P_{org} content is also controlled by redox settings in the bottom water

layers (Tribouillard et al., 2006). Phosphorus is also tightly related to Fe (Planavsky et al., 2010), and some researchers suggest that the high Fe concentration in water mass could constrain the primary productivity and hence, the rate of OM influx in sediments (Mills et al., 2004). It is believed (Papineau, 2010; Lenton et al., 2014; Laakso and Schrag, 2014; Horton, 2015) that in the Precambrian the primary productivity and C_{org} burial rate in sediments were sensitive to the continental phosphorus flux during intense weathering of mafic igneous rocks ascribed to the large igneous provinces. The degree of enrichment of sedimentary rocks in P (Enrichment Factor, EF) can be calcu-

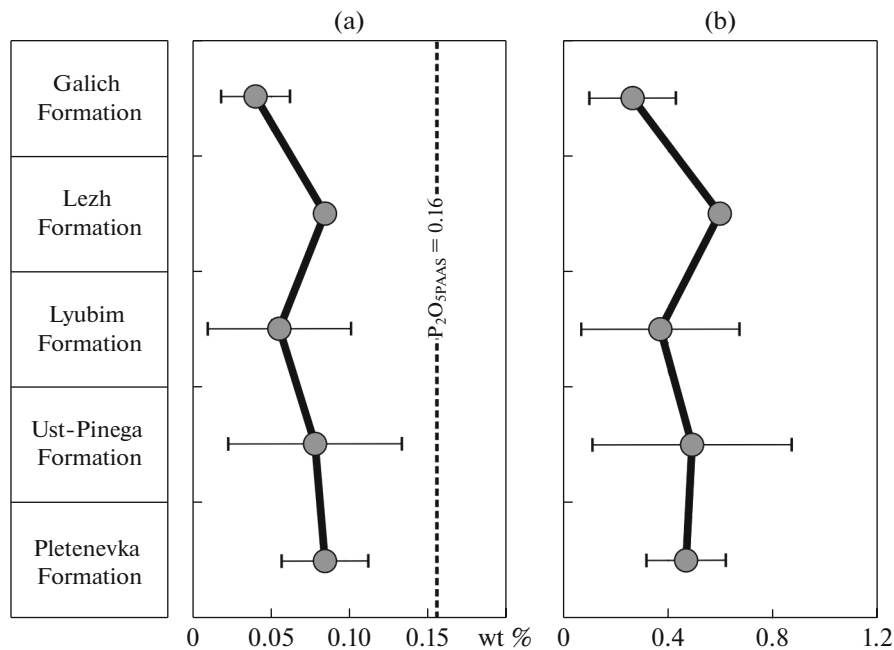


Fig. 10. Variations of average contents of P₂O₅ (a) and average EF_{P₂O₅} values (b) in the clay rocks from different Upper Vendian and Lower Cambrian lithostratigraphic units in the central part of the Moscow syncline. For symbols, see Figs. 3 and 5.

lated using different formulas. In this rock, this parameter is calculated using the following equation: $EF = (P_2O_{5\text{dsample}}/Al_2O_{3\text{sample}})/(P_2O_{5\text{PAAS}}/Al_2O_{3\text{PAAS}})$, i.e., the enrichment factor is calculated relative to PAAS (Taylor and McLennan, 1985).

