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Geochemistry of Upper Vendian and Lower Cambrian Clay Rocks in the Moscow Syneclise: Some Traditional and Modern Approaches

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Abstract—The article discusses some geochemical characteristics of Upper Vendian and Lower Cambrian (hereafter, Upper Vendian–Lower Cambrian) clay rocks that make up the base of the Moscow syneclise. It is shown that there was no significant change in the clay rock composition during several tens of million years of the geological history under consideration. Based on the typical Zr/Sc and Th/Sc values, the petrogenic nature of the fine-grained aluminosiliciclastics of mudstones and mudstone-type clays is substantiated. This conclusion is also confirmed by the CIA/WIP values. In general, according to some parameters of their composition, Upper Vendian and Lower Cambrian clay rocks of the Moscow syneclise are closer to granitoids; according to other parameters, to basic igneous rocks. Thus, compared with the average Late Proterozoic basalts, the clay rocks are markedly enriched in K_2O and Rb, Th, Zr, Hf, Nb, and Ta, whereas the average Archean granitoids have notably lower concentrations of TiO_2, FeO, MgO, Sc, V, Cr, Co, and Ni. Positions of data points of the Upper Vendian–Lower Cambrian clay rocks on the La/Sc–Th/Co, La/Th–Th/Yb, Sc–Th/Sc, and other diagrams confirm the above statement. The chondrite-normalized lanthanide distribution in clay rocks is close to the PAAS lanthanide spectrum. It is suggested that the suspended material was transported to the sedimentation area by: (1) large rivers with source areas composed of rock complexes of different composition; (2) rivers that drained provenances composed mainly of sedimentary rocks. The average CIA values inherent in the Upper Vendian–Lower Cambrian clay rocks of the Moscow syneclise are comparable to those typical for the suspended particulate matter (SPM) in modern large rivers of the humid subtropical and tropical climate, as well as in rivers of dry tropical climate regions. Localization of data points of mudstones and mudstone-type clays on the SiO_2–(Na_2O + K_2O + MgO + CaO), Al_2O_3–(Na_2O + K_2O + MgO + CaO), and CIA–WIP diagrams suggests that the main characteristics of their composition was governed by the paleoclimate. The series of α-coefficients characteristic of the Upper Vendian–Lower Cambrian clay rocks in the Moscow syneclise is quite similar to those for the fine-grained SPM of modern large river systems in southern Africa.

Keywords: clay rocks, Moscow syneclise, geochemistry, main features of the accumulation of Upper Vendian–Lower Cambrian sedimentary sequences

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INTRODUCTION

One of the main factors determining the appearance of sedimentary associations is, as is known, the climate, which largely controls the features of matter differentiation during exogenesis (Chumakov, 2015 and others; *Klimat* ..., 2004; *Metody* ..., 1985; Monin and Shishkov, 1979; Sinitsyn, 1980; Ronov and Balukhovsky, 1981; Strakhov, 1963, 1968, and others; Yasamanov, 1985; Zharkov, 1978 and others). The present paper continues our works devoted to the Late Precambrian paleoclimatic reconstructions based on the lithogeochemical approaches and methods (Kotova et al., 2016; Maslov, 2010a, 2010b, 2022; Maslov and Podkovyrov, 2023; Maslov et al., 2003, 2016; Podkovyrov and Maslov, 2022; Podkovyrov et al., 2015, 2022, and others). We tried with a certain degree of conditionality to use the techniques currently used for studying the fine-grained aluminosiliciclastic/pelitic sediments of modern large alluvial systems in Africa, China, Hindustan and some other regions of the world.

It is known that rocks (the fine-grained variety included) of such systems in continental environments are represented usually by a material with the mineral and chemical composition integrating the parameters of both modern and previous (if the sedimentary or metasedimentary rocks are present in paleodrainage areas) weathering, as well as the processing of sediments after their accumulation (Dellinger et al., 2014;

Dinis et al., 2020; Gaillardet et al., 1999; Garzanti and Resentini, 2016; Garzanti et al., 2013a; Guo et al., 2018; Viers et al., 2009). The formation of the fine-grained terrigenous river sediments is controlled by a combination of various factors (rock composition in paleosource areas, recycling, introduction of material from various climatic zones, postsedimentary transformations, and others) (Allen, 2017; Borges et al., 2008; Fedo et al., 1995; Garzanti et al., 2013a, 2013b, 2014, 2022; Johnsson, 1993; Jury, 2010; Setti et al., 2014; van der Lubbe et al., 2016; and others). Despite a rather long history of the discussion of this issue, identification of the last climatic signal from its common chain is still considered a very difficult task in sedimentary geochemistry (Cox et al., 1995; Cruz et al., 2022; Dinis et al., 2020; Gaillardet et al., 1999; Garzanti et al., 2014, 2021, 2022; and others). Nevertheless, the riverine fine-grained aluminosiliciclastic sediments (along with the closely related sediments of the estuarine coast and the coastal and shallow-marine sediments) have been considered in recent decades as "excellent archives of the environment of the geological past", with the mineral, chemical, and isotopic composition preserving paleoclimatic records corresponding to their accumulation period (Dinis et al., 2017, 2020; Garzanti et al., 2014; Guo et al., 2018; He et al., 2020; Porter, 2001; Schatz et al., 2015; Yang et al., 2004; and others). In this regard, the interest of researchers has grown markedly in recent years for the comprehensive study of modern sediments of large river systems in Africa and some other regions draining the compositionally diverse provenance rock complexes in a markedly variable climate (Cruz et al., 2021, 2022; Dinis et al., 2020; Dupré et al., 1996; Garçon and Chauvel, 2014; Garzanti et al., 2011, 2013a, 2013b, 2014, 2018, 2021a, 2021b; He et al., 2020; Just et al., 2014; Le Pera et al., 2001; Maharana et al., 2018; Setti et al., 2014; Singh, 2009; van der Lubbe et al., 2014, 2016; Vezzoli et al., 2016; and others). The approaches developed recently for studying the continental sediments as a result of these works and the obtained results (some of which are discussed below) contributed to the formation of new directions for studying the influence of climate on the formation of intracontinental and coastal sediments. As for the marine sedimentary sequences traditionally used for these purposes, a point of view has appeared recently: the modern climate signal can be lost in the fine-grained/clayey sediments in marine environments, since the differentiation of minerals by morphology and other parameters, the mixing of material from areas of different climates, and authigenesis can change their composition to a certain extent (Borges et al., 2008; Dinis et al., 2020; Garzanti et al., 2011, 2014; Thiry, 2000; von Eynatten, 2012, 2016; and references therein).

FEATURES OF THE FINE SUSPENDED PARTICULATE MATTER OF RIVERS IN SOUTHERN AFRICA: BRIEF OVERVIEW

Southern Africa is characterized by the well-defined longitudinal (from subhumid Mozambique to hyperarid Namibia) and latitudinal (from humid Angola to arid Botswana) climatic gradients (Garzanti et al., 2014; Jury, 2010; McCarthy et al., 2000). The rivers flowing here carry huge volumes of the clastic material to coastal areas of the Atlantic and Indian oceans. For example, only the Orange River transports annually about 60000000 t of the suspended and entrained material to the Atlantic margin of Africa (Compton and Maake, 2007). The prolonged mechanical processing of such material in the river and coastal (high-energy littoral included) environments does not change significantly its composition and properties (Garzanti et al., 2015). As a result, the shallow-sea sediments can retain the continental characteristics. This is indicated, in particular, by the data available for sediments on the southeastern coast of Africa (Hahn et al., 2018 and references therein).

The Zambezi River (length 2575 km, drainage area 1.4×10^6 km^2), the largest river in southern Africa, drains crystalline rocks, plateau basalts of the Karoo Supergroup. It also flows among the Kalahari Desert sands. In its upper course, the fine suspended particulate matter (SPM) contains abundant quartz and K-feldspar along with the subordinate plagioclases. The clay fraction includes the predominant smectite (its content grows down the river) along with the subordinate kaolinite and illite. Due to the diluting effect of quartz (Garzanti et al., 2022), the content of most rare and trace elements in this SPM is depleted relative to the upper continental crust (UCC) and the average post-Archean Australian shale (PAAS). In middle reaches of the Zambezi River, the proportion of plagioclase and iron oxides in the fine SPM increases, the amount of kaolinite decreases, and some increase in the content of Fe, Mg, Ca, Na, Sr, Ti, Eu, V, Cr, Mn, Co, Ni, Cu and P is noted due to the erosion of mafic volcanic rocks below the Victoria Waterfalls. According to (Garzanti et al., 2022), the CIA value is 83 in the fine (<32 μm) SPM in upper reaches of the Zambezi River and only 62 above the Victoria Waterfalls. At its middle course, the CIA value decreases to 69 in the fine SPM and is about 71 in the lower course.

Sources of the Okavango River (1600 m long, 8×10^5 km^2) are located in a humid belt. The river ends in the Kalahari Desert with the world's largest intracontinental delta consisting of the seasonally flooded plains, numerous channels, and swamps (Gumbricht et al., 2004). The Okavango River delta has an area of about 15000 km^2. During floods, its area increases to 20000 km^2, which is about 4 or 5% of the area of the Moscow Syneclise under consideration. The fine SPM of the Okavango River contains abundant quartz and K-feldspar; the subordinate plagioclase, and occasional calcite, probably, inherited from the plagioclase-rich soils. Clay minerals are composed of the predominant smectite (its content increases down the river) along with the subordinate kaolinite and illite. Due to the dilution by quartz, most of the rare and trace elements are relatively depleted relative to UCC and PAAS (Garzanti et al., 2014).

The Orange River (2430 km, ~10^6 km^2) flows mainly through arid climate areas. The drainage area in its upper reaches is composed of terrigenous rocks and basalts of the Karoo Supergroup. The Vaal River (1460 km), the main tributary, flows among the Neoarchean and Paleoproterozoic rocks. Below its confluence, the Orange River crosses the Mesoproterozoic metasedimentary and metavolcanic rocks (Becker et al., 2006). The fine SPM of the Orange River is dominated by the erosion products of clay rocks of the Karoo Supergroup (Compton and Menace, 2007; Garzanti et al., 2014) and the predominant illite. The average CIA value calculated for this material is 57, based on the data in (Konta, 1985; Savenko, 2006).

The southern tributaries of the Limpopo River (length 1750 km, 4.4×10^5 km^2) drain the Precambrian Kaapvaal Craton. The northern tributaries drain the Zimbabwe Craton, sedimentary formations and plateau basalts of the Karoo Supergroup. In Mozambique, the Elephant River flows into the Limpopo River (560 km) that crosses the Paleoproterozoic Bushveld Complex. These rivers carry a fine SPM enriched in Fe, Mg, Ca, Sc, Cr, Mn, Co, Ni, and Cu due to the predominant erosion of igneous basic rocks. The Limpopo River SPM is also enriched in Na, K, Sr, Ba, and Ti. The average CI value for the fine SPM is ≤50 (!!) in the Elephant River and 60 in the Limpopo River. The SPM in some tributaries of the Limpopo River, which erode rocks of the crystalline basement, is characterized by CIA ~70 (Garzanti et al., 2014).

