Alkali Earth Elements in Vendian–Cambrian Clayey Rocks, the East European Platform

S. B. Felitsyn

Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences, nab. Makarova 2, St. Petersburg, 199034 Russia e-mail: felitsyn@peterlink.ru

Received May 24, 2005

Abstract—Low Sr and Ca contents in fine-grained terrigenous rocks of the Vendian sedimentary cover in the East European Platform may be related to the following reasons: (1) the absence of authigenic carbonates in Vendian mudstones owing to desalination of epiplatformal sedimentary basins; (2) significant contribution of the chemically weathered rocks in the formation of the Vendian cover of the East European Platform.

DOI: 10.1134/S0024490206040067

INTRODUCTION

Important Late Precambrian–Early Cambrian biotic events are accompanied by the reorganization of geochemical cycle and variations in carbon, sulfur, and strontium isotopic compositions of sedimentary rocks (Logan et al., 1995; Braiser and Lidsay, 2001). Models of the biosphere-hydrosphere system are traditionally used to explain variations in the phosphorus cycle and carbon and sulfur isotopic compositions (Cook and Shergold, 1984; Braiser, 1992a), whereas increase in the ⁸⁷Sr/⁸⁶Sr value in oceanic water at the end of Precambrian is attributed to increase in the erosion rate of radiogenic Sr-rich rocks during the Pan-African orogeny (Derry et al., 1994). Attempts were made to create models combining all known geological-geochemical features of rocks formed at the Precambrian-Phanerozoic boundary (Sochava, 1992).

These models are based on isotope–geochemical data on Late Precambrian and Early Cambrian carbonate sequences.

Vendian stratotype sections of the East European Platform are only composed of terrigenous sediments. Unlike the underlying and overlying sediments, Vendian sequences of the East European Platform do not contain carbonates, and authigenic calcite is absent in clayey rocks of these sequences. Pioneer investigations of the composition of basement and sedimentary sequences of the Russian Platform under the supervision of A.P. Vinogradov and A.B. Ronov revealed that Vendian mudstones have unusually low contents of alkali earth elements and CO₂, as compared to the Riphean and Phanerozoic shales. The detailed study of compositional variations in mudstones throughout the Vendian sequence of the East European Platform (Sochava et al., 1992, 1994) completely confirmed the depletion of clayey rocks in alkali earth elements. Further investigations made it possible to distinguish the levels with extremely low contents of Ca (0.26 wt %) and Sr (~70 μ g/g) in Upper Vendian reference sections (Felitsyn, 2004). This geochemical feature of Vendian clayey rocks of the East European Platform suggests the influence of Vendian sedimentogenesis on the cycle of alkali earth elements in Late Precambrian.

The aim of the present work is to analyze the distribution of alkali earth elements in the largest Vendian structures of the East European Platform. Since Ca, Sr, and Na are most mobile during the continental chemical weathering and can migrate as cations (Nesbitt et al., 1980), variations in the Sr and Ca contents across the section in fine-grained terrigenous sediments should reflect variations in the geochemical cycle of elements mentioned above.

MATERIALS AND METHODS

Element content data on fine-grained terrigenous rocks were taken from the PRECSED database compiled under the supervision of A.V. Sochava at the Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences. The sampling was supplemented with 650 analyses of major element contents in mudstones from the reference Vendian sections of the East European Platform and Sinian system of the South Chinese Craton. The analyses were carried out using the conventional chemical method at the Experimental-Methodical Expedition of the Sevzapgeologiya Industrial Geological Association. Average error in the determination of Ca, Mg, and Na contents was no more than 7%. Principles of the database compilation and some results of its processing were published in (Sochava et al., 1992, 1994). Therefore, we present below only data on samples corresponding to the problem formulated in this article.

The bulk mass of Vendian clayey rocks (more than 95%) in the East European Platform was deposited in the Late Vendian. In order to characterize these rocks, we used data on the chemical composition of mudstones of the Redkino and Povarovka groups and lower part of the Baltic Group in the largest Vendian structures (Moscow syneclise; Lvov-Kishinev, Mezen, and Shkapovo–Shikhany depressions). The Sr content in the basement rocks was determined for borehole samples from the Lvov-Kishinev depression and northwestern and central parts of the Moscow syneclise. The samples were taken at a depth of no less than 20 m below the pre-Vendian erosion surface and characterized by the lack of signs of supergene alterations. In addition, we used the following materials: unpublished data of M. Moczydlowska on the composition of clayey rocks of the Upper Vendian Bialopole, Lublin, and Wludawa formations of the Lublin slope (borehole Lopenik IG-1, Helm area, eastern Poland); data on lithologies and stratigraphy of Vendian rocks on the Lublin slope (Strauss et al., 1997); and data on the chemical composition of mudstones from the upper part of the Visingso Group, Vättern basin, southern Sweden. The mudstone sequence (580 m) mainly consists of clayey rocks with a high content of organic carbon and units of phosphate nodules in the upper part. Sandstones and dolomites are subordinate (less than 30% of the section). Sediments of the upper part of the Visingso Group were deposited in a shallow-water marine basin (Morad and Vidal, 1989). Their microfossil assemblage testifies to the Late Riphean-Early Vendian age (Knoll and Vidal, 1980). The presence of phosphorites suggests that the sediments are younger, because the unit of similar phosphorite-bearing sediments in Vendian sequences of Ukraine is considered a regional lithological marker of Upper Vendian rocks and is used to correlate sections (Velikanov, 1986).

We analyzed mudstones of the Zherba, Tinnaya, and Moty formations of the Yudoma Complex—stratigraphic analogue of the Upper Vendian of the East European Platform in the Siberia (Sokolov, 1997). The studied samples characterize the western and eastern slopes of the Anabar Shield, Aldan massif, Olenek uplift, Nepa–Botuoba anteclise, and the Uchur–Maya region. The stratigraphy and composition of Late Cambrian terrigenous rocks of the Siberian are reported in (Sochava et al., 1994).

