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Vendian Volcanism, Weathering, and Phosphorus Cycle Variation in the East European Platform

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Abstract—Two geochemical types of volcanic ash are recognized in the Redkino Horizon of the East European Platform based on the systematics of trace elements. The first type developed in the northeastern area of the platform is characterized by Ni/Cr and Ce/Yb ratios typical of the silicic tephra of recent volcanic eruptions in the Kuril–Kamchatka and Aleutian island-arc systems. The respective ratios in ash of the second type are typical of volcanics from the lower Vendian Berestovets Formation. Depletion of the upper Vendian pelites of the East European Platform in Ca, Sr and P (relative to the PAAS) indicates the continental chemical weathering of provenance.

INTRODUCTION

Volcanic ashes are ubiquitous in terrigenous rocks of the upper Vendian Redkino Group of the Moscow Syneclise and the Lvov–Kishinev, Mezen, Upper Kama, and Shkapovo–Shikhany basins (Aksenov, 1998). The volume of pyroclastic material delivered to the sedimentary basin of the East European Platform in the late Vendian attains n 10^4 km^3 (Felitsyn and Sochava, 1996). The U–Pb zircon age of volcanic ash from the upper Vendian Vaizitsa Beds of the Ust-Pinega Formation in the Mezen Basin (Zimnii Coast of the White Sea) is estimated as 553.3 ± 0.3 Ma (Martin *et al.*, 2000). Aksenov and Volkova (1969) discovered that tephra-bearing members are abundant in the upper Vendian Redkino Group and the elemental composition of the Redkino volcanic ash became a subject of detailed studies (Borchwardt and Felitsyn, 1992; Felitsyn and Sochava, 1996; Felitsyn and Kir'yanov, 2002; and others).

At present, the andesite–dacite–rhyolite volcanism at the convergent continental margins is regarded as the major source of tephra delivered to the sedimentary basins (Sharpton and Ward, 1990). Attempts to correlate late Vendian tephra units of the Podolian reference district with the subduction-related explosive volcanism in the southwestern East European Platform meet certain difficulties. Since 615 Ma ago, the Baltica, Laurentia, and Amazonia plates began to pull apart. The consequently rifting produced the embryonal Japetus and Tornquist oceans 565–550 Ma ago (Bingen *et al.*, 1998; Poprawa *et al.*, 1999). In terms of the mineral composition and major oxide chemistry, upper Vendian terrigenous rocks at the western margin of Baltica (in the present-day coordinates) are similar to those from the modern continental rifts dominated by intraplatform sources of clastic materials (Sochava *et al.*, 1992; McCann, 1998). Therefore, the supply of pyroclastic material into the epiplatformal basins from an island-arc system located at the western margin of the East European Platform in the late Vendian seems unrealistic.

At the same time, the lower Vendian of the Belarus Anteclise (Rataichitsa Formation), Volhynian Basin (Berestovets Formation), and Lyublin slope of eastern Poland (Slawatycze Formation) is composed of flood basalts that occupy an area of more than 200000 km^2. The volume of the retained volcanic pile is as much as n 10^4 km^3 (Makhnach and Veretennikov, 1970; Volovnik, 1990). The lava flows largely consist of normative olivine–hypersthene and highly alkaline quartz tholeiites and alkali basalts (Juskowiakowa, 1971). Andesite-dacite and rhyolite lavas with explosion coefficient equal to 85% are subordinate (Volovnik, 1990). The U–Pb zircon age of the trachyandesitic ash of the lower Vendian Slawatycze Formation on the Lyublin slope is estimated as 551 ± 4 Ma (Compston *et al.*, 1995). Relationships between the volcanic ash of the Redkino Group and flood basalts of the Volhynian Group were not considered, because the existing correlation schemes (Velikanov, 1985; Sokolov, 1997) suggest that tephra units of the Yaryshev Formation in the Podolian reference section are separated from the much older Berestovets volcanics by the Mogilev Formation.

This work presents the systematics of some chemical elements in the Vendian volcanics and fine-grained terrigenous rocks of the East European Platform is discussed in order to define the geochemical signature of volcanic ashes from the Redkino Horizon and the enclosing fine-grained terrigenous rocks.