In Namibia, the rivers are usually ephemeral and subjected to long-term droughts. The drained provenances are composed of plateau basalts of the Upper Karoo Supergroup, Mesoproterozoic metamorphic rocks, and Neoproterozoic–Cambrian sedimentary rocks. Granite intrusions of different ages are also eroded. The fine SPM is composed of the predominant illite (80–87%) and the subordinate kaolinite (9–11%) and smectite (4–9%). The rivers in northern Namibia erode the Etendek plateau basalts and quartz latites. Clay minerals are in the fine SPM are dominated by smectite. The CIA value ranges from 43 to 76. Average values of the chemical indices ($CIA_{average}$ 53 ± 9, $WIP^1_{average}$ 58 ± 8) reflect a slight intensification of weathering. In general, the southern Africa is marked by a slight depletion of the alkaline and alkaline earth metals in the fine SPM compared to rivers in the equatorial regions (Garzanti et al., 2013a, 2013b, 2014).

The river systems in southern Africa clearly show that any large drainage basin includes various complexes of the source of fine aluminosiliciclastic material (sedimentary sequences included) that underwent one or more cycles of sedimentation. As a result, the mineral and chemical composition of the newly formed detritus reflects both the present and previous weathering settings. Results of the analysis of WIP, CIA, and α values are used to discriminate them in (Garzanti et al., 2014, 2022 and others). If quartz is added to the sediment (recycled material, its source is mainly fossil Kalahari dunes), the WIP value decreases linearly, whereas the CIA and α values do not change (Garzanti et al., 2013a, 2013b). For the fine SPM in the Okavango and Zambezi rivers, this approach allows us to identify assimilation of the repeatedly recycled material (in the SPM of the first sedimentation cycle, the CIA/WIP values vary from 0.6 for rivers in the arid Namibia to 1...2 for the Limpopo River, with the drainage areas mainly located in a subhumid climate.

When studying modern sediments of large river systems in Africa and other regions, authors abroad often use the weathering indices (αE) for mobile elements (E). These parameters appeared first in (Gaillardet et al., 1999). They are calculated by comparing the concentrations of mobile elements with the concentration of some immobile elements (Al, Ti, Th, Sm or Nd) with similar properties in the sample and UCC. It was shown in (Garzanti et al., 2010) that weathering indices, calculated not on the basis of Al, strongly depend on the hydraulic sorting processes. Therefore, it was proposed to calculate such indices only using Al ($\alpha^{Al}E = (Al/E)_{sample}/(Al/E)_{UCC}$) in (Garzanti et al., 2013a, 2013b; Guo et al., 2018; Maslov and Podkovyrov, 2023). If $\alpha^{Al}E > 1$, the content of element E is depleted relative to UCC; at $\alpha^{Al}E < 1$, it is enriched. The fine SPM in the rivers of southern Africa is most strongly depleted in Na ($\alpha^{Al}Na$ varies from 2 to 5 in the arid Namibia, from 3 to 10 in the Limpopo and Zambezi rivers, and from 13 to 28 in the Upper Zambezi and Okavango (Garzanti et al., 2013a). Average $\alpha^{Al}Sr$ values are higher than $\alpha^{Al}K$ and $\alpha^{Al}Ca$. The values of $\alpha^{Al}Ba$, $\alpha^{Al}Mg$, and $\alpha^{Al}Rb$ rarely exceed 2, indicating a slight decrease of these elements. Thus, various components of sediments in many regions show a fairly typical mobility succession: $\alpha^{Al}Na \gg \alpha^{Al}Sr > \alpha^{Al}K > \alpha^{Al}Ca > \alpha^{Al}Ba > \alpha^{Al}Mg \geq \alpha^{Al}Rb \geq \alpha^{Al}Cs$ (Bouchez et al., 2011; Gaillardet et al., 2003; Garzanti et al., 2014).

Taking into account the facts based on the PRECSED data bank (IGDD RAS, St. Petersburg) pertaining to contents of the major oxides, as well as the pioneer information related to the distribution of rare and trace elements in the Upper Vendian–Lower Cambrian clay rocks in the Moscow syneclise, we again attempted to reconstruct the rock composition in provenances and to analyze the relationship between the processes of weathering and recycling in

[1] WIP, Weathering Index of Parker = (100 × (Na/0.35 + Mg/0.9 + K/0.25 + Ca/0.7) (Parker, 1970).

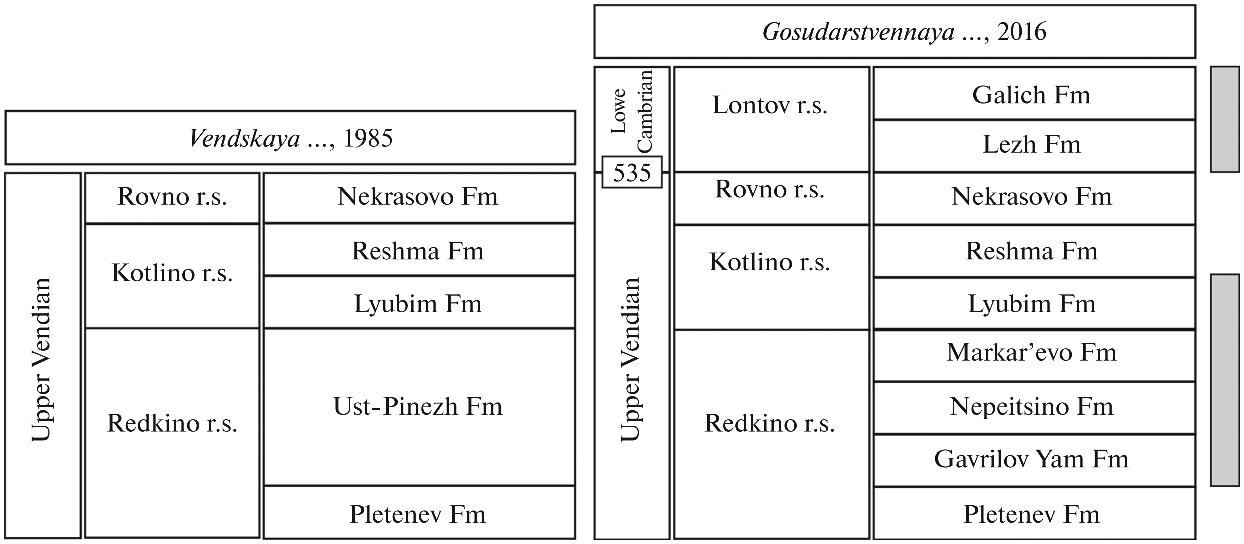

Fig. 1. Stratigraphic division of the Upper Vendian–Lower Cambrian Moscow syneclise, according to (*Gosudarstvennaya* ..., 2016; *Vendskaya* ..., 1985). Age of the Vendian/Cambrian boundary is given in Ma. Gray boxes on the right show the section interval, with the clay rocks characterized by the analytical data. r.s.—regional stage; Fm—Formation.

the formation of the specified sedimentary sequence. Unfortunately, these issues of sedimentary geology (currently crucial) are not almost discussed in our geological literature. This publication is an attempt to fill this gap to some extent.

LITHOSTRATIGRAPHY OF THE UPPER VENDIAN–LOWER CAMBRIAN, COMPOSITION OF CLAY ROCKS AND CONDITIONS OF THEIR ACCUMULATION

According to (*Vendskaya* ..., 1985), the Upper Vendian Valdai Group unites the Pletenev, Ust-Pinezh, Lyubim, and Reshma formations (Fig. 1). The Pletenev Formation (thickness up to 50 m or more) is composed of gravelites, coarse- and fine-grained variegated sandstones, siltstones, and dark gray black mudstones. It conformably overlaps the crystalline basement rocks of the East European Platform (EEP) and Riphean rocks in aulacogens, but its belonging to the Upper Vendian is debatable. The Ust-Pinega Formation (300–400 m) is represented by dark greenish gray and gray, as well as chocolate-brown mudstones, among which one can see interlayers and packages of gray-colored siltstones and sandstones. The Formation transgressively overlaps basement rocks of the EEP, Riphean, and Pletenev Formation. The Pletenev and Ust-Pinezh formations correspond to the Upper Vendian Redkino regional stage. The Lyubim Formation (up to 480 m) unites sandstones, siltstones, gravelites, and conglomerates, as well as greenish and dark gray or variegated mudstones. In the central part of Moscow syneclise, it conformably overlies rocks of the Ust-Pinezh formation, grades on flanks to the crystalline basement rocks, and truncates the underlying rocks (*Vendskaya* ..., 1985). The Reshma Formation (up to 230 m or more) is composed of red and variegated sandstones, siltstones, mudstones, and mudstone-type clays. The Reshma Formation is absent in our sample set. The Lyubim and Reshma formations belong to the Kotlino regional stage. Rocks of the Nekrasovo Formation (10...20–100 m) unconformably overlie the Reshma Formation (Rovno regional stage, Baltic Group) composed of the variegated and red-colored sandstones along with the interlayers of siltstones and clay rocks (*Gosudarstvennaya* ..., 2016). This unit is also absent in our sample set.

In the Explanatory Note to the stratigraphic scheme of Vendian rocks in the Moscow syneclise (Kuz'menko and Burzin, 1996), the Ust-Pinezh Formation is divided into three (Gavrilov-Yam, Nepeitsino, and Makar'evo formations, whereas the lower subformation of the Lyubim Formation is included into the Makar'evo Formation. The Upper Vendian is also accepted almost similarly in the Explanatory Note to the State Geological Map (scale 1 : 1000000, Sheet O-37, Yaroslavl) (*Gosudarstvennaya* ..., 2016) (Fig. 1).

The Vendian is overlain conformably by the Lower Cambrian Lezh Formation (40...>100 m) (*Gosudarstvennaya* ..., 2016). This unit is composed of greenish, bluish, dark gray, and red-colored clay rocks, siltstones, and sandstones. Its lower part contains glauconite. The Lezh Formation is conformably overlain by the Lower Cambrian Galich formation (20...100 m or more), which is composed of greenish and bluish gray mudstones and mudstone-type clays in the upper part, but siltstones and sandstones with glauconite in the lower part.

According to Explanatory Note to the Map of Precambrian rocks in the Russian Platform and its framing (*Karta* ..., 1983), rocks of the Reshma formation contain shrinkage cracks, clay pellets, authigenic barite, and pseudomorphoses after halite, and these rocks are characterized by the gypsification and cross-layering of individual regional stages. It is obvious that the Reshma level is hardly composed of basinal sediments.

According to (Aksenov, 1985 and references therein), sediments of the Ust-Pinezh and Lyubim formations were deposited mainly in shallow-marine environments. Boundaries of the modern terrain of these formations are almost universally erosional. The Reshma time is characterized by the coastal and shallow-marine sedimentation, as well as the accumulation of continental sediments, suggesting that the sedimentation area of the specified time could resemble the huge Okavango River delta or several such deltas. The presence of glauconite in the Lower Cambrian rocks suggests their shallow-marine genesis.

According to (Kuz'menko et al., 1996), the beginning of the Gavrilov Yam time was marked by a basinal setting and the deposition of mainly fine-grained terrigenous sediments over most of the Moscow syneclise area. In the Nepeitsino time, the water area was decreased slightly, but sediments were accumulated in normal marine conditions. In the Lyubim period, the basin was likely desalinated, and the marine setting gave way to the swamp-lagoon conditions in the northeastern areas. In the Reshma time, these settings also dominated in central areas of the syneclise. A new transgression took place during the Nekrasovo period.