In order to characterize Upper Precambrian finegrained terrigenous rocks of the South Chinese Craton, we used data on the Sinian stratotype section in the Huangling anticline (30 km north of the town of Yichang, Hubei Province, China). In the Yangtze canyon area, the Sinian carbonate sequence (~1100 m thick) overlies the Early Proterozoic Kunlien gneisses and Huangling granites. The U–Pb zircon age of granites is 819 ± 7 Ma (Ma et al., 1989). The Sinian finegrained terrigenous rocks include mudstones of the Dengying and Doushantou formations that account for 10% of the section. The Upper Sinian Dengying and Doushantou formations are considered stratigraphic analogue of the Upper Vendian of the East European Platform and the Yudoma Complex of the Siberian Craton (Sokolov, 1997).

In addition to the PRECSED database, we used analyses of Sr and Ba concentrations in 1200 clayey rock samples by the energy-dispersive X-ray fluorescence analysis (EDFA) at the Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences. The average relative measurement error was less than 7% (3σ) in the concentration range of 50–499 µg/g and less than 4% in the concentration range of 500– 999 µg/g.

RESULTS

Table 1 presents the contents of alkali earth elements in the Upper Vendian and Lower Cambrian clayey rocks in the largest Vendian structures of the East European Platform. The stratigraphic subdivision is given after (Sokolov, 1997). The Ca, Sr, and Ba contents in the fine-grained terrigenous rocks from all areas of the platform are significantly lower than those in the standard Composite Post-Archean Shales (PAAS): Ca 0.93 wt %, Cr 200 μ g/g, and Ba 650 μ g/g (Taylor and McLennan, 1985). The Ca content in the Vendian mudstones from different structural zones based on the study of intricately mixed samples (Ronov and Kazakov, 1983) corresponds to data in Table 1. The Ca content is 4.3 wt % in the bulk shale sample from the sedimentary cover of the East European Platform (Migdisov et al., 1994). Thus, the Upper Vendian and Lower Cambrian mudstones and clays are significantly depleted in Ca and Sr relative to the representative PAAS samples. Mudstones of the Povarovka Group (and Kanilov Group, a stratigraphic analogue of the Povarovka Group in the Lvov–Kishinev depression) show the lowest contents of Ca, Ba, and Sr as compared to the underlying Redkino Group and the overlying Cambrian clayey rocks.

We have detected regularity in the areal distribution of Ca and, especially, Sr in the Vendian rocks of the East European Platform. According to the IR-MS analysis data, mudstone fraction $1-2 \mu m$ (80% illite and 20% chlorite) from the middle part of the Stappogiedde Formation (Varanger Peninsula, northern Norway) contains 47 μ g/g Sr (Gorokhov et al., 2001). The Ca content in 26 bulk mudstone samples from the middle part of the Stappogiedde Formation varies from 0.21 to 0.34 wt % (A. Sochava, personal communication). According to the Neoproterozoic correlation schemes of Baltica (Vidal and Moczydlowska, 1995), the middle and upper parts of the Stappogiedde Formation correspond to the Upper Vendian Lublin and Wludawa formations on the Lublin slope of east Poland. In the Vendian mudstones from the northeastern part of the German basin (within the North Arkon block sandwiched between the Bornholm and Rügen islands), where the Vendian sequence is 55 m thick (Franke, 1993), the

Stratigraphic position	Mg, wt %	Ca, wt %	Sr, μg/g	Ba, µg/g				
Central part of the Moscow syneclise								
Lower Cambrian	1.13 ± 0.38 (30)	0.28 ± 0.18 (30)	79 ± 11 (79)	433 ± 87 (59)				
Povarovka Group	1.08 ± 0.24 (84)	0.24 ± 0.08 (84)	77 ± 14 (102)	$356 \pm 40 (38)$				
Redkino Group	1.39 ± 0.13 (183)	0.42 ± 0.06 (183)	$102 \pm 21 (165)$	497 ± 111 (13)				
Northwestern part of the Moscow syneclise								
Lower Cambrian	1.03 ± 0.42 (74)	0.21 ± 0.11 (74)	87 ± 18 (52)	483 ± 103 (74)				
Povarovka Group	0.81 ± 0.42 (80)	0.24 ± 0.14 (80)	76 ± 14 (40)	426 ± 92 (5)				
Redkino Group	0.74 ± 0.34 (56)	0.29 ± 0.11 (56)	84 ± 33 (18)	680 ± 247 (12)				
Mezen and Shkapovo–Shikhany depressions								
Povarovka Group	1.28 ± 0.41 (238)	0.21 ± 0.09 (239)	74 ± 12 (181)	383 ± 46 (100)				
Redkino Group	1.81 ± 0.35 (94)	0.47 ± 0.13 (94)	96 ± 26 (51)	485 ± 92 (102)				
Lvov–Kishinev depression								
Lower Cambrian	1.23 ± 0.28 (52)	0.51 ± 0.29 (52)	107 ± 47 (24)	448 ± 78 (52)				
Kanilov Group	1.40 ± 0.36 (133)	0.40 ± 0.17 (133)	97 ± 26 (191)	428 ± 51 (75)				
Mogilev–Podol'sk Group	1.33 ± 0.28 (192)	0.54 ± 0.23 (192)	156 ± 37 (205)	597 ± 103 (49)				

Table 1. Abundance of alkali earth elements in the Vendian and Lower Cambrian clayey rocks from various areas of the East European Platform

Note: Average values and standard deviations $(X \pm 2\sigma)$ are given. Number of analyses is shown in parentheses.

Table 2.	Average content	is of Ca (wt %) and	d Sr (μg/g) and	the Al ₂ O ₃ /Na	a ₂ O ratio in	Vendian clayey	rocks from	various areas
of the Ea	ast European Platf	form			-			

Location of the area	Ca	Sr	Al ₂ O ₃ /Na ₂ O	
Vättern Basin	_	58	_	
North German basin*	0.30	55	65	
Mezen basin	0.29	78	16	
Northwestern Moscow syneclise	0.19	78	92	
Central Moscow syneclise	0.36	89	15	
Southwestern East European Platform, Lublin slope	0.47	110	14	
Southwestern East European Platform, Lvov–Kishinev depression	0.53	127	22	

* Data from (McCann, 1998).