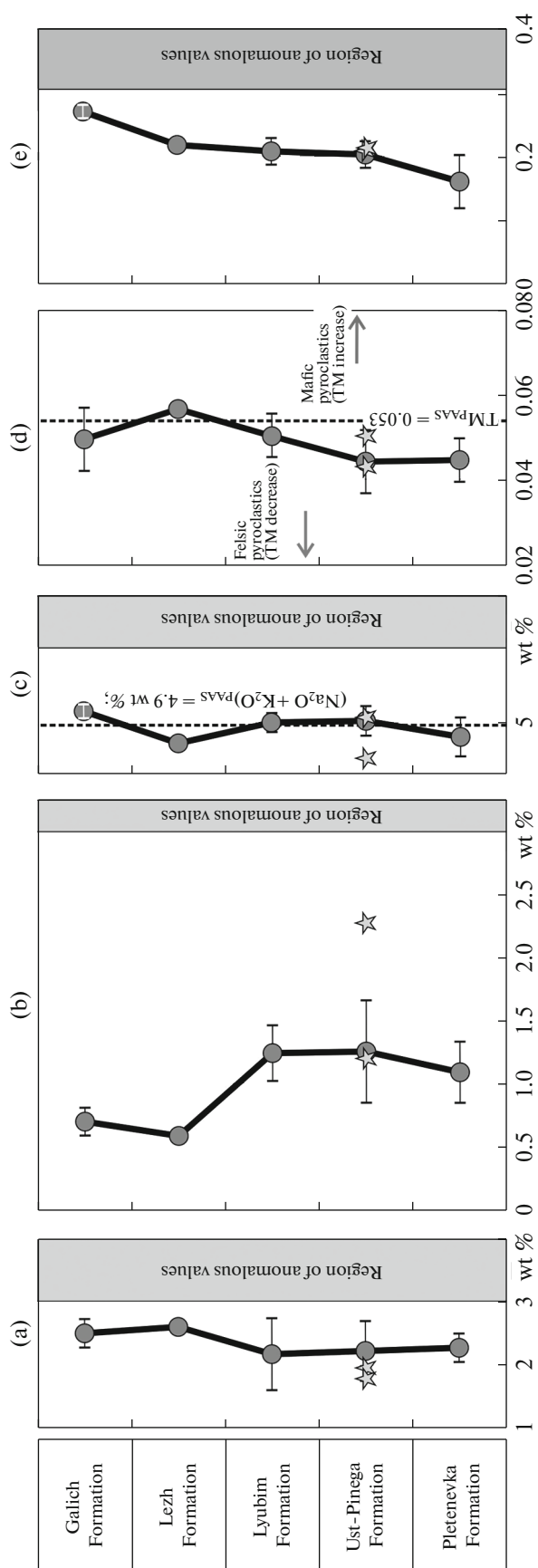
The average content of phosphorus oxide in the Upper Vendian and Lower Cambrian clayey rocks in the central part of the Moscow syncline varies from 0.04 ± 0.02 (Galich Formation) to 0.09 ± 0.03 wt % (Pletenevka Formation), which is much lower than the P₂O₅ content in PAAS (0.16 wt %). This parameter, with allowance for error, practically shows no systematic variations throughout the sequence (Fig. 10a). Correspondingly, the average EF_{P₂O₅} values also display no any changes (Fig. 10b). The maximum EF_{P₂O₅} value typical of mudstones of the Lezh Formation (0.60) is much lower than 1, which indicates a sufficiently low bioproductivity of the basin at the beginning of the Early Cambrian. Even lower values of the considered parameter were determined for the Upper Vendian clay rocks (0.37–0.50), in spite of the “abundance” of organic films in the mudstones of the Kotlin horizon (Vendian..., 1985).

The average EF_{P₂O₅} value for the Upper Vendian mudstones of the Baltic monocline (Starorusskaya, Vasileostrovskaya, and Voronkovskaya formations) accounts for 0.84 ± 1.03 (minimum – 0.12, maximum – 5.69). The Lower Cambrian clayey rocks from the same structure (Lomonosovskaya and Siverskaya formations) also have slightly lower average enrichment factors for phosphorus oxide (0.59 ± 0.37) and maximum value of this parameter (EF_{P₂O₅} = 2.55). The

Upper Vendian clayey rocks of the Shkapovo–Shikhany basin (Baikibashev, Staropetrovskaya, and Karlinskaya formations) in contrast show higher EF_{P₂O₅} average (1.36 ± 1.90) and EF_{P₂O₅} maximum (9.74). The EF_{P₂O₅} values in the Upper Vendian mudstones of the Belomorian–Kuloi plateau show more homogeneous distribution (EF_{P₂O₅} average – 0.79 ± 0.57), although minimum and maximum values of this parameter also demonstrate a wide scatter (0.13–3.13). Analysis of these data shows that sedimentation areas existing in the Upper Vendian–Lower Cambrian in the central and northern parts of the East European Platform did not reveal any marked bioproductivity. In the eastern part of the platform, in the Shkapovo–Shikhany basin, it was slightly greater.

The Upper Vendian sediments in the central, northern, and eastern parts of the East European Platform are frequently considered as “tuffogenic–terrigenous” rocks (Lagutenkova, 1963; Aksenov, 1998; Grazhdankin, 2003; Kheraskova et al., 2005a, 2005b, 2006; and others). Given the fact that the identification of volcanogenic admixture, including “camouflaged” pyroclastics, in sedimentary rocks, is one of the most urgent problem in lithochemistry (Yudovich and Ketris, 2000), it is very important to consider this point in more detail.