The sedimentation conditions in the Moscow syneclise during the Late Vendian are scrutinized in (Kheraskova et al., 2005a). For example, the Gavrilov Yam Formation is divided into the tuffite–sand–siltstone, tuffaceous mudstone, siltstone–tuffite–clay, tuff–tuffaceous pelite and tuff, tuff–tuffaceous pelite–clay (gray) and sand facies. Let us focus only on some of these facies. For example, the tuffite–sand–siltstone facies is represented by an alternation of variegated sandstones and siltstones with diverse flow structures. The sand facies is composed of monotonous gray-colored, often coarse-grained sandstones with an admixture of pebble and gravel. These sediments were probably deposited in a coastal shallow–water zone. The Nepeitsino and Makar'evo formations are represented by the tuffite–tuff–pelite–siltstone and tuffite–mudstone facies. The first facies is characterized by the horizontal and wavy-layered structures, whereas the sandy and silty material often composes thin lenses related to the activity of small currents, according to (Kheraskova et al., 2005a). Good rounding of the clastic material may indicate both its long-range transport and repeated redeposition of sediments in the shallow–water zone. The Lyubim and Reshma formations are also represented by two (sand–siltstone–tuffaceous pelite and tuff–tuffaceous pelite–mudstone) facies. The first facies is characteristic of intra-basin uplifts and underwater fans. Sandstones and siltstones in this facies are characterized by the wavy and cross-layered structures, as well as wave ripples. The second facies tends to depressions in the basin. Siltstones and fine-grained sandstones in its sections appear only near intra-basin uplifts. They are characterized mainly by the horizontal and subhorizontal structures, as well as gentle cross-wavy layering.

According to (Grazhdankin et al., 2010), the Gavrilov Yam and lower Nepeitsino subformation is composed of thin-layered mudstones with interlayers of volcanic tuffs, as well as thin intercalations of siltstones and mudstones with sandstone interlayers. The Makar'evo Formation, which is present mainly in the northeastern Moscow syneclise, is composed of thin-layered mudstones and siltstones alternating with sandstones. Various regional stages of the Nepeitsino and Makar'evo formations are overlain transgressively by variegated rocks of the Lyubim Formation. On the southern, southwestern, and northwestern limbs of the Moscow syneclise, the lower part of the Lyubim Formation includes quartz sandstones, probably, deposited during the repeated rewashing of bottom sediments on a spacious sand shoal.

Mudstones of the Ust-Pinezh Formation are composed of kaolinite, mixed-layer minerals of the illite-smectite type, and chlorite (Aksenov and Volkova, 1969; Kheraskova et al., 2005a; Kuz'menko et al., 1994). The Lyubim, Reshma, and Nekrasovo formations are dominated by illite clays (Kheraskova et al., 2005a). Mudstones of the Lezh and Galich formations are also dominated by illite with the smectite admixture (Kheraskova et al., 2005b, 2006). According to the (Gorokhov et al., 2005), the fine aluminosiliciclastic material in the Upper Vendian clay rocks of the Moscow syneclise was derived mainly from the Riphean sedimentary rocks.

According to (Pyrrus, 1980), the main components of Upper Vendian clay rocks are represented by illite, chlorites, kaolinite, and mixed-layer minerals (illite-smectite). The basal levels of the Kotlino regional stage include a notable amount of kaolinite, which may be associated with intense humid weathering in the provenances. Based on analysis of the average content of clay minerals "in some sections", E.A. Pyrrus made the following conclusion: at the beginning of the Late Vendian, chlorite entered the sedimentation area from the northeast and southeast; the mixed-layer minerals, from the east; and kaolinite, from the west. In the Rovno time, kaolinite was delivered from the west and northwest, whereas chlorite is transported from the southeast. Similar pathways of the clay mineral migration are inherent in the Lontovo time. Therefore, E.A. Pyrrus (1980) assumed that the Late Vendian–Early Cambrian history of the western Moscow syneclise was marked by the existence of a spa-

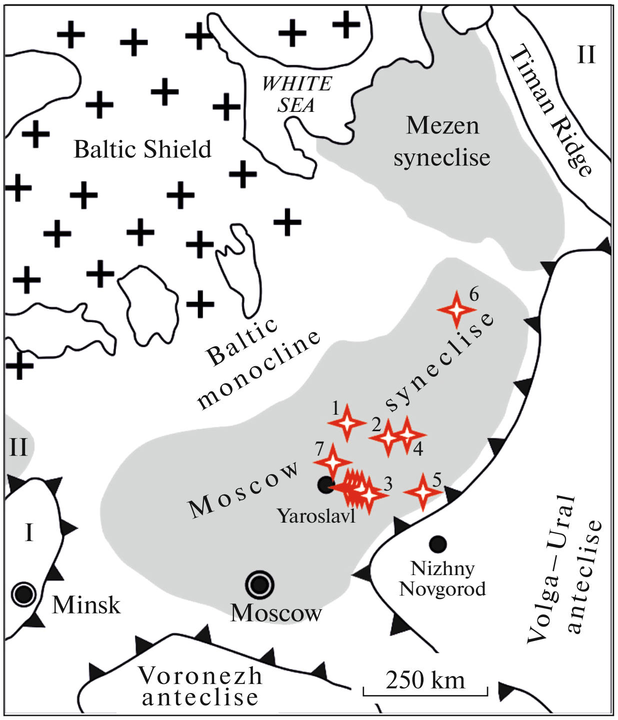

Fig. 2. Main tectonic elements of the East European Platform, modified after (Biske, 2019; Chistyakova et al., 2020; Podkovyrov et al., 2022), and the position of wells (asterisks) that recovered the Upper Vendian–Lower Cambrian rocks in the Moscow syneclise. (I) Belarusian anteclise; (II) Timan–Pechora Plate. Wells: (1) Danilovskaya 11; (2) Orekhovo 3; (3) Gavrilov Yam 1, 2, 3, 4, and 5; (4) Galich; (5) Medvedevskaya 1; (6) Krasavino 2; (7) Marino 1.

cious, poorly dissected continent/land that underwent chemical weathering in a humid climate. Probably, this continent/land served as the main source of the "frontal flow" of kaolinite.

The mineral composition of the Upper Vendian clay rocks at margins of the Moscow syneclise, especially where the Vendian rocks overlie the crystalline basement and weathering crusts (Savko, 1988; Tikhomirova et al., 1971), differs somewhat from the composition discussed above. According to (Savko, 1988), the amount of kaolinite in sediments decreases from the southern limb of the syneclise to its central part.

A detailed study of the mineral composition of the Upper Vendian–Cambrian clay rocks in the western EEP regions (Lithuania, Poland, western Belarus, Podolia, and others) was undertaken in (Jewuła et al., 2022). Based on the X-ray structural analysis, these authors performed a quantitative analysis of the composition of clays and mudstones. They found that quartz, orthoclase, microcline, Na- and Ca-plagioclase, micas ($2M_1$ and trioctahedral), hematite, goethite, kaolinite, illite $1M_d$, illite–smectite, pyrite, and berthierine occur mainly in clay rocks. It was shown that the kaolinite content in clay rocks increases from the Volyn level (average for all regions ~10%) to the Redkino level (~16%) and then decreases (about 8% in Cambrian clays). It is specially noted that both traditional geochemical and new mineralogical indicators proposed by the authors suggest the accumulation of these sediments during prominent chemical weathering, with the formation of kaolinite (indicator of hot humid climate) in the weathering crusts. This is also evidenced by the composition of Meso- and Neoproterozoic paleosoils developed on the Volyn basalts and crystalline basement rocks (Kremer et al., 2018; Liivamagi et al., 2018, 2021). In general, dioctahedral smectite prevailed at the bottom and kaolinite and hematite prevailed at the top. The increased kaolinite content in clay rocks can be related to the erosion of upper horizons of paleosols (Jewuła et al., 2022; Liivamagi et al., 2021) or by local "kaolinite weathering" of Vendian rocks (Bojanowski et al., 2020; Dudzisz et al., 2021; Jewuła et al., 2022).

Calculation of the hydrolyzate module, HM (Yudovich and Ketris, 2000), and the chemical index of alteration, CIA (Nesbitt and Young, 1982), allowed us to judge the paleoclimate during the formation of these rocks (Podkovyrov et al., 2022). For example, average CIA values in clay rocks correspond to the interval 72–77; i.e., the fine aluminosiliciclastic material was derived, probably, from areas with a relatively warm climate.

FACTUAL MATERIAL AND DISCUSSION

Deep wells Gavrilov Yam 1–Gavrilov Yam 5, Orekhovo 3, Danilovskaya 11, Krasavino 2, and others, which recovered rocks of the Valdai and Baltic groups in the central Moscow syneclise (Fig. 2), were sampled by A.V. Sochava and V.N. Podkovyrov in 1989 and 1992–1994. We accepted the stratigraphic division of Upper Vendian rocks in accordance with the concept in (*Vendskaya* ..., 1985). Unfortunately, it is impossible to "adopt" the samples taken at that time into the Vendian subdivision schemes accepted at present (see, for example, *Gosudarstvennaya* ..., 2016). Therefore, we operate further with the formation names adopted at that time.

Contents of the major oxides in clay rocks were determined in the late 1980s-early 1990s by the "wet chemistry" method in the Central Laboratory of the Northwestern PGO (Krasnoe Selo). The content of rare and trace elements in this sample set was determined by the ICP-MS method in the Central Laboratory of VSEGEI (St. Petersburg).

General lithogeochemical features of clay rocks

In this work, we used data on the bulk chemical composition (major oxides) of 98 clay rock samples and the content of rare and trace elements in 39 samples. Table 1 presents some information pertaining to

Table 1. Contents of the major oxides (wt %), as well as rare and trace elements (ppm), in representative samples of the Upper Vendian–Lower Cambrian clay rocks in the Moscow syneclise