Sr content varies from 53 to 58 μ g/g (McCann, 1998). Mudstones from the upper part of the Visingso Group are also characterized by an extremely low Sr content (58 ± 8 μ g/g, *n* = 10). Table 2 shows Ca and Sr contents and Al₂O₃/Na₂O ratio in the Vendian mudstones from different areas of the Baltic plate. The mudstones demonstrate increase in the Sr and Ca contents by four and two times, respectively, over a distance of ~2500 km extending from the northernmost field of Late Cambrian clayey rocks (Varanger Peninsula) to the southernmost field (Podolia).

Losses of Ca and Sr during the formation of the Vendian clayey rocks in the East European Platform are significantly higher relative to similar Late Precambrian sediments in the Siberian and South Chinese cratons (Table 3). Validity of the comparison of chemical compositions of the basement rocks and Upper Precambrian clayey rocks is justified by the following fact: in all three ancient platforms, Upper Precambrian sedimentary complexes record the onset of the platformal evolution stage of lithospheric blocks, and the sedimentary rocks immediately overlie the basement. In terms of Na and Mg contents, the Vendian mudstones of the East European Platform do not apparently differ from mudstones of the Siberian and South Chinese cratons. The Al₂O₃/Na₂O ratio is 47 ± 12 (n = 86) in mudstones of the Yudoma Complex of the Siberian Craton and 41 ± 9 (n = 42) in Sinian mudstones of the Yangtze canyon district.

These data indicate a certain geochemical anomaly of the Vendian clayey rocks in the East European Platform: mudstones are depleted in Sr and Ca (and, to a

Object	MgO	CaO	Na ₂ O	Sr	Al ₂ O ₃ /Na ₂ O
Vendian of the East European Platform	2.3 (872)	0.61 (872)	0.74 (872)	82 (1094)	20
Basement of the East European Platform (Ronov and Migdisov, 1970)	2.3	2.9	2.6	252 (35)*	
Yudoma Complex of the Siberian Craton	3.0 (86)	1.1 (86)	0.83 (86)	143 (121)	47
Basement of the Siberian Craton (Sochava, 1986)	2.3	3.7	3.3	260	
Sinian system of the South Chinese Craton, Yangtze can- yons	2.2 (42)	1.1 (42)	0.70 (42)	146 (31)	41
Basement of the South Chinese Craton, Yangtze canyons (Kunlien gneisses and Huangling granites)	2.1 (18)	3.8 (18)	3.4 (18)	238 (18)	
Average Post-Archean Composite Shale (Taylor and McLennan, 1985)	2.2	1.3	1.2	200	
Modern upper continental crust (Taylor and McLennan, 1985)	2.2	4.2	3.9	350	

Table 3. Contents of MgO, CaO, Na₂O (wt %), and Sr (μ g/g) in basement rocks and Late Precambrian clayey rocks of the East European, Siberian, and South Chinese cratons

* Original data. Number of analyses is shown in parentheses.

lesser extent, in Ba), but they are similar to coeval clayey rocks from the Siberian and South Chinese cratons and to the average PAAS in terms of Mg and Na contents.

CALCIUM AND STRONTIUM DEPLETION IN THE VENDIAN MUDSTONES OF THE EAST EUROPEAN PLATFORM

Low Ca and Sr contents in the Vendian mudstones distinctly correlate with the absence of authigenic calcite in them and the predominance of minerals, which lose alkali earth elements during weathering. According to (Ronov et al., 1990), the kaolinite content in the Vendian mudstones is 20 wt %, which is significantly higher than that in the Riphean and Phanerozoic clayey rocks (10 and 13 wt %, respectively). The predominance of clay minerals with low contents of alkali and alkali earth elements is corroborated by K2O/Al2O3 values in the Vendian mudstones (0.21, n = 872). Similar values are typical of the recycled clayey sediments (Cox and Lowe, 1995), whereas erosion of the basement rocks and/or folded framing is considered a decisive factor in the formation of the Vendian sedimentary cover of the East European Platform (Bekker, 1988; Sochava et al., 1992). Based on 1094 EDFA determinations (present communication), the average Rb content in the Vendian clavey rocks of the East European Platform is 174 μ g/g. Correspondingly, the Rb/Sr ratio in them is 2.1, which is significantly higher than 0.8 in the average PAAS (Taylor and McLennan, 1985).

The absence of carbonates in the Vendian of the East European Platform was presumably caused by desalination of epiplatformal basins, which was previously established for the Moscow syneclise (Ronov and Kazakov, 1983; Pirrus, 1989; Afanas'eva et al., 1995) and the Lvov–Kishinev depression (Ryabenko, 1988;

LITHOLOGY AND MINERAL RESOURCES Vol. 41 No. 4 2006

Shnyukov, 1993), with maximum desalination in the Povarovka time. The Ca and Sr distribution in mudstones (Table 1) is consistent with the previous lithological and mineralogical data indicating that the Vendian basins of the East European Platform had low salinity, which prevented the precipitation of authigenic calcite. The nature of low salinity in the Upper Vendian basins of the East European Platform is unclear. However, the desalination of subsurface waters is consistent with the model of stratified Late Precambrian ocean characterized by restricted mass exchange between units with different contents of nutrient elements (Cook and Shergold, 1984; Brasier, 1992a; Yang et al., 1999; Gaucher, 2000). This assumption is based on the fact that low salinity is noted both for basins in the central part of the platform (central Moscow syneclise) and for the shelf of its western margin (the Lvov-Kishinev depression and the Lublin slope).