MATERIALS AND METHODS

This work is based on results of the study of volcanic ash and fine-grained terrigenous rocks from the Redkino Group in various localities of the East Euro-

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pean Platform. The principles of sampling, lithological and petrographic descriptions of the samples, and contents of the major and trace elements (Co, Zr, Hf, Y, Th, Rb, and REE) are given in (Borchwardt and Felitsyn, 1992; Sochava *et al.*, 1992; Felitsyn and Sochava, 1996). For comparison, we also investigated the systematics of trace elements in erosion products of the lower Vendian volcanics represented by flood basalts of the Berestovets Formation and volcanomictic sandstones of the Grushka Formation in the Lvov–Kishinev Basin (Kopeliovich, 1965; Sochava *et al.*, 1992). The results obtained were compared with the composition of tephra from Quaternary–Recent eruptions in the Kuril–Kamchatka and Aleutian island arcs and with Neoproterozoic (Sinian) volcanic ash from the Liantnuo Formation (Sinian section) along banks of the Yangtze River in the Yichang area (Hubei Province, southern China).

The minor elements were determined with the INAA method at the Institute of Precambrian Geology and Geochronology and the Department of Nuclear Geophysics (Geological Faculty, St. Petersburg State University). The weighed samples (12–55 mg) were placed into quartz ampules[DR1] and irradiated by a epithermal neutron flux for 48 h with a flux density of 5×10^{13} neutron cm^2 sec^{-1} in research channels of a VVR-M reactor at the St. Petersburg Institute of Nuclear Physics, Russian Academy of Sciences, Gatchina. Standard samples BCR-1, AGV-1, SG-1, SGD-1, and RZS-3 were also simultaneously irradiated. Measurements were carried out with Ge(Li) and Ge detectors in 7 and 30 days after activation. The average relative uncertainty of determinations was <4% for Co, Sc, La, and Th; <7% for Cr and Yb; and <15% for Ni.

Major elements were determined in sedimentary rocks by chemical analysis in the laboratory of the Experimental-Methodical Expedition, Sevzapgeologiya Industrial-Geological Association, St. Petersburg. Phosphorus was determined in the same laboratory with the colorimetric method. The average relative uncertainty was <10% at the P_2O_5 content of 0.01–0.1 wt % and <7% at higher contents (0.1–1.0 wt %). The PRECSED database compiled at the Institute of Precambrian Geology and Geochronology under the supervision of A.V. Sochava was also used.The Sr content was determined by the energy-dispersive XRF spectrometry (K_α, 14.16 keV) at the Experimental-Methodical Expedition, St. Petersburg. The characteristic radiation was excited with a ^{109}Cd (22.1 keV) radionuclide source and recorded with a semiconductor Si(Li) detector. The average relative uncertainty within the concentration range of 50–499 ppm did not exceed 7% (3σ).

TRACE ELEMENT SYSTEMATICS IN VENDIAN VOLCANICS

Based on INAA data, we selected a group of elements characterized by concentration variation in upper Vendian ashes of different localities in the East European Platform. The volcanic ash from the Bronnitsa Beds of the Yaryshev Formation in the Lvov–Kishinev Basin contains much less Cr (6.9 ± 2.4 ppm) relative to the tephra from the southeastern Belomorian region (31.5 ± 17.6 ppm) ($x \pm 1\sigma$). The average Ni content in volcanic ashes from the southwestern and northeastern parts of the platform is virtually the same (~15 ppm). Therefore, the Ni/Cr ratio in ashes varies from 2.2 ± 0.84 in the Bronnitsa ash (Podolian section) to 0.52 ± 0.16 in ashes from the Lyamitsa, Verkhov, and Vaizitsa beds that correspond to volcanosedimentary units I, II, and III, respectively, in the Belomorian section (Aksenov and Volkova, 1969). The lowest Ni and Cr contents were detected in the ash interlayers (1–2 mm) from the lower part of the Ust-Pinega Formation in Borehole Krasavino-2 (unit I, after Aksenov and Volkova, 1969). The Ni/Cr ratio in this ash is 2.0–3.5 (Table 1).

The Ni/Cr ratio correlates with the REE fractionation rate. The chondrite-normalized Ce/Yb_{CN} ratio decreases from 8.4 ± 0.75 in the Bronnitsa ash of Podolia (the CN value is 0.957 ppm for Ce and 0.248 ppm for Yb, after Evensen *et al.*, 1978) to 3.3 ± 0.77 in the volcanic ash from the Ust-Pinega Formation of the Belomorian section. The REE distribution in the Upper Vendian ash of the East European Platform is presented in (Borchwardt and Felitsyn, 1992).