Component	Formation										
	Ust-Pinega									Lyubim	
	sample										
	970-3	970-4	970-12	970-16	970-27	972-23	930-9	931-14	939-7	931-30	972-4
SiO_2	57.35	57.72	58.20	56.70	55.43	60.65	62.89	59.65	58.38	63.33	57.47
TiO_2	0.61	0.65	0.79	0.92	0.81	0.80	1.00	0.83	0.92	0.95	0.81
Al_2O_3	18.86	19.07	19.69	19.36	19.28	19.68	17.34	17.89	19.72	17.36	18.31
FeO*	7.34	6.63	6.64	8.06	7.92	5.54	7.02	7.58	6.75	5.95	8.04
MnO	0.03	0.03	0.04	0.11	0.12	0.06	0.05	0.12	0.05	0.03	0.06
MgO	2.10	2.19	1.91	1.73	2.07	1.84	2.09	3.01	2.46	2.40	2.30
CaO	0.39	0.39	0.45	0.41	0.57	0.38	0.29	0.39	0.50	0.41	1.39
Na_2O	1.23	1.23	1.08	0.95	1.05	1.10	1.47	1.88	1.66	1.17	1.42
K_2O	4.22	4.00	3.41	3.52	3.81	3.79	3.90	4.39	4.80	3.94	3.71
P_2O_5	0.06	0.02	0.02	0.02	0.07	0.05	0.09	0.13	0.12	0.11	0.70
LOI	7.31	7.58	7.29	7.74	8.37	5.61	3.37	3.63	4.13	3.85	5.30
Total	101.84	101.91	101.05	100.31	99.85	99.64	99.56	99.79	99.49	99.55	99.63
Sc	15.00	15.20	13.80	16.60	14.70	15.90	14.70	12.90	18.40	12.90	16.60
V	114.00	156.00	110.00	124.00	127.00	118.00	112.00	116.00	160.00	99.40	117.00
Cr	70.60	81.50	79.20	86.80	87.20	78.60	73.90	78.60	81.00	83.70	81.40
Co	26.60	17.60	14.00	16.50	16.00	14.30	14.00	21.20	23.10	21.30	21.30
Ni	28.70	37.90	23.40	36.00	30.10	31.80	32.10	38.50	47.80	40.70	38.50
Rb	156.00	166.00	156.00	174.00	187.00	167.00	168.00	160.00	146.00	134.00	166.00
Sr	85.80	74.20	82.90	92.50	110.00	93.60	93.80	78.70	153.00	68.20	94.70
Y	27.70	29.20	27.20	37.50	28.60	27.90	31.30	25.60	35.20	25.80	39.70
Zr	143.00	146.00	185.00	185.00	162.00	164.00	215.00	154.00	163.00	245.00	243.00
Nb	15.40	15.40	19.60	20.40	19.50	16.70	19.40	16.60	19.20	18.30	20.60
Cs	7.35	8.60	7.69	8.57	9.49	8.37	7.73	8.15	8.32	5.77	7.44
Ba	403.00	337.00	401.00	374.00	336.00	311.00	339.00	384.00	2000.0	382.00	361.00
La	42.70	45.30	45.10	54.50	56.00	45.70	51.50	41.90	49.00	36.10	53.70
Ce	83.30	88.30	84.00	112.00	110.00	90.30	104.00	83.70	101.00	70.40	113.00
Pr	9.32	10.60	9.80	13.60	12.90	10.70	12.40	9.67	12.40	8.25	13.90
Nd	32.40	38.80	33.10	50.30	44.90	38.70	44.20	34.00	48.50	30.00	54.50
Sm	5.55	7.31	5.66	10.00	7.59	7.22	8.04	6.11	11.10	5.43	12.20
Eu	1.07	1.29	1.05	1.89	1.30	1.33	1.41	1.15	2.57	1.05	2.27
Gd	4.95	6.00	4.82	8.56	6.15	6.09	6.34	5.11	9.78	4.77	10.30
Tb	0.81	0.92	0.79	1.33	0.93	0.94	1.00	0.80	1.51	0.77	1.53
Dy	4.97	5.40	5.01	7.63	5.35	5.55	5.86	4.67	7.95	4.64	8.35
Ho	1.06	1.11	1.06	1.49	1.11	1.10	1.20	0.99	1.44	0.97	1.55
Er	3.26	3.18	3.26	4.15	3.31	3.28	3.54	2.91	3.76	2.95	4.29
Tm	0.50	0.48	0.49	0.62	0.49	0.49	0.51	0.44	0.52	0.45	0.61
Yb	3.32	3.17	3.17	3.88	3.20	3.27	3.46	2.92	3.21	3.05	3.96
Lu	0.52	0.46	0.48	0.58	0.49	0.46	0.52	0.44	0.51	0.47	0.59
Hf	4.46	4.51	5.87	6.01	5.29	5.08	6.49	4.58	4.87	7.51	6.59
Pb	17.60	53.40	22.90	24.20	15.20	20.00	6.09	7.88	26.30	30.70	26.30
Th	11.00	11.60	12.90	14.50	13.00	12.40	14.00	12.00	13.10	11.50	14.00
U	2.26	3.72	2.47	2.69	2.45	2.24	2.59	1.93	1.72	2.42	3.40

Table 1. (Contd.)

Component	Formation										
	Lyubim					Lezh		Galich			
	sample										
	972-6	972-13	972-42	972-45	972-49	930-48	930-49	930-52	971-4	971-7	971-9
SiO_2	56.34	57.33	62.62	59.00	61.26	63.12	65.99	62.71	57.72	56.19	62.61
TiO_2	0.82	0.90	0.93	0.94	0.91	0.97	0.87	0.93	1.02	0.80	0.68
Al_2O_3	18.26	18.08	18.79	21.14	18.35	15.91	14.98	16.64	18.87	18.89	16.25
FeO*	10.71	11.07	5.66	5.51	6.42	8.02	5.00	7.25	7.78	9.21	7.36
MnO	0.05	0.05	0.05	0.04	0.05	0.07	0.05	0.05	0.10	0.02	0.03
MgO	2.59	2.21	1.42	1.79	1.68	2.63	1.88	2.37	2.58	2.85	2.47
CaO	0.33	0.21	0.26	0.25	0.27	0.54	1.12	0.24	0.88	0.26	0.26
Na_2O	1.20	1.20	1.05	1.14	1.23	0.26	0.86	0.65	0.80	0.80	0.56
K_2O	3.86	3.85	3.24	3.81	3.48	3.69	3.39	4.53	4.67	5.16	4.51
P_2O_5	0.02	0.02	0.02	0.02	0.02	0.26	0.08	0.07	0.04	0.02	0.02
LOI	5.33	4.57	5.48	5.89	5.83	4.03	5.28	4.07	5.04	5.31	4.75
Total	99.56	99.54	100.01	99.58	100.14	99.55	100.46	99.79	99.82	99.73	99.69
Sc	17.30	16.00	18.60	17.30	14.20	14.50	10.70	14.00	14.50	14.70	13.30
V	135.00	131.00	120.00	123.00	108.00	95.80	61.50	123.00	135.00	131.00	117.00
Cr	87.50	86.10	82.10	85.90	77.50	81.90	46.30	84.90	82.70	89.30	79.70
Co	25.50	19.70	17.00	24.90	15.60	34.80	50.70	25.70	20.70	60.40	39.00
Ni	40.50	39.00	25.60	39.00	24.30	44.80	28.40	40.30	36.60	46.50	38.10
Rb	180.00	187.00	153.00	178.00	155.00	146.00	93.90	175.00	170.00	180.00	154.00
Sr	90.40	91.90	75.00	86.20	80.90	93.00	74.40	80.80	67.40	73.90	61.90
Y	36.00	33.40	39.70	34.20	34.40	40.60	26.90	35.30	31.70	29.00	30.10
Zr	164.00	161.00	240.00	222.00	227.00	280.00	403.00	189.00	182.00	145.00	220.00
Nb	18.30	18.00	21.40	21.70	19.60	21.10	16.20	19.00	17.80	16.70	17.20
Cs	8.94	9.39	8.05	9.75	7.52	7.45	4.05	8.33	8.07	8.63	7.16
Ba	358.00	373.00	321.00	346.00	336.00	407.00	324.00	380.00	400.00	380.00	427.00
La	60.10	54.90	52.00	52.30	50.60	54.30	33.20	48.40	45.60	45.80	41.20
Ce	127.00	111.00	103.00	101.00	104.00	107.00	69.30	97.30	91.40	87.80	84.10
Pr	15.20	12.80	12.20	11.80	12.40	14.20	8.18	11.80	10.80	10.40	10.10
Nd	54.80	45.50	44.00	42.30	45.30	57.20	30.70	43.70	38.50	37.40	37.30
Sm	9.17	7.62	8.61	7.73	8.69	13.70	5.66	8.29	7.04	6.76	7.09
Eu	1.57	1.37	1.60	1.40	1.56	2.70	1.03	1.54	1.31	1.25	1.35
Gd	6.92	6.33	7.54	6.64	7.18	11.60	4.88	7.22	5.89	5.62	5.89
Tb	1.08	1.03	1.25	1.07	1.13	1.54	0.77	1.12	0.94	0.88	0.93
Dy	6.56	6.19	7.55	6.49	6.60	8.18	4.72	6.53	5.68	5.29	5.48
Ho	1.35	1.26	1.54	1.31	1.30	1.51	0.96	1.28	1.16	1.07	1.12
Er	3.92	3.72	4.53	3.92	3.79	4.30	2.97	3.84	3.49	3.22	3.26
Tm	0.57	0.54	0.67	0.58	0.56	0.62	0.45	0.56	0.53	0.47	0.50
Yb	3.69	3.58	4.54	3.82	3.65	4.02	3.04	3.59	3.38	3.10	3.25
Lu	0.52	0.54	0.68	0.57	0.53	0.60	0.47	0.52	0.51	0.47	0.47
Hf	5.16	4.82	7.20	6.92	6.79	8.30	11.30	5.83	5.71	4.54	6.58
Pb	44.40	32.80	27.40	48.00	39.30	47.00	36.40	31.30	28.00	35.80	35.00
Th	14.50	14.70	13.80	15.00	13.40	12.60	9.46	12.80	12.50	12.40	11.60
U	2.50	2.64	3.06	3.45	2.85	3.23	2.57	2.78	2.63	2.23	2.39

representative mudstone samples from the Ust-Pinezh, Lyubim, Lezh and Galich formations. Since it is difficult to give a complete description of these samples because of the limited volume of journal article, we will focus only on the main points.

Hereafter, we consider mainly the data on rock units furnished with more than two samples. Taking into account the standard deviation, average SiO_2 contents in clay rocks of the Ust-Pinega, Lyubim, and Galich formations are comparable: 57.85 ± 3.27, 59.81 ± 2.96, and 60.65 ± 2.66 wt %, respectively). This statement is also valid for Al_2O_3 (18.82 ± 1.57, 18.14 ± 1.15, and 17.54 ± 1.10 wt %, respectively), $Fe_2O_3^*$ (i.e., total Fe), MgO (2.27 ± 0.45, 2.28 ± 0.52, and 2.50 ± 0.21 wt %, respectively), and CaO (0.61 ± 0.50, 0.38 ± 0.24, and 0.34 ± 0.22 wt %, respectively). At the same time, mudstones of the Galich Formation are depleted in $Na_2O_{average}$, relative to the Upper Vendian clay rocks—0.70 ± 0.09 vs. 1.27 ± 0.41 wt % (Ust-Pinezh level) and 1.26 ± 0.21 wt % (Lyubim level). The average K_2O content in them is slightly higher (4.76 ± 0.22 wt %) than in mudstones of the Ust-Pinezh (3.86 ± 0.46 wt %) and Lyubim (3.81 ± 0.29 wt %) formations.

Let us note that we use hereafter only the analytical data on rocks with the SiO_2 content <66 wt %. In the normal alkalinity (NAM)–FM diagram (Yudovich and Ketris, 2000), i.e., $(K_2O + Na_2O)/Al_2O_3$–$(Fe_2O_3^* + MgO)/SiO_2$ diagram, average compositional data points of various lithostratigraphic divisions of the Upper Vendian–Lower Cambrian clay rocks in the Moscow syneclise are concentrated in the overlap area of classification fields II (mainly smectite with kaolinite and illite clays) and V (chlorite–smectite–illite clays) or near the specified area (Fig. 3a). This pattern somewhat contrasts with the concept about a significant share of kaolinite in the rocks under consideration. The distribution of average points of mudstones and mudstone-type clays in the K/Al–Mg/Al diagram (Turgeon and Brumsack, 2006) indicates the predominance of illite in their composition with a subordinate role of kaolinite. In rocks of the Galich Formation, the role of illite is higher than in the underlying formations (Fig. 3b). All these facts suggest that there was no significant change in the composition of clay rocks during the considered, several tens of million years long, time interval.