In the air-dry clayey material of present-day bottom sediments of the Gulf of Finland (Baltic Sea), the contents of characteristic elements are as follows: Ca 0.65 ± 14 wt %, Sr 178 \pm 18 µg/g, and Ba 610 \pm 105 µg/g (average from 44 EDFA analyses; A. Kol'tsov, personal communication). These values are significantly higher than those in the Vendian mudstones of the East European Platform, although the Gulf of Finland can be considered an analogue of epiplatformal Vendian basins in the East European Platform in terms of salinity and climatic conditions. At present, Quaternary glacial deposits and Early Paleozoic sedimentary rocks (including carbonates) are the main sources of clastic material in the Gulf of Finland, and authigenic calcite is absent in the bottom sediments. Therefore, the observed depletion of the Vendian mudstones in Ca and Sr is an indicator of not only low salinity of the Late Vendian basin, but also of the absence of carbonate rocks in the provenances.

The relatively high Mg contents in the Vendian clayey rocks of the East European Platform are attributed to the significant contribution of volcanogenic rocks in the Vendian sedimentary cover formation (Bekker, 1988; Sochava et al., 1992; Felitsyn and Sochava, 1996; Felitsyn, 2004). The chlorite content in the average sample of Vendian clayey rocks of the East European Platform is 5%, which is higher than that in the Riphean (1%) and Paleozoic (3%) mudstones (Ronov et al., 1990). Although the mineral composition of clayey rocks was determined by the semiquantitative method, increase in the chlorite content in the Vendian mudstones, relative to the Riphean rocks, seems to be significant and can be considered an indirect evidence for a higher contribution of volcanogenic material in the Vendian clayey rocks as compared to the Riphean one.

Mobility of Ba in the supergene zone is constrained by its adsorption on clay minerals, while the presentday oceanic cycle of Ba is mainly defined by biogenic carbonates and organic matter, since most $BaSO_4$ in the surface waters is related to the biogenic calcite and organic matter (Dehairs et al., 1980). Therefore, the Ba distribution in the Vendian sedimentary cover of the East European Platform cannot be unambiguously explained, especially, when one takes into consideration principle differences between the structures of biota and trophic chains in the Precambrian and Phanerozoic. In the present-day environment, increase in the Ba influx into sediments is related to the increase in bioproductivity (Braiser, 1992b) and the sorption of Ba by the decomposing organic matter in water column. In kerogens extracted by acid maceration from the Vendian clayey rocks of the East European Platform (Felitsyn and Pshenichnova, 1992; Felitsyn et al., 1998), the Ba content determined by the INAA data (present work) is $420 \pm 160 \,\mu\text{g/g}$ (*n* = 13) in the Redkino Group. $240 \pm 95 \ \mu g/g \ (n = 8)$ in the Povarovka Group. In the Lower Cambrian clayey rocks, the Ba content is $510 \pm$ 100 μ g/g (n = 4). Bioproductivity in the epiplatformal basins decreased in the Povarovka time, as is evident from the lowest Ba content in organic matter dissemination of the corresponding stratigraphic level. Some decrease in the Ba content in mudstones of the Povarovka Group, relative to the underlying and overlying beds (Table 1), is also attributed to the decrease of Ba inflow to the bottom of desalinated sedimentation basins in the East European Platform, since Na_2SO_4 is the major component of the buried Ba influx (Dehairs et al., 1980).

ALKALI EARTH ELEMENTS IN THE UPPER PRECAMBRIAN CLAYEY ROCKS OF THE SOUTH CHINESE AND SIBERIAN CRATONS

Formation conditions of the mature terrigenous material in the Siberian and South Chinese cratons correspond to their low-latitude position in the Late Precambrian-Early Cambrian, as follows from paleogeographic reconstructions in (McKerrou et al., 1992; Torsvik et al., 1995). In averaged samples of the Vendian mudstones of the East European Platform, the Al₂O₃/Na₂O value ranges from 16 (Ronov et al., 1999) to 20 (Sochava et al., 1994). In the Vendian mudstones of the near-equatorial Siberian and South Chinese cratons, this ratio is 47 and 41, respectively. Based on the Al_2O_3/Na_2O value (<30), most Vendian clayey rocks of the East European Platform pertains to low-maturity sediments, except for mudstones from the northwestern Moscow syneclise and German basin with $Al_2O_3/Na_2O >$ 60, which is typical of high-maturity clayey rocks. The Vendian fine-grained terrigenous rocks of the Siberian and South Chinese cratons correspond to moderatematurity sediments $(30 < Al_2O_3/Na_2O < 60)$ (Akul'shina, 1985).

Although the Vendian mudstones of the Siberian and South Chinese cratons are more mature than those of the East European Platform, the former rocks have significantly higher Ca and Sr contents owing to normal marine conditions in the Siberian and South Chinese basins dominated by carbonate sedimentation in the Late Precambrian. Mudstone samples from these basins contain authigenic calcite (2-4%).

Results presented above are consistent with data on the maximum mobility of Ca and Sr (higher than Na mobility) at the earliest stages of the continental chemical weathering during the decomposition of calcic plagioclases (Kronberg et al., 1979; Duddy, 1980; Nesbitt et al., 1980; Stefansson and Gislason, 2001). Strontium is the most mobile alkali earth element. Its mobility in supergene conditions was higher than that of Ca during the formation of Late Precambrian terrigenous sedimentary sequences in all three platforms. Therefore, the delivery of Sr from provenances to Panthalassa was intense. However, unlike the East European Platform, carbonate platforms were characterized by precipitation of Sr in the epiplatformal basins. For example, in limestones of the Doushantou Formation and lower part of the Dengying Formation of the Sinian sequence in the Yangtze canyon area, the average Sr content is $940 \pm 130 \,\mu\text{g/g} \,(n = 26).$

SOURCES OF CLASTIC MATERIAL IN THE VENDIAN STRUCTURES OF THE EAST EUROPEAN PLATFORM

Results presented in this communication indicate the specificity of chemical composition of the Vendian mudstones of the East European Platform. Low maturity of the fine-grained terrigenous sediments is associated with low contents of Ca and Sr. The problem of Ca (and Sr) depletion in the sedimentary cover of the East European Platform seems to be even more impressive, because the sedimentary cover is enriched in Ca, relative to the upper continental crust (Galimov, 1975; Ronov, 1980). In the East European Platform, accumulation of the Vendian sediments in areas with weakly differentiated relief was accompanied by the formation of kaolinitic weathering crusts in stable parts of denudation zones and the significant contribution of material from provenances located beyond the platform (Sochava et al., 1992; Shnyukov, 1993). The presence of erosion products of juvenile volcanic rocks in the Upper Vendian sedimentary cover of the East European Platform has been established by mineralogical (Kopeliovich, 1965) and geochemical (Sochava et al., 1992; Felitsyn, 2004) data. These data indicate that provenances located beyond the platform began to play a significant role since the Povarovka time.