The presence of volcanogenic admixture in sedimentary rocks is determined using diverse lithochemical approaches in addition to traditional petrographic method. In particular, it is believed that the presence of volcanogenic admixture in clay rocks is indicated by



MgO > 3 and (Na₂O + K₂O) > 8 wt %. This also follows from a positive correlation between FM and TM, IM and TM, and a negative correlation between NAM and FM modules. A positive correlation between FM and TM and Na₂O/K₂O > 1 in sedimentary rocks suggest the presence of mafic and mafic–intermediate pyroclastics (Yudovich and Ketris, 2000). The high MgO/CaO, AM, TM, and IM values also give grounds to suggest that “seemingly common sedimentary rocks” contain volcanic products (Yudovich and Ketris, 2000, 2015; *Diagnostics...*, 2012). The presence of exhalative components and feldspathic pyroclastics can be reconstructed from (SM + PM) and IM, while the presence of mafic pyroclastics is indicated by an increase of TM and IM (Yudovich et al., 2018).

It is believed that PM ≥ 0.31, (PM + SM) > 0.40, and AM > 0.27 could indicate the presence of potassium feldspar/felsic pyroclastics in clay rocks. However, it should be kept in mind that the presence of finely ground K-feldspar in clays frequently is caused by peculiar weathering in arid settings and it is practically indistinguishable from felsic pyroclastics. Yudovich et al. (1986) noted that the Na₂O > 3 wt % in clayey rocks indicates significant contribution of felsic plagioclases. A significant positive correlation of K₂O with TiO₂ and MgO likely indicates the presence of alkali basaltic/mafic pyroclastics and their weathering products.

Below, we attempted to use some of mentioned criteria for analysis of bulk chemical composition of clayey rocks of the Upper Vendian as well as Lezh and Galich formations, which macroscopically look as “common sedimentary rocks” (Fig. 11). In particular, the average MgO content varies from 2.17 ± 0.57 (Lyubim Formation) to 2.60 wt % (Lezh Formation), which is lower than boundary value (3 wt %) discriminating the “common clayey rocks” (the MgO content in PAAS is 2.20 wt %) from rocks bearing pyroclastic admixture. Felsic volcanic tuffs from the Ust-Pinega Formation have MgO 1.76–1.95 wt %. The average Na₂O content in the Upper Vendian mudstones varies from 1.10 ± 0.24 (Pletenevka Formation) to 1.26 ± 0.40 wt % (Ust-Pinega Formation). The volcanic tuffs in the Ust-Pinega sequence have variable contents of Na₂O (1.22–2.28 wt %), which, however, are insufficiently high to plot in the field of “anomalous” Na₂O contents for fine-grained clastic rocks. In the Lower Cambrian clayey rocks, the average Na₂O content is twice lower. The parameter (Na₂O + K₂O)_{average} in the

Fig. 11. Variations of average contents of MgO (a), Na₂O (b), (Na₂O + K₂O) (c), and average values of indicator TiO₂/Al₂O₃ (d) and K₂O/Al₂O₃ (e) ratios in the clay rocks of different Upper Vendian and Lower Cambrian lithostratigraphic units in the central part of the Moscow syncline (gray background shows the regions of “anomalous” contents and values of definite parameters, see text for explanation). For symbols, see Figs. 3 and 5.

clayey rocks of the whole considered interval is comparable with its value in PAAS (4.19–5.46 and 4.90), whereas values of $\text{Na}_2\text{O} > 8 \text{ wt } \%$ are regarded to be anomalous. The average TM values for clay rocks of the Valdai Group and Lower Cambrian vary from 0.044 to 0.056. In PAAS, this parameter accounts for 0.053. The TM values (0.050 and 0.043) for volcanic tuffs in sections of the Ust-Pinega Formation are statistically indistinguishable from $\text{TM}_{\text{average}}$ (0.044 ± 0.007) for “common sedimentary rocks” of this level. The average $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ values for Upper Vendian and Lower Cambrian clayey rocks in the central part of the Moscow syncline also are much lower (0.16–0.27), falling beyond the field with anomalous values ($\text{PM} > 0.31$).

All these facts indicate that macroscopically “common mudstones and mudstone-like clays” from the Upper Vendian and Lower Cambrian sequences of the central part of the Moscow syncline cannot be considered as rocks with “camouflaged” pyroclastics. Moreover, in terms of most lithochemical parameters, this is not also the case for volcanic tuffs (!) sampled from the Ust-Pinega sequence in hole Krasavino 2. The same conclusion was made from lithochemical studies of Upper Vendian sediments of the Baltic monocline, the western flank of the Moscow syncline (Kotova and Podkovyrov, 2020; Podkovyrov and Kotova, 2020).