Based on comparison of contents of the major oxides in the Upper Vendian–Lower Cambrian clay rocks of the Moscow syneclise with the PAAS (Taylor and McLennan, 1985), the average content of SiO_2, Al_2O_3, MgO, K_2O, and Na_2O in the Ust-Pinezh mudstones is comparable to PAAS. Relative to PAAS, the average TiO_2 content is slightly lower, whereas the P_2O_5 and CaO contents are notably lower. The average FeO* content is 1.17 ± 0.27 PAAS. Approximately similar distribution of the major oxides is also characteristic of the Lyubim clay rocks. Relative to PAAS, the Lezh mudstones are slightly depleted in Al_2O_3 (0.88 PAAS) and Na_2O (0.49 PAAS), but slightly enriched in $MgO_{average}$ (1.18 PAAS). The distribution of other oxides resembles the pattern observed in the Upper Vendian mudstones. Finally, average SiO_2 and Al_2O_3 contents in the Galich clay rocks are comparable to the PAAS values. Average content of FeO*, MgO, and K_2O in them is slightly higher than in PAAS (1.14 ± 0.15, 1.14 ± 0.10, and 1.29 ± 0.06 wt %, respectively), and the content of TiO_2, CaO, Na_2O, and P_2O_5 is slightly or significantly lower than in PAAS (0.87 ± 0.14, 0.26 ± 0.17, 0.58 ± 0.08, and 0.25 ± 0.15 wt %, respectively).

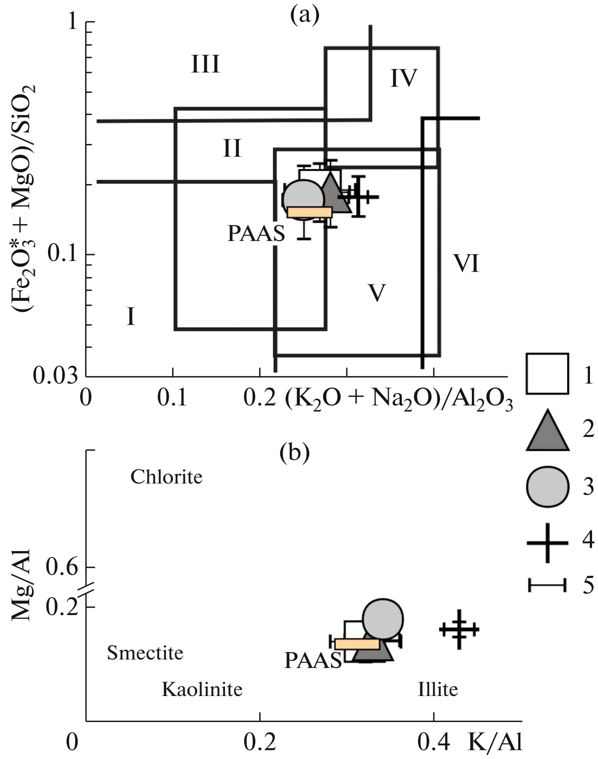

Fig. 3. Positions of the averaged compositional data points of clay rocks of various Upper Vendian–Lower Cambrian lithostratigraphic divisions on diagrams $(K_2O + Na_2O)/Al_2O_3$–$(Fe_2O_3^* + MgO)/SiO_2$ (a) and K/Al–Mg/Al (b). (1–4) Average compositions of mudstones: (1) Ust-Pinezh Formation; (2) Lyubim Formation; (3) Lezh Formation; (4) Galich Formation; (5) standard deviation (± 1σ). (a) (I–VI) clay rock composition fields: (I) predominantly kaolinite, (II) predominantly smectite with an admixture of kaolinite and illite, (III) predominantly chlorite with an admixture of Fe-illite, (IV) chlorite–illite, (V) chlorite–smectite–illite, (VI) illite with a significant feldspar dissemination.

Unfortunately, it is now difficult to specify the rock complexes, eroded during the accumulation of the Upper Vendian–Lower Cambrian sedimentary sequences, in the above-listed works. Therefore, so we draw all possible conclusions hereinafter, as usual, as

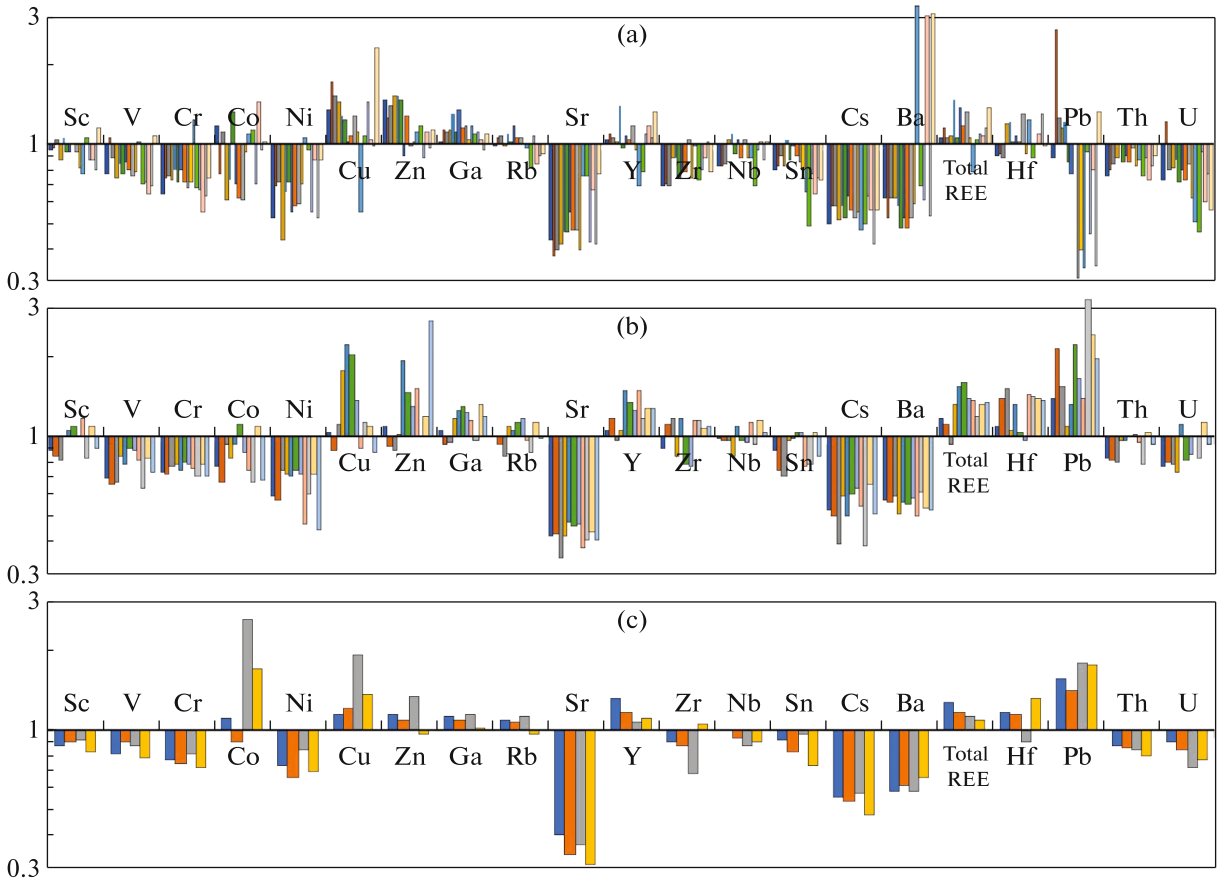

Fig. 4. Comparison of the content of rare and trace elements in mudstones of the Ust-Pinezh (a), Lyubim (b), and Galich (c) formations with their concentrations in PAAS, according to (Taylor and McLennan, 1985). The number of columns in the element cells corresponds to the number of analyzed samples.

reference average data on the chemical composition of Archean granites and Late Proterozoic basalts (Condie, 1993). This allows us to see that the studied clay rocks differ from Archean granitoids by notably higher contents of TiO_2, FeO, and MgO, whereas the Na_2O content in granitoids is higher. Comparison with the composition of basalts demonstrates that the clay rocks are characterized by significantly lower CaO contents and, conversely, notably higher concentrations of K_2O. Thus, the Upper Vendian–Lower Cambrian mudstones are closer to granitoids based on some composition parameters, but closer to mafic igneous rocks based on other parameters.

Clay rocks of the Ust-Pinezh, Lyubim, and Galich formations have comparable average concentrations of Sc, Cr (its maximum content is notably higher in the Ust-Pinezh mudstones), Rb, Y, Zr, Cs, Th, and total REE. At the same time, the Ust-Pinezh clay rocks have higher average concentrations of Sr than the mudstones of other two formations (103.54 ± 27.31 ppm vs. 84.25 ± 7.66 and 71.00 ± 8.17 ppm). Mudstones of the Galich Formation have a higher average Co content (36.45 ± 17.75 vs. 20.95 ± 5.49 and 19.04 ± 3.58 ppm). Average total REE content is 214.12 ± 29.77 in the Ust-Pinezh clay rocks, 236.75 ± 33.48 in the Lyubim mudstones, and 215.87 ± 14.43 ppm in the Galich mudstones.

Comparison of the contents of rare and trace elements in mudstones of the Ust-Pinezh and Lyubim formations with the contents in PAAS (Figs. 4a, 4b) showed that the rocks of both formations are relatively depleted in V, Cr, Co, Ni, Sr, Sn, Cs, Ba, Th, and U relative to PAAS. The contents of Cu, Zn and Ga, on the contrary, are higher. The Lyubim mudstones differ from the Ust-Pinezh variety by higher concentrations of Y, total REE, Hf, and Pb than in PAAS. Clay rocks of the Galich Formation have slightly increased average concentrations of Co, Cu, and Pb relative to PAAS. On the contrary, the average content of Sr, Cs, and Ba in them ranges from 0.36 to 0.61 PAAS (Fig. 4c).

Another important tool for lithogeochemical studies is the comparison of contents the of major oxides, as well as rare and trace elements, in clay rocks with the content in UCC (Rudnick and Gao, 2003). The contents of K_2O, Rb, Cs, Be, LREE, Eu, HREE, Y, Nb, Ta, FeO*, Co, Ni, and Cu are higher (relative to

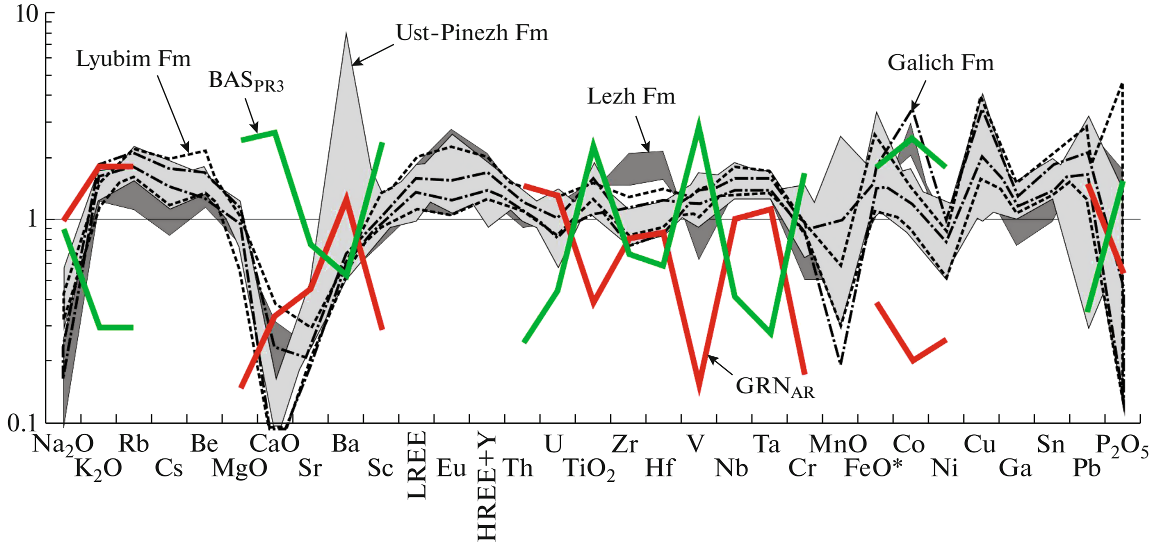

Fig. 5. The UCC-normalized concentrations of some major oxides along with rare and trace elements in the Upper Vendian–Lower Cambrian clay rocks of the Moscow syneclise, as well as in average Archean granites (GRN_{AR}) and Upper Proterozoic basalts (BAS_{PR3}), according to (Condie, 1993).