Thus, the sedimentation basins accumulated clastic materials of different degrees of maturity. The Baikalide surrounding of the platform delivered relatively low-maturity sediments of the molassoid formation (Bekker, 1983, 1988), whereas the basement inliers delivered products of intense chemical weathering. In the Vendian basins, the most mature clayey rocks are found in areas mainly related to the delivery of material from the Baltic Shield during the Late Vendian (northwestern Moscow syneclise and eastern German basin). Hence, the contribution of material from provenances located within and beyond the platform was different for various parts of a single epiplatformal basin. Relatively low-maturity terrigenous sediments of the molassold formation dominated in the marginal troughs of the platformal periphery (Varanger Peninsula, Mezen depression, Lublin slope, and Lvov-Kishinev depression), while the clastic material was mainly derived from the Hyperborean and Galician fold systems (Bekker, 1988). Areal variations in the Sr content can be related to the combination of two factors: (1) various role of provenances located in the Baltic Shield (maximal in the northwestern part of the platform and minimal in the central part of the Moscow syneclise); (2) influence of climatic zoning on the intensity of chemical weathering. Salinity regime in the Vendian epiplatformal basins prevented the precipitation of authigenic calcite. Therefore, the Vendian sedimentary cover is significantly depleted in Ca and Sr.

According to conceptual models of relationships between the tectonic activity, volcanism, atmospheric CO_2 content, weathering, and geochemical cycles (Fisher, 1986; Sochava, 1992), the rate of chemical weathering is maximal during transgressions, which accompanied the breakup of supercontinents (e.g., Rodinia and Pangea). The Vendian transgression was one of the largest transgressions in the Earth's history, and this episode was manifested in almost all ancient platforms (Sokolov, 1997). In the East European Platform, the maximum transgression took place in the Redkino time (Aksenov, 1998). The presence of terrigenous sediments with the lowest Ca and Sr contents in the Povarovka and Kanilov groups is consistent with the concept of maximum chemical weathering during the largest transgression in the East European Platform regardless of the provenance type (within or beyond the platform).

INFLUENCE OF VENDIAN SEDIMENTOGENESIS ON CALCIUM AND STRONTIUM CYCLES

The degree of the study and preservation of the Vendian fine-grained rocks of the East European Platform make it possible to estimate the amount of Sr and Ca, which were not removed from geochemical cycle with platformal sediments. The amount of Sr and Ca buried with fine-grained terrigenous rocks during the formation of the Post Archean Shale from the upper continental crust accounts for ~60 and 30%, respectively, of their contents in the provenances (Table 3). Comparison of Ca and Sr contents in the basement of the Siberian and South Chinese cratons versus mudstones of the Yudoma complex and Sinian system yield similar values. In the Vendian terrigenous rocks of the East European Platform, Sr and Ca account for only 30 and 20%, respectively, of their contents in the basement. If Sr and Ca transported from provenances to platformal clayey rocks account for ~60 and 30% of their contents in the provenances, their concentrations in the Vendian mudstones should be equal to 150 μ g/g and ~0.8 wt %, respectively. These values are the lower estimates, because we have supposed only intraplatformal provenances. The presence of volcanics of the folded framing in the provenances during the formation of the Vendian sedimentary cover (Sochava et al., 1992; Felitsyn, 2004) implies higher Ca and Sr contents in the denudation areas.

Datings of tuffs from the Lower Vendian Slawatycze Formation of the Lublin slope, eastern Poland (551 ± 4 Ma) (Compston et al., 1995) and from the Upper Vendian Ust–Pinega Formation at the Zimnii Coast of the White Sea (553.3 ± 0.3 Ma) (Martin et al., 2000) indicate that the Vendian clastic sediments of the East European Platform were mainly accumulated in ~10 Ma. Given that the volume of Vendian rocks is 0.5×10^6 km³ (Ronov et al., 1990), the rate of terrigenous material sedimentation in the East European Platform in Late Precambrian was 0.12×10^{15} g/yr.

Deficiency of Sr and Ca in the Vendian clayey rocks (discrepancy between calculated and observed contents) is 70 µg/g and 0.36 wt %. The excess amounts of Sr and Ca delivered to the oceanic basin during the Vendian, as deduced from their deficits in the clayey rocks, was no less than 0.09×10^{18} and 3.6×10^{18} g, respectively. It should be emphasized that these values define precisely the "excess" amounts of Sr and Ca, which were not removed from the cycle together with authigenic carbonates in epiplatformal basins of the East European Platform. The calcite content of 1-2 wt % in the sedimentary cover of the East European Platform would have been sufficient to remove the calculated amounts of Sr and Ca from the geochemical cycle with

authigenic calcite. Taking into consideration the formation duration (~10 Ma) and volume of the Upper Vendian sedimentary cover, the excess annual runoff of Sr and Ca from the Eastern European Platform was 0.01×10^{12} and 0.4×10^{12} g/yr, respectively.

The present-day annual Sr runoff is $(1.9-2.0) \times 10^{12}$ g/yr (Chaudhuri and Clauer, 1986); i.e., the annual delivery of Sr and Ca from the East European Platform to oceanic reservoir at the end of Precambrian was less than 1 and 0.2%, respectively, of the present-day continental runoff. The average Ca and Sr contents in the present-day river water are 15 and 0.07 µg/g, respectively (Voitkevich et al., 1990). Thus, the annual river runoff of ~140 km³/yr from the East European Platform at the end of Precambrian is sufficient to remove the amounts of Ca and Sr indicated above. Such a runoff value is trivial and typical of many modern large rivers in the world with a drainage area of less than $n \times 10^6$ km².