CONCLUSIONS

Based on $(\text{K}_2\text{O} + \text{Na}_2\text{O})/\text{Al}_2\text{O}_3$ and $(\text{Fe}_2\text{O}_3^* + \text{MgO})/\text{SiO}_2$ ratios, the studied clay rocks of the Upper Vendian, as well as Lower Cambrian Lezh and Galich formations in the central part of the Moscow syncline are ascribed mainly to the smectite clays with admixture of kaolinite and illite and to chlorite–smectite–illite clays with a sufficiently homogenous bulk chemical composition. Volcanic tuffs associated with them in the Ust-Pinega Formation have $(\text{Fe}_2\text{O}_3^* + \text{MgO})/\text{SiO}_2 < 0.01$, which make them different from “common” clay rocks. The above conclusion on the homogenous composition of the Upper Vendian and Lower Cambrian rocks is also confirmed by the position of data points of mudstones and mudstone-like clays in the $\text{K}/\text{Al}–\text{Mg}/\text{Al}$ classification diagram.

The $\text{K}_2\text{O}/\text{Na}_2\text{O}$ and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios typical of clayey rocks indicate that they were not subjected to the postsedimentation K–metasomatism and silicification, which modify the chemical composition of clastic rocks of Precambrian sedimentary sequences. The average $\text{SiO}_2/\text{Al}_2\text{O}_3$ values in the clayey rocks of the Lyubim–Galich interval, within the errors, are slightly higher than those of mudstones of the Pletenevka–Ust-Pinega interval. The average $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios are significantly higher in the Lower Cambrian clayey rocks.

The Upper Vendian and Lower Cambrian sediments in the axial part of the Moscow syncline con-

tain both petrogenic (mudstones of the Ust-Pinega Formation) and lithogenic clayey rocks, in which significant part of sedimentary material passed through more than one sedimentary cycle (mudstones and mudstone-like clays of the Pletenevka, Lyubim, and Galich formations).

The PAAS-normalized distribution patterns of major rock-forming oxides in the clayey rocks from the lower levels of the section of the central part of the Moscow syncline are similar, differing mainly in phosphorus, which compared to PAAS varies in both sides in the Upper Vendian rocks and is usually lower in the Lower Cambrian rocks.

Sources of fine aluminosiliciclastics for the Upper Vendian and Lower Cambrian clay rocks in the axial part of the Moscow syncline were rocks of the crystalline basement of the East European platform and sedimentary and metasedimentary rocks underlying the studied rocks. Thereby, the composition or proportions of the indicated rocks on the paleocatchment areas likely slightly changed during this interval.

A significant overlap of fields of Upper Vendian and Lower Cambrian clayey rocks of the axial zone of the Moscow syncline, Baltic monocline, northwestern Mezen syncline and Shkapovo–Shikhany basin in the diagram $(\text{CaO} + \text{MgO})–\text{SiO}_2/10–(\text{Na}_2\text{O} + \text{K}_2\text{O})$ suggests that sedimentary basins existing at that time in the East European platform were fed from paleocatchment areas of similar composition.

Based on the average CIA values typical of clayey rocks of the Upper Vendian as well as the Lezh and Galich formations, the source rocks of fine aluminosiliciclastics were eroded under relatively warm climate. Significant changes of climatic settings on the Late Vendian–Early Cambrian paleocatchment areas surrounding the Moscow syncline basin were not established.

Analysis of the average values of paleoproductivity indicators for clayey rocks of different formations revealed the low bioproductivity in sedimentation areas existing in the Upper Vendian–Lower Cambrian in the central and northern areas of the East European Platform. In the east of the platform, in the Shkapovo–Shikhany basin bordering with the Mezen piedmont basin, the bioproductivity was likely slightly higher.

The average values of some indicator ratios suggest that the mudstones and mudstone-like clays composing the most part of the Upper Vendian–Lower Cambrian formations in the central part of the Moscow syncline practically do not contain “camouflaged” pyroclastics.

ACKNOWLEDGMENTS

We are grateful to N.S. Glushkova for preparation of figures for this paper.

FUNDING

These studies were performed in the framework of the State Task of the IPGG RAS (FMUW-2021-0003) and GIN RAS (0135-2019-0043). The study of “camouflaged” pyroclastics was supported by the Russian Science Foundation (project no. 19-17-00099).

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Translated by M. Bogina