UCC) in the Upper Vendian–Lower Cambrian rocks of the Moscow syneclise. The Na_2O and CaO contents are significantly lower. Notable variations are inherent to Ba, MnO, and P_2O_5. Compared with the average Late Proterozoic basalts, the mudstones contain significantly more K_2O, Rb, Th, Zr, Hf, Nb, and Ta. On the contrary, concentrations of TiO_2, MgO, CaO, Sc, V, and Cr are significantly higher in basalts. In comparison with the mudstones under consideration, average Archean granitoids have notably lower concentrations of TiO_2, FeO, MgO, Sc, V, Cr, Co, and Ni (Fig. 5).

The chondrite-normalized (Taylor and McLennan, 1985) REE distribution in the Upper Vendian–Lower Cambrian clay rocks of the Moscow syneclise are very close to the analogous PAAS pattern (Fig. 6a). For example, the average $(La/Yb)_N$ value is 9.91 ± 0.99 for the Ust-Pinezh mudstones and 9.15 for PAAS. Average $(La/Yb)_N$ value for clay rocks of the Lyubim, Lezh, and Galich formations is 9.34 ± 1.10, 8.25, and 9.19 ± 0.59, respectively. Depletion of HREE in them is almost lacking. Average value of the negative Eu anomaly varies from 0.61 ± 0.01 (Lyubim Formation) to 0.66 ± 0.16 (Ust-Pinezh Formation). In PAAS, Eu/Eu* is 0.65. Interestingly, the LREE distribution in clay rocks does not differ basically from the distribution in the average Archean granitoids, whereas the HREE distribution is comparable to that in Late Proterozoic basalts.

Type of the aluminosiliciclastic material in clay rocks

Issue of the type of aluminosiliciclastic (petrogenic/lithogenic) material composing the Upper Vendian–Lower Cambrian clay rocks is already discussed in (Podkovyrov et al., 2022). Analysis of the relationship of lithochemical modules in the Ust-Pinezh clay rocks revealed a positive correlation between TM and IM (correlation coefficient, $r = 0.20$), but a negative correlation between NAM and HM[2] ($r = -0.38$). Thus, in accordance with (Yudovich and Ketris, 2000), we believe that mudstones of this level under consideration are composed mainly of material poorly transformed during sedimentogenesis. Mudstones of the Lyubim and Galich formations, which show a negative correlation between both module pairs (r_{TM-IM} –0.11, r_{NAM-HM} –0.21 and $r_{TM-IM} = -0.06$, r_{NAM-HM} –0.56), apparently contain a significant proportion of the material notably transformed in comparison with the parent rocks (Podkovyrov et al., 2022). At the same time, when analyzing these ratios, we did not take into account critical values of the correlation coefficients for a particular level of significance.

If we use this approach, the value of r_{TM-IM} for the Ust-Pinezh clay rocks cannot be considered significant. At the same time, the petrogenic nature of the material composing mudstones also becomes debatable. This conclusion is also valid for the r_{TM-IM} and r_{NAM-HM} values characterizing clay rocks of the Lyubim and Galich formations. All these facts suggest that the ratios of various lithochemical modules do not allow in our case to correctly judge the type of aluminosiliciclastic material composing the studied clay

[2] TM, titanium module = TiO_2/Al_2O_3; IM, iron module = $(Fe_2O_3^* + MnO)/(Al_2O_3 + TiO_2)$; NAM, normalized alkalinity module = $(Na_2O + K_2O)/Al_2O_3$; HM, hydrolyzate module = $(Al_2O_3 + TiO_2 + Fe_2O_3^* + MnO)/SiO_2$ (Yudovich and Ketris, 2000]. All modules are calculated based on wt %.

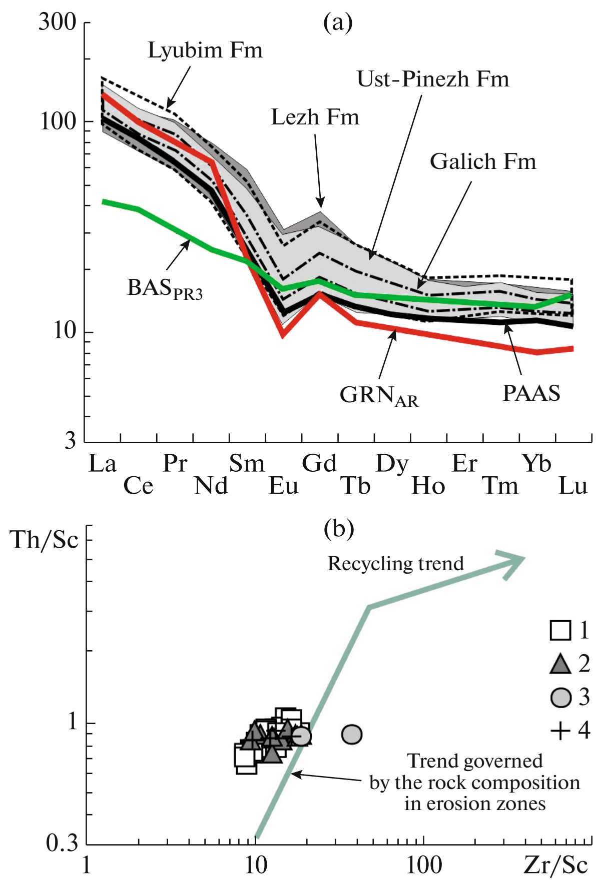

Fig. 6. The chondrite-normalized REE distribution in the Upper Vendian–Lower Cambrian clay rocks of the Moscow syneclise, as well as in PAAS (Taylor and McLennan, 1985), average Archean granites (GRN$_{AR}$), and Upper Proterozoic basalts (BAS$_{PR3}$), according to (Condie, 1993) (a), and the distribution of points of composition of clay rocks Upper Vendian–Lower Cambrian on the Zr/Sc–Th/Sc diagram (b). (1) Ust-Pinezh Formation; (2) Lyubim Formation; (3) Lezh Formation; (4) Galich Formation.

rocks. However, there is another approach to the solution of this issue based on the analysis of the Zr/Sc and Th/Sc values characteristic of clay rocks (McLennan et al., 1993). The mudstones and mudstone-type clays under consideration are characterized by the values of both these parameters typical for rocks with the composition controlled by the composition of rocks in the erosion areas (Fig. bb). This conclusion is essential for further constructions. The rather compact arrangement of data points of clay rocks of different lithostratigraphic divisions on the Zr/Sc–Th/Sc plot suggests a significant similarity in their composition.

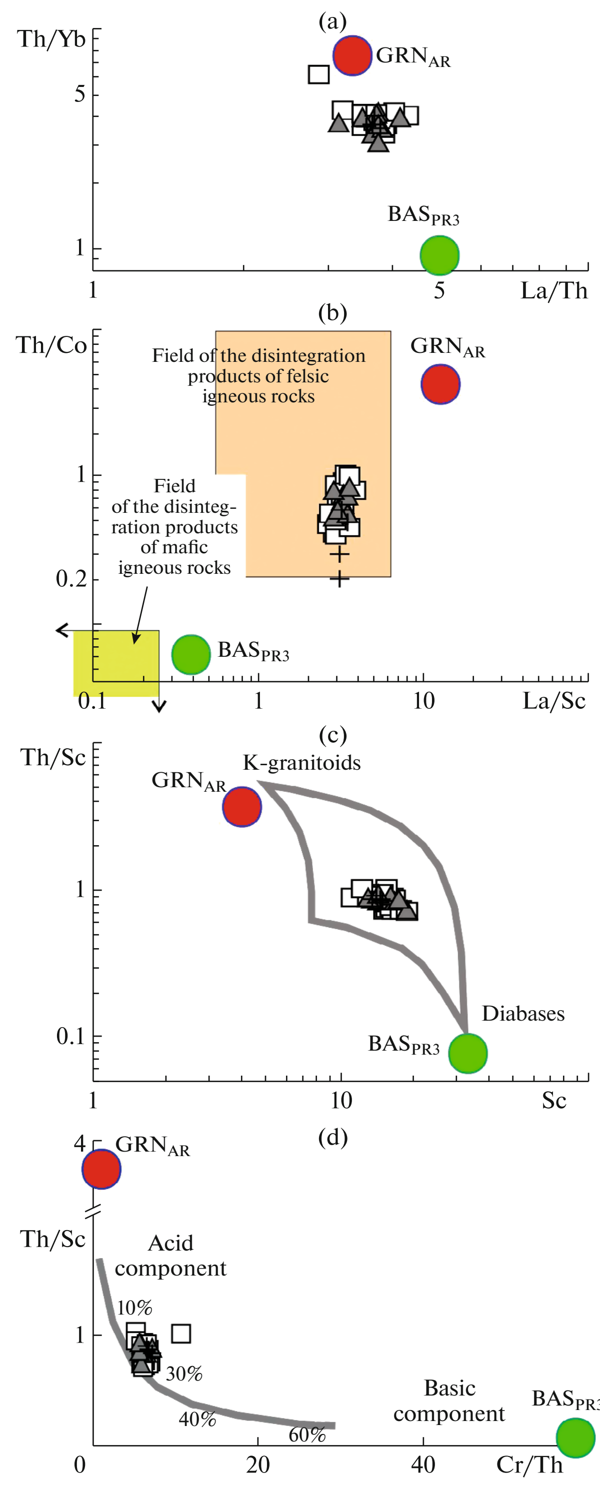

Fig. 7. Localization of the data points of the Upper Vendian–Lower Cambrian clay rocks in the Moscow syneclise, as well as reference data points of the average Archean granites (GRN$_{AR}$) and Upper Proterozoic basalts (BAS$_{PR3}$), according to (Kondi, 1993), on diagrams La/Th–Th/Yb (McLennan et al., 1980) (a), La/Sc–Th/Co (Cullers, 2002) (b), Sc–Th/Sc (Fedo et al., 1997; Bhat and Gosha, 2001) (c), and Cr/Th–Th/Sc (Bracciali et al., 2007; Condi and Wronkiewicz, 1990) (d). Legend as in Fig. 6.