CONCLUSIONS

The Vendian fine-grained sediments of the East European Platform are depleted in Ca and Sr, relative to the more mature coeval clayey rocks of the Siberian and South Chinese cratons. The specific compositional signature of the Vendian mudstones is most probably related to the significant contribution of erosion products of basement inliers subjected to intense chemical weathering and the low salinity of the Vendian epiplatformal basins of Baltica, which was responsible for the absence of authigenic calcite in the Vendian mudstones.

Although the amount of Sr delivered from the provenance during the formation of Upper Precambrian sedimentary cover of the East European Platform was less than the continental Sr runoff in the Phanerozoic ranging from 1 \times 10¹⁰ mol/yr to 3.5 \times 10¹⁰ mol/yr (Kump, 1989), the general impact of the Vendian sedimentogenesis on the Sr geochemical cycle could be much more significant. According to (Akul'shina, 1985), the Vendian epoch of intense chemical weathering and weathering crust formation was a global event recorded in mature clayey materials and weathering profiles around the world. According to the model of geochemical cycle presented in (Sochava, 1992), the chemical decomposition of cratonic rocks governs the Sr isotopic composition of oceanic reservoir during the epochs of high rates of delivery of acid-forming components together with volcanic products into atmosphere. Increase of the CO₂ content in atmosphere and intensification of chemical weathering are likely to be responsible for the specific evolution of sedimentation, as well as Sr and C isotopic compositions of carbonates in Late Precambrian basins surrounding the Amazonian Craton (Alvarenga et al., 2004; Gaucher et al., 2004). High ⁸⁷Sr/⁸⁶Sr ratios in the oceanic crust are typical of the epoch of the global Vendian transgression when the rate of chemical weathering attained the maximum, according to the models in (Fisher, 1986; Sochava, 1992).

At present, ~20% of continental Sr runoff is delivered from provenances containing rocks with 87 Sr/ 86 Sr > 0.715, i.e., from ancient shields (Holland, 1989). During the Vendian transgression, the ancient shields, the most stable blocks of the continental crust, continued to deliver clastic material. Therefore, their contribution to the continental Sr runoff could be significantly higher than at the present time. Let us assume that the area of shields in the Vendian was $\sim 25 \text{ mln km}^2$ and the ⁸⁷Sr/⁸⁶Sr value in rocks therein was ~0.730. In this case, in order to increase the 87Sr/86Sr ratio in seawater from 0.7072 in the Early Vendian to 0.7087 in the Early Cambrian, Sr should be annually removed from the shield rock volume of 1.1 km³ with the chemical weathering intensity similar to that during the formation of the Vendian clayey rocks in the East European Platform. The rate of chemical weathering of the basement inliers is estimated at 0.04 mm/yr, which is comparable with the present-day rate of the chemical weathering in the humid tropical climate (Kukal, 1987). Therefore, increase in the ⁸⁷Sr/⁸⁶Sr ratio of seawater at the end of Precambrian can be related not only with the Pan-African orogeny, but also with increase in the delivery of radiogenic Sr from continents owing to the denudation of weathering profiles in ancient shields at the end of Precambrian.

ACKNOWLEDGMENTS

The author is grateful to A. A. Kol'tsov for the analytical determinations and to M. Moczydlowska for samples and analytical data placed at our disposal.

This work was supported by the Russian Foundation for Basic Research, project no. 03-05-64062.

REFERENCES

Aksenov, E.M., Geological Evolution of the East European Craton in the Late Proterozoic, *Doctoral (Geol.–Miner.) Dissertation*, St. Petersburg: Inst. Geol. Geokhim. Dokembr. Ross. Akad. Nauk, 1998.

Afanas'eva, M.S., Burzin, M.B., Mikhailova, M.V., and Kuz'menko, Yu.T., Depositional Environment of Potential Oil Source Rocks, *Geol. Nefti Gaza*, 1995, no. 4, pp. 42–48. Akul'shina, E.P., *Glinistoe veshchestvo i osadochnyi rudogenez* (Clayey Substance and Sedimentary Ore Genesis), Novosibirsk: Nauka, 1985.

Alvarenga, C.J.S., Santos, R.V., and Dantas, E.L., C–O–Sr Isotopic Stratigraphy of Cap Carbonates Overlying Marinoan-Age Glacial Diamectites in the Paraguay Belt, Brazil, *Precambrian Res.*, 2004, vol. 130, pp. 1–21.

Bekker, Yu.R., Karta dokembriiskikh formatsii Russkoi platformy i ee skladchatogo obramleniya. Masshtab 1:2500000. Ob"yasnitel'naya zapiska (Map of Precambrian Rock Associations of the Russian Platform and Its Folded Framing. Scale 1:2500000. Explanatory Note), Leningrad: Vses. Geol. Inst., 1983. Bekker, Yu.R., *Molassy dokembriya* (Precambrian Molasses), Leningrad: Nedra, 1988.

Brasier, M.D., Nutrient-Enriched Waters and the Early Skeletal Fossil Record, *J. Geol. Soc. London*, 1992a, vol. 149, pp. 621–629.

Brasier, M.D., Paleoceanography and Changes in the Biological Cycling of Phosphorus across the Precambrian–Cambrian Boundary, in *Origin and Early Evolution of the Metazoa*, New York: Plenum, 1992b, pp. 483–523.

Brasier, M. and Lindsay, J., Did Supercontinental Amalgamation Trigger the "Cambrian Explosion," in *The Ecology of the Cambrian Radiation*, New York: Columbia Univ. Press, 2001, pp. 69–89.

Chaudhuri, S. and Clauer, N., Fluctuations of Isotopic Composition in Seawater during the Phanerozoic Eon, *Chem. Geol.*, 1986, vol. 59, pp. 293–304.

Compston, W., Sambridge, M.S., Reinfrank, R., et al., Numerical Ages of Volcanic Rocks and the Earliest Faunal Zone within the Late Precambrian of East Poland, *J. Geol. Soc. London*, 1995, vol. 152, pp. 599–611.