Sources of the fine aluminosiliclastic material

In most of the discriminant diagrams (La/Sc–Th/Co, La/Th–Th/Yb, Sc–Th/Sc, and others(see (Maslov et al., 2020) for their overview) traditionally

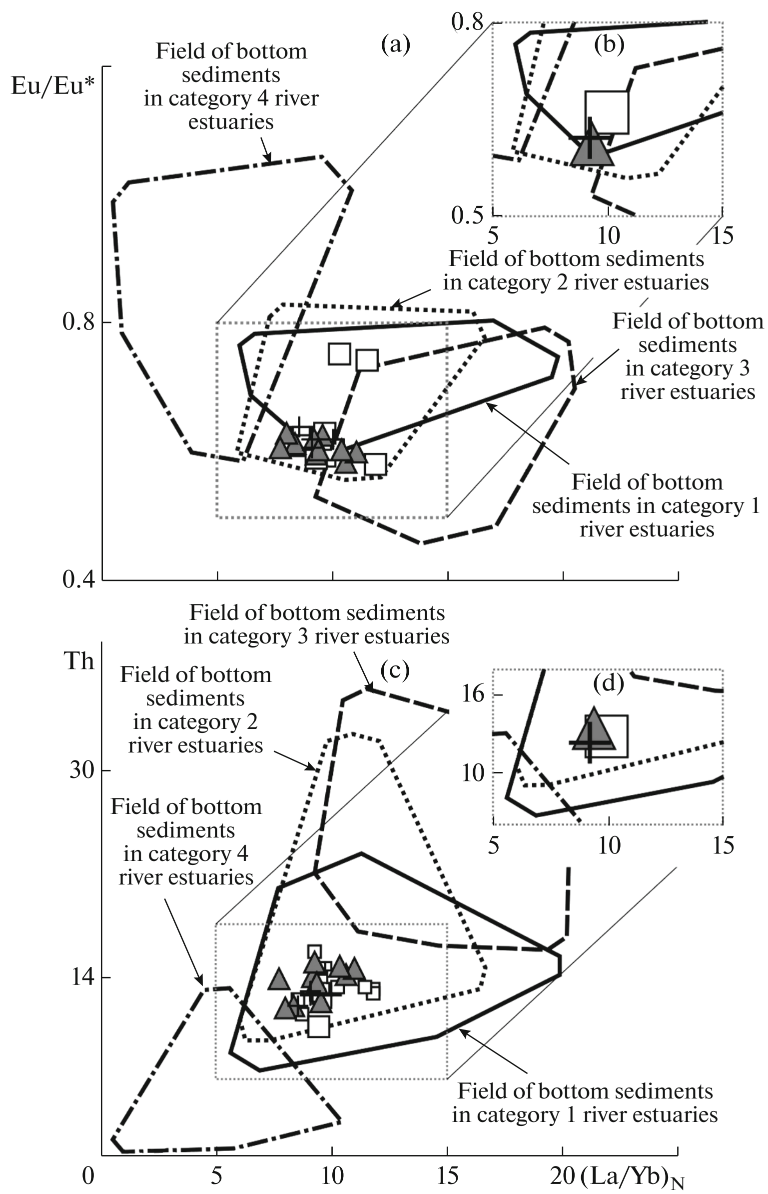

Fig. 8. Positions of individual (a, c) and averaged (b, d) compositional data points of the Upper Vendian–Lower Cambrian clay rocks on the diagrams $(La/Yb)_N$–Eu/Eu* and $(La/Yb)_N$–Th. Legend as in Fig. 6.

used for the reconstruction of the composition of source rocks of fine aluminosiliciclastic materials, data points of the Upper Vendian–Lower Cambrian clay rocks are located approximately between the reference data points of Archean granitoids and Late Proterozoic basalts (Figs. 7a–7c). Like the above-discussed relationship with PAAS and UCC, this fact suggests an approximately equal contribution of both sources to the composition of the studied sample set. Distribution of data points of mudstones in the Cr/Th–Th/Sc diagram (Fig. 7d) indicates, however, apparently a large proportion (up to 70–90%) of the disintegration products of felsic igneous rocks, as well as metasedimentary shales and gneisses. Analysis of ratios of the major oxides in clay rocks suggests the involvement erosion products of both sedimentary and metasedimentary rocks in their formation (Podkovyrov et al., 2022).

This statement confirms the concepts in (Gorokhov et al., 2005) about the significant contribution of destruction products of the underlying Riphean sedimentary rocks to the composition of the Upper Vendian–Lower Cambrian clays . In all diagrams (Fig. 7), data points of the clay rocks in different formations show a compact arrangement, suggesting that rock complexes eroded in drainage areas during the Late Vendian–Early Cambrian did not undergo notable alterations. We made a similar conclusion in (Pod-

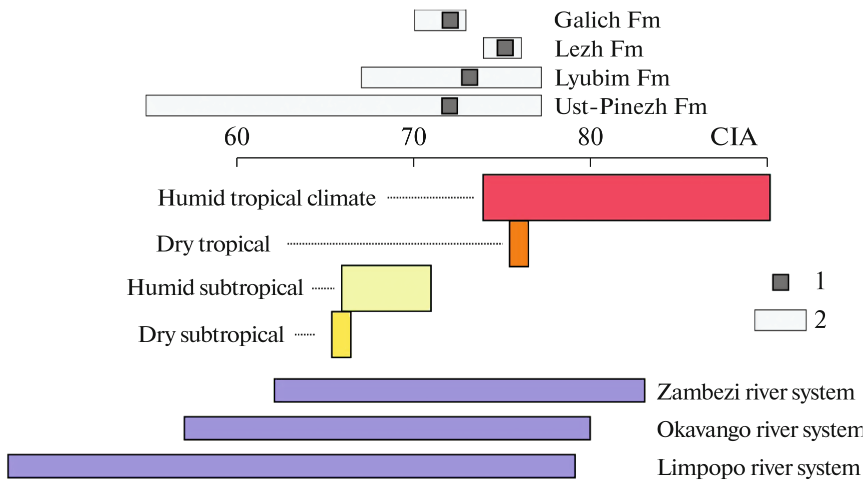

Fig. 9. Comparison of the average, minimum, and maximum CIA values typical for the Upper Vendian–Lower Cambrian clay rocks in the Moscow syneclise with the values typical for the fine SPM of modern rivers in different climatic conditions, according to (McLennan, 1993). The CIA values for the fine SPM of river systems in southern Africa are adopted from (Garzanti et al., 2014). (1) average CIA value; (2) minimum and maximum CIA values.

kovyrov et al., 2022) based on the analysis of lithochemical data.

Types of river systems transporting the fine aluminosiliclastic material into the basin

In the $(La/Yb)_N$–Eu/Eu* and $(La/Yb)_N$–Th diagrams (Maslov and Shevchenko, 2019) showing the fields of fine aluminosiliciclastic material characteristic of estuarine areas of different types of modern rivers (Bayon et al., 2015), data points of clay rocks of the Ust-Pinezh, Lyubim, Lezh, and Galich formations are concentrated in the fields of large rivers (category 1) and rivers draining source areas composed mainly of sedimentary rocks (category 2) (Fig. 8). Hence, the source areas of such river systems were quite large; i.e., they could be composed of rock complexes of different composition, which is typical for river systems in southern Africa.

According to the approach proposed in (González-Álvarez and Kerrich, 2012), the establishment of categories of river systems, which transported the fine aluminosiliciclastic material to the sedimentation area, makes it possible to compare the CIA values typical for the latter deposits with the values typical for the fine-grained sediments of various modern large river systems. Certainly, this approach is not devoid of pitfalls (Maslov, 2021 and references therein), since large rivers can cross several climatic zones. Therefore, variations of the CIA and other similar indices can be associated with the influence of tectonics on sedimentation processes, different duration of the detrital material existence in drainage areas, and with different composition of rocks in provenances drained by different sectors of the river system—as shown above, crystalline complexes in the upper reaches, sedimentary rocks or basalt plateaus in the middle reaches, and so on.

It is known that modern large river systems are marked by the following CIA values of SPM: ~51 (St. Lawrence River, tundra and taiga zone) and 54–64 (rivers of temperate humid climate, such as Danube, Mississippi, and others) to 90–95 (rivers of tropical climate, such as Congo, Niger, and others) (González-Álvarez and Kerrich, 2012; McLennan, 1993). Average CIA values for clay rocks of different Upper Vendian–Lower Cambrian formations in the Moscow syneclise vary in the range of 72–76 (Fig. 9). Such CIA values are characteristic of the SPM in modern large rivers of the humid subtropical and tropical regions, as well as rivers of the dry tropical climate regions (Yellow River, Orinoco, Nile, and others). Individual mudstone samples of the Ust-Pinezh Formation demonstrate a wider range of CIA values (56–77) than for clay rocks of the overlapping lithostratigraphic divisions (e.g., 67–77 in the Lyubim Formation). This circumstance is likely related to the insufficiently intensive and uniform transformation of catchment areas of that epoch by the processes of chemical weathering. Unlike the Vendian–Lower Cambrian clay rocks of the Moscow syneclise, the fine SPM of large river systems in southern Africa are characterized by a significant scatter of minimum and maximum CIA values, e.g., 62–83 for the Zambezi river system, 57–80 for the Okavango, and 47–79 for the Limpopo river. This scatter is significantly greater than the average CIA estimates (McLennan, 1993) for rivers of different climates and is related to the scale of their source areas located in different climatic zones and different composition of rock complexes therein.

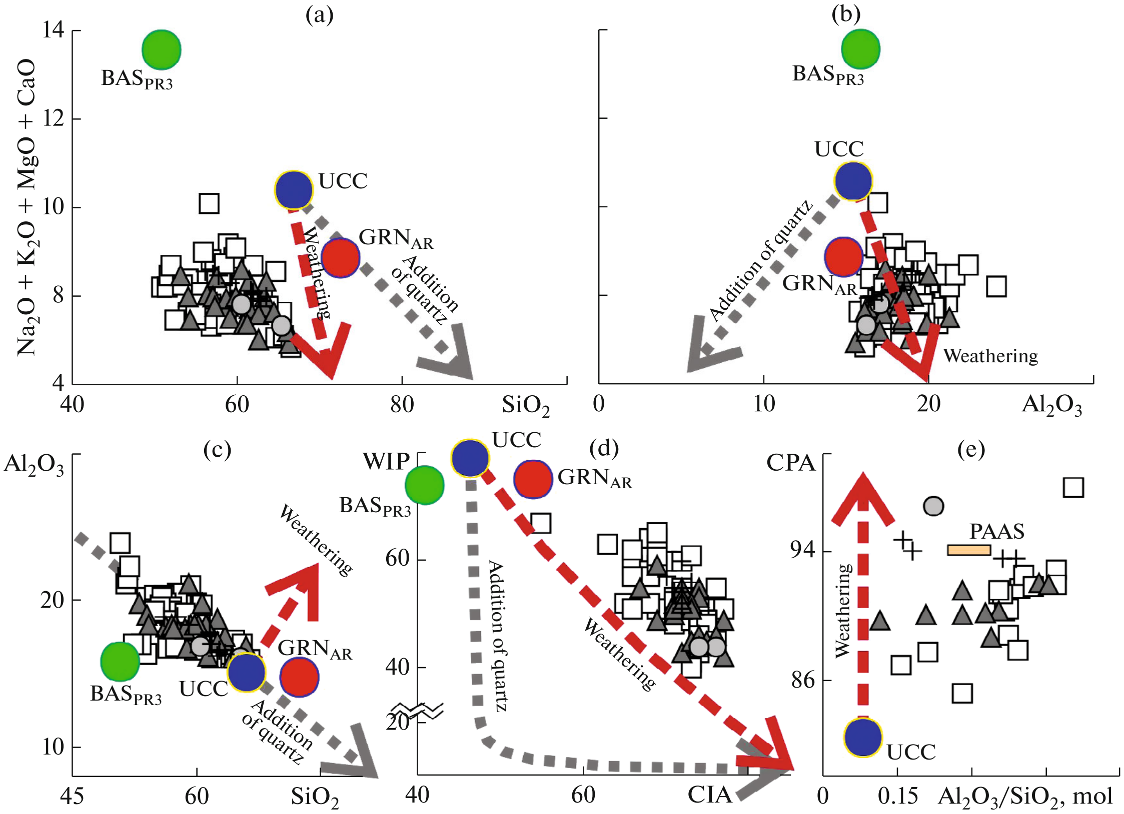

Fig. 10. Distribution of individual data points of the Upper Vendian–Lower Cambrian clay rocks, as well as reference data points of the upper continental crust, UCC (Rudnick and Gao, 2003), average Archean granites (GRN$_{AR}$) and Upper Proterozoic basalts (BAS$_{PR3}$), according to (Condie, 1993), on diagrams according to (Garzanti et al., 2014): SiO_2–($Na_2O + K_2O + MgO + CaO$) (a), Al_2O_3–($Na_2O + K_2O + MgO + CaO$) (b), SiO_2–Al_2O_3 (c), and CIA–WIP (d); and on diagram Al_2O_3/SiO_2– CPA (e) (Bosq et al., 2020). Legend as in Fig. 6.

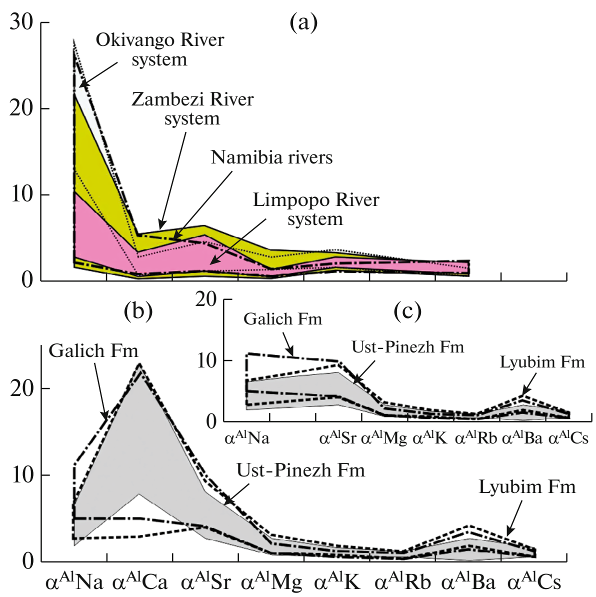

Fig. 11. Values of parameter $\alpha^{Al}E$ in the pelitic sediments (<32 μm fraction) in river systems of southern African (a), according to (Garzanti et al., 2014), and in Upper Vendian–Lower Cambrian clay rocks of the Moscow syneclise (b, c).

Relationship of the processes of weathering and recycling

The relationship of weathering and recycling processes in the formation of the Upper Vendian–Lower Cambrian clay rocks in the Moscow syneclise is another issue that can be considered taking into account the approaches developed for studying sediments of modern river systems in southern Africa. For example, according to (Garzanti et al., 2014, 2022 and others), it was shown that the addition of quartz to the reference UCC composition leads to a gradual increase of SiO_2 in sands, whereas the process of weathering leads to a decrease of mobile metals relative to Si and Al in both sands and silts. In our case, data points of the Upper Vendian–Lower Cambrian mudstones and mudstone-type clays on the SiO_2–($Na_2O + K_2O + MgO + CaO$), Al_2O_3–($Na_2O + K_2O + MgO + CaO$), and CIA–WIP diagrams (Figs. 10a, 10b, 10d) are located near or directly on the weathering trends. Their distribution is slightly different in the SiO_2–Al_2O_3 (Garzanti et al., 2014) and Al_2O_3/SiO_2–CPA (Bosq et al., 2020) diagrams (Figs. 10c, 10e). However, even here, absence of the influence of recycling processes on the clay rock composition is obvious in the first case and a notable difference in their composition from UCC (most likely, due to weathering processes) is seen in the second case. The composition of the fine aluminosiliciclastic material under consideration differs slightly from the composition of parent rocks—this conclusion is also supported by average CIA/WIP values typical for clay rocks: 1.40 ± 0.20 (Ust-Pinezh Formation), 1.45 ± 0.16 (Lyubim Formation, 1.73 (Lezh Formation), and 1.33 ± 0.07 (Galich formation).

In contrast to illustrations given in (Garzanti et al., 2014), Fig. 11 in our paper is based on the analytical data pertaining to the <32 μm fraction of pelitic silts in several rivers of southern Africa and the contents of Na, Ca, Sr, Mg, K, Rb, Ba, and Cs in clay rocks in the Upper Vendian–Lower Cambrian rocks of the Moscow syneclise. It is clearly seen that most of the fine SPM of modern African river systems (probably, except the Limpopo River) differ from the Upper Vendian–Lower Cambrian clay rocks by significantly higher α^{Al}Na values. On the contrary, the α^{Al}Ca values in the Upper Vendian–Lower Cambrian clay rocks of the Moscow syneclise vary in the range of 3.1–20.1. This range is notably higher than the typical value for the SPM of modern rivers in southern Africa and is related to the initial deficiency of CaO in the mudstones. If this parameter is excluded, the remaining series of α coefficients for the Upper Vendian–Lower Cambrian clay rocks will be close to a similar series for African rivers. With respect to the characteristic small α^{Al}Sr maximum (2.7–5.8), this series is close to the values typical for the Limpopo and Zambezi SPM.

CONCLUSIONS

The above factual material and its discussion allow us to draw several conclusions. First, it is obvious that there was no significant change in the composition of clay rocks formed in the modern Moscow syneclise during the several tens of million years of the geological history under consideration.

Second, the composition of the Upper Vendian–Lower Cambrian mudstones is closer to granitoids according to some parameters, but to mafic igneous rocks according to other parameters, indicating the participation of erosion products of both rock associations, as well as underlying sedimentary and metasedimentary rocks, in their composition. This conclusion is supported by peculiarities of the distribution of rare and trace elements in the Upper Vendian–Lower Cambrian clay rocks of the Moscow syneclise. Thus, compared with the average Late Proterozoic basalts, they contain notably more K_2O, Rb, Th, Zr, Hf, Nb, and Ta, whereas the concentrations of TiO_2, MgO, CaO, Sc, V, and Cr are significantly higher in basalts. Compared with mudstones, average Archean granitoids have notably lower concentrations of TiO_2, FeO, MgO, Sc, V, Cr, Co, and Ni.

Third, the chondrite-normalized REE distribution in clay rocks are close to the pattern in PAAS lanthanides—$(La/Yb)_N$ varies, on average, from 9.91 to 8.25. Average Eu/Eu* varies from 0.61 to 0.66. All these facts also suggest that the mudstones include destruction products of both felsic and mafic igneous rocks. Positions of data points of the Upper Vendian–Lower Cambrian clay rocks on the La/Sc–Th/Co, La/Th–Th/Yb, Sc–Th/Sc, and other discriminant diagrams confirm the above statement. In addition, the distribution of data points of mudstones on the Cr/Th–Th/Sc diagram indicates that the share of destruction products of the felsic igneous rocks could be as high as 70–90%.

Fourth, data on the relationship between geochemical parameters in the Upper Vendian–Lower Cambrian clay rocks of the Moscow syneclise do not allow us to draw a definite conclusion about the petrogenic or lithogenic nature of the aluminosiliciclastic material. However, its generally insignificant compositional difference from the parent rocks is supported by the Zr/Sc and Th/Sc values typical of mudstones and mudstone-type clays, with data points clustered near the field of clay rocks governed by the rock composition in paleosource areas.

Fifth, the distribution of data points of the Upper Vendian–Lower Cambrian mudstones in the Moscow syneclise in the $(La/Yb)_N$–Eu/Eu* and $(La/Yb)_N$–Th diagrams near the composition fields of fine aluminosiliciclastic material, which is typical for estuarine areas of different types of modern rivers, suggests that the SPM was transported to the sedimentation area by large rivers, whose catchment areas should be composed of different rock complexes (this is typical for the river systems of southern Africa), and by rivers draining source areas composed mainly of sedimentary rocks. At first glance, the CIA values, inherent to the Upper Vendian–Lower Cambrian clay rocks of the Moscow syneclise, values peculiar are more comparable with the values typical for the SPM in modern large rivers of the humid subtropical and tropical climate, as well as rivers of dry tropical climate areas. However, the scatter of minimum and maximum CIA values in the fine SPM of large river systems in southern Africa is significantly wider than in clay rocks of the Ust-Pinezh–Galich sedimentary sequence. Hence, this parameter depends in the latter case on both climate and composition of the source areas—such relationship is lacking for the Upper Vendian–Lower Cambrian rocks. Localization of data points of the Upper Vendian–Lower Cambrian mudstones and mudstone–type clays on the SiO_2–(Na_2O + K_2O + MgO + CaO), Al_2O_3–(Na_2O + K_2O + MgO + CaO) and CIA–WIP diagrams near the trends of weathering suggests that it was the paleoclimate that governed the main characteristics of their composition. Their specific CIA/WIP values serve as another argument in favor of the petrogenic nature of the fine aluminosiliciclastic material therein.

Sixth, most of the fine SPM of river systems in southern Africa (probably, except the Limpopo River) differ from the Upper Vendian–Lower Cambrian clay rocks of the Moscow syneclise by significantly higher α^{Al}Na values. Hence, their parent rocks underwent a generally stronger chemical weathering than the rocks that served as sources of the fine aluminosiliciclastic material for the clay rocks under consideration. On the contrary, the α^{Al}Ca values in clay rocks are notably higher (3.1–20.1) (typical for the fine riverine SPM), but this is related to the initial deficiency of CaO in the mudstones. If the parameter like α^{Al}Ca is omitted, as suggested above, then the remaining series of α coefficients for the Vendian–Lower Cambrian clay rocks in the Moscow syneclise will be similar to counterparts for the African rivers. Even the maximum α^{Al}Sr (2.7–5.8) brings this series closer to values typical for the fine SPM in the Limpopo and Zambezi rivers.

Upper Vendian–Lower Cambrian mudstones of the Moscow syneclise are at an early stage of catagenesis, and sediments in the African rivers have not even passed diagenesis. Moreover, clay minerals are quite sensitive to changes in environmental parameters during lithogenesis. Therefore, according to many experts, direct comparisons of sediments and sedimentary rocks should be treated with great caution. If the approach under consideration is applied, we are likely "saved" by at least one circumstance—despite the diversity of individual characteristics, a significant similarity in the content and distribution of the major oxides, as well as rare and trace elements, in reference objects /clay rocks/ shales (NASC, PAAS, RPSC, and others) and our samples.

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