Cook, P.J. and Shergold, J.H., Phosphorus, Phosphorites and Skeletal Evolution at the Precambrian-Cambrian Boundary, *Nature*, 1984, vol. 308, pp. 231–236.

Cox, R. and Lowe, D.R., A Conceptual Review of Regional-Scale Controls on the Composition of Clastic Sediment and the Co-Evolution of Continental Blocks and Their Sedimentary Cover, J. Sediment. Res., 1995, vol. A65, pp. 1–12.

Dehairs, F., Chesselet, R., and Jedwab, J., Discrete Suspended Particles of Barite and the Barium Cycle in the Open Ocean, *Earth Planet. Sci. Lett.*, 1980, vol. 49, pp. 528–530.

Derry, L.A., Brasier, M.D., Corfield, R.M., and Rozanov, A.Yu., Sr and C Isotopes in Lower Cambrian Carbonates from the Siberian Craton: A Paleoenvironmental Record during the "Cambrian Explosion", *Earth Planet. Sci. Lett.*, 1994, vol. 128, pp. 671–681.

Duddy, I.R., Redistribution and Fractionation of Rare-Earth Elements in a Weathering Profile, *Chem. Geol.*, 1980, vol. 30, pp. 363–381.

Felitsyn, S.B., Vendian Volcanism, Weathering, and Phosphorus Cycle Variation in the East European Platform, *Litol. Polezn. Iskop.*, 2004, vol. 39, no. 4, pp. 375–386 [*Lithol. Miner. Resour.* (Engl. Transl.), 2004, vol. 39, no. 4, pp. 322–333].

Felitsyn, S.B. and Pshenichnova, T.G., Gold Content and Thermal History of Kerogen and Organic Megafossils in Upper Vendian Sequences of the Russian Platform, *Dokl. Akad. Nauk*, 1992, vol. 325, no. 2, pp. 374–377.

Felitsyn, S.B. and Sochava, A.V., Eu/Eu* in Upper Vendian Mudstones of the East European Platform, *Dokl. Akad. Nauk*, 1996, vol. 351, no. 4, pp. 521–524 [*Dokl. Earth Sci.* (Engl. Transl.), 1996, vol. 351A, no. 9, pp. 1381–1384].

Felitsyn, S.B., Vidal, G., and Moczydlowska, M., Trace Elements and Sr and C Isotopic Signatures in Late Neoproterozoic and Earliest Cambrian Sedimentary Organic Matter from Siliciclastic Successions in the East European Platform, *Geol. Mag.*, 1998, vol. 135, pp. 537–551.

Fisher, A. The Two Phanerozoic Supercycles, in *Catastrophes and Earth History*, Princeton: Princeton Univ. Press, 1984. Translated under the title *Katastrofy v istorii Zemli*, Moscow: Mir, 1986, pp. 133–155.

Franke, D., The Southern Border of Baltic—A Review of the Present State of Knowledge, *Precambrian Res.*, 1993, vol. 64, pp. 419–430.

Galimov E.M. The Cause of Calcium Excess and Sodium Deficiency in the Earth's Sedimentary Cover, *Geokhimiya*, 1975, vol. 13, no. 8, pp. 1251–1257.

Gaucher, C., Sedimentology, Palaeontology and the Stratigraphy of the Arroyo del Soldado Group (Vendian to Cambrian, Uruguay), *Beringeria*, 2000, vol. 26, pp. 1–120.

Gaucher, C., Sial, A.N., Blanco, G., and Sprechmann, P., Chemostratigraphy of the Lower Arroyo del Soldado Group (Vendian, Uruguay) and Palaeoclimatic Implications, *Gondwana Res.*, 2004, vol. 7, pp. 715–730.

Gorokhov, I.M., Siedlecka, A., Roberts, D., et al., Rb–Sr Dating of Diagenetic Illite in Neoproterozoic Shales, Varanger Peninsula, Northern Norway, *Geol. Mag.*, 2001, vol. 138, pp. 541–562.

Holland, H.D., *The Chemical Evolution of the Atmosphere* and Oceans, Princeton: Princeton Univ. Press, 1984. Translated under the title *Khimicheskaya evolyutsiya okeanov i* atmosfery, Moscow: Mir, 1989.

Knoll, A. and Vidal, G., Late Proterozoic Vase-Shaped Microfossils from the Visingso Beds, Sweden, *Geol. Foren. Stockholm Forh.*, 1980, vol. 102, pp. 207–211.

Kopeliovich, A.V., *Epigenesis of Ancient Sequences in the Southwestern Russian Platform*, Moscow: Nauka, 1965.

Kronberg, B.I., Fyfe, W.S., Leonardos, O.H., and Santos, A.M., The Chemistry of Some Brasilian Soils: Element Mobility during Intense Weathering, *Chem. Geol.*, 1979, vol. 24, pp. 211–230.

Kukal, Z., *Rychlost geologickych procesu*, Praha: Academia, 1983. Translated under the title *Skorost' geologicheskikh protsessov*, Moscow: Mir, 1987.

Kump, L.R., Alternative Modeling Approaches to the Geochemical Cycles of Carbon, Sulfur, and Strontium Isotopes, *Am. J. Sci.*, 1989, vol. 289, pp. 390–410.

Logan, G.A., Hayes, J.M., Hieshima, G.B., and Summons, R.E., Terminal Proterozoic Reorganization of Biogeochemical Cycles, *Nature*, 1995, vol. 376, pp. 53–56.

Ma, G.G., Zhang, Z.C., Li, H.Q., et al., A Geochronostratigraphical Study of the Sinian System in Yangtze Platform, *Bull. Yichang Inst. Geol. Mineral Resources, Chinese Acad. Geol. Sci.*, 1989, vol. 14, pp. 114–124.

Martin, N.W., Grazhdankin, D.V., and Bowring, S.A., Age of Neoproterozoic Bilaterian Body and Trace Fossils, White Sea, Russia: Implications for Metazoan Evolution, *Science*, 2000, vol. 288, pp. 841–845.

McCann, T., Lower Palaeozoic Evolution of the North East German Basin/Baltica Borderland, *Geol. Mag.*, 1998, vol. 135, pp. 129–143.

McKerrow, W.S., Scotese, C.R., and Brasier, M.D., Early Cambrian Continental Reconstructions, *J. Geol. Soc. London*, 1992, vol. 149, pp. 599–606.

Migdisov, A.A., Balashov, Yu.A., Sharkov, I.V., et al., Distribution of Rare Earth Elements in Major Lithological Types of Rocks in Sedimentary Cover of the Russian Platform, *Geokhimiya*, 1994, vol. 32, no. 6, pp. 789–803.

Morad, S. and Vidal, G., Proterozoic Mn-Oxide Precipitation by Planktonic Plant Protists (Acritarchs), *Geol. Mag.*, 1989, vol. 126, pp. 301–305. Nesbitt, H.W., Markovics, G., and Price, R.C., Chemical Processes Affecting Alkalis and Alkaline Earths during Continental Weathering, *Geochim. Cosmochim. Acta*, 1980, vol. 44, pp. 1659–1666.

Pirrus, E.A., Nodules in the Vendian Complex of the East European Craton, in *Konkretsii dokembriya* (Precambrian Nodules), Leningrad: Nauka, 1989, pp. 79–85.

Ronov, A.B., Osadochnaya obolochka Zemli (kolichestvennye zakonomernosti stroeniya, sostava i evolyutsii) (The Earth's Sedimentary Cover: Quantitative Regularities in Structure, Composition, and Evolution), Moscow: Nauka, 1980.

Ronov, A.B. and Kazakov, G.A., Distribution of Late Proterozoic Sedimentation in the Russian Platform, *Litol. Polezn. Iskop.*, 1983, vol. 18, no. 6, pp. 108–135.

Ronov, A.B. and Migdisov, A.A., Evolution of the Chemical Composition of Rocks in Shields and Sedimentary Cover of the Russian and North American Platforms, *Geokhimiya*, 1970, vol. 8, no. 4, pp. 403–438.

Ronov, A.B., Migdisov, A.A., and Khane, K., Distribution and Composition of Clays in the Sedimentary Cover of the Russian Platform, *Geokhimiya*, 1990, vol. 28, no. 4, pp. 467– 482.

Ryabenko, V.A., *Biostratigrafiya i paleogeograficheskie rekonstruktsii dokembriya Ukrainy* (Biostratigraphy and Paleogeographic Reconstruction of the Precambrian in the Ukraine), Kiev: Naukova Dumka, 1988.

Shnyukov, E.F., *Geologicheskaya istoriya territorii Ukrainy. Dokembrii* (Geological History of the Ukrainian Territory: Precambrian), Kiev: Naukova Dumka, 1993.

Sochava, A.V., *Petrokhimiya verkhnego arkheya i proterozoya zapada Vitimo-Aldanskogo shchita* (Upper Archean and Proterozoic Petrochemistry of the Western Vitim–Aldan Shield), Leningrad: Nauka, 1986.

Sochava, A.V., Quasi-Constant Model of Geochemical Cycle and Biosphere Evolution at the Precambrian–Phanerozoic Boundary, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1992, no. 6, pp. 41–56.

Sochava, A.V., Korenchuk, L.V., Pirrus, E.A., and Felitsyn, S.B., Geochemistry of Upper Vendian Rocks in the Russian Platform, *Litol. Polezn. Iskop.*, 1992, vol. 27, no. 2, pp. 71–89.

Sochava, A.V., Podkovyrov, V.N., and Felitsyn, S.B., Late Precambrian Evolution of Terrigenous Rock Composition, *Stratigr. Geol. Korrelyatsiya*, 1994, vol. 2, no. 2, pp. 3–21.

Sokolov, B.S., *Ocherki stanovleniya venda* (Essays on the Vendian Evolution), Moscow: KMK Scientific Press Ltd, 1997.

Stefansson, A. and Gislason, S.R., Chemical Weathering of Basalts, Southwest Iceland: Effect of Rock Crystallinity and Secondary Minerals on Chemical Fluxes to the Ocean, *Am. J. Sci.*, 2001, vol. 301, pp. 513–556.

Strauss, H., Vidal, G., Moczydlowska, M., and Paczecna, J., Carbon Isotope Geochemistry and Palaeontology of Neoproterozoic to Early Cambrian Siliciclastic Successions in the East European Platform, Poland, *Geol. Mag.*, 1997, vol. 134, pp. 1–16.

Taylor, S.R. and McLennan, S.M., *The Continental Crust: Its Composition and Evolution*, Oxford: Blackwell, 1985.

Torsvik, T.H., Lohmann, K.C., and Sturt, B.A., Vendian Glaciations and Their Relation to the Dispersal of Rodinia: Paleomagnetic Constraints, *Geology*, 1995, vol. 24, pp. 727–730.

Velikanov, V.N., Vendian Phosphorite Nodules of the Ukraine: Implications for Stratigraphic Correlation and Paleotectonic Reconstruction, in *Konkretsii i konkretsionnyi analiz dokembriya* (Precambrian Nodules and Nodule Analysis), Leningrad: Inst. Geol. Geokhim. Dokembr. Akad Nauk SSSR, 1986, pp. 18–20.

Vidal, G. and Moczydlowska, M., The Neoproterozoic of Baltica—Stratigraphy, Paleobiology and General Geological Evolution, *Precambrian Res.*, 1995, vol. 73, pp. 197–216.

Voitkevich, G.V., Kokin, A.V., Miroshnikov, A.E., and Prokhorov, V.G., *Spravochnik po geokhimii* (Handbook of Geochemistry), Moscow: Nedra, 1990.

Yang, J.D., Sun, W.G., Wang, Z.G., et al., Variations in Sr and C Isotopes and Ce Anomalies in Successions from China: Evidence for the Oxygenation of Neoproterozoic Seawater, *Precambrian Res.*, 1999, vol. 93, pp. 215–233.