Two fields of data points are rather definitely recognized in the Ni/Cr–Ce/Yb_{CN} plot. The volcanic ash from the Ust-Pinega Formation of the Belomorian section falls into the field of andesitic–rhyolitic tephra related to Quaternary–Recent eruptions of volcanoes in the Kuril–Kamchatka and Aleutian island-arc systems. Tephra of the latter region are marked by strong variations of Ni (from 1 to 21 ppm) and Cr (from 2 to 66 ppm), Ni/Cr = 0.41, and Ce/Yb_{CN} = 3.4. These values fit the respective ratios for volcanics of modern island arcs (Taylor and McLennan, 1985). The compositions of volcanic ash from the lower Sinian Liantnuo Formation (southern China) fall into the same field (Fig. 1).

Data points of the upper Vendian volcanic ash of the Bronnitsa Beds from Podolia with high Ce/Yb_{CN} values and Ni/Cr > 1.0 are localized in the Ni/Cr–Ce/Yb_{CN} plot together with the vent-facies basalts of the Berestovets Formation (Ovadno–Ratno volcanic field), the volcanomictic sandstone of the lower Vendian Grushka Formation, and the volcanic ash of unit I of the Ust-Pinega Formation (Borehole Krasavino-2).

The distribution of trace elements in the Vendian volcanics of the East European Platform testifies to the presence of two geochemical types of volcanic ash. The first type characterized by high $(Ce/Yb)_{CN}$ and Ni/Cr ratios includes the Bronnitsa ash in the Podolian section and unit I in the northern area of the Moscow Syneclise), suggesting their analogy with basalts of the Berestovets Formation and volcanomictic sandstones of the lower Vendian Grushka Formation. The second type

Table 1. Ni and Cr contents and chondrite-normalized Ce/Yb ratio in Late Precambrian volcanics of the East European Platform and tephra of the recent island-arc volcanoes

Sample no.	Depth, m	Ni, ppm	Cr, ppm	Ce/Yb_{CN}	Ni/Cr
Basalt from the Berestovets Formation (Volhynian Group, Ovadno–Ratno field), BoreholeRatno-1, Volhynia District, Ukraine					
BORP-1	541	42	31	8.0	1.4
BORP-2	530	34	25	6.7	1.4
Sandstone from the Grushka Formation (Volhynian Group, Lvov–Kishinev Basin), Borehole 3628, Denisovka Village, Khmelnitska District, Ukraine					
701-22	415	50	31	6.1	1.7
701-25	399	76	40	6.0	1.9
Volcanic ash of the Bronnitsa Beds, Yaryshev Formation (Valdai Group, Lvov–Kishinev Basin), Borehole 3643, Chukheli Village, Khmelnitska District, Ukraine					
700-76	384	57	56	7.8	1.0
Borehole 60, Rybnitsa, Moldova					
735-67	561	11	9	9.6	1.2
735-66	563	23	8	7.8	2.8
735-63	569	11	9	9.6	1.2
735-60	573	13	7	8.0	1.9
735-58	576	12	4	8.8	3.0
Outcrop near the Borshchev Yar Village, Vinnitsa District, Ukraine					
710-17A	–	10	3	7.8	3.4
710-17B	–	18	8	7.8	2.3
Volcanic ash from unit I, Ust-Pinega Formation, Borehole Krasavino-2, northeastern Moscow Syneclise, 15 km north of Velikii Ustyug					
939-56A	2237	7	2	7.1	3.5
939-56B	2237.2	8	4	6.7	2.0
Volcanic ash from the Lyamitsa (unit I), Verkhov (unit II), and Vaizitsa (unit III) beds, Ust-Pinega Formation, Borehole Tuchkino-1, Mezen Basin, Onega Peninsula					
1000-189 (unit III)	645	28	35	3.6	0.80
1000-193 (unit III)	653	20	40	4.4	0.50
1000-194 (unit III)	654	30	80	1.7	0.38
1000-200 (unit II)	693	4	7	3.1	0.57
1000-200a (unit II)	694	8	15	3.6	0.53
1000-201 (unit II)	695	20	30	3.6	0.67
1000-233 (unit I)	908	7	15	3.6	0.47
1000-240 (unit I)	915	9	30	3.1	0.30
Volcanic ash from the Liantnuo Formation, base of the Sinian System near Yichang, Hubei Province, southern China					
KYA-10	–	12	25	5.7	0.50
KYA-5	–	6	10	2.7	0.60
KYA-9	–	5	12	4.1	0.42
KYA-7	–	9	40	3.4	0.21
KYA-8	–	2	15	2.9	0.13
KYA-2	–	4	15	4.4	0.27
Average value of 69 young volcanic ash samples (andesite, dacite, and rhyolite) from the Kuril–Kamchatka and Aleutian island-arc systems					
		6.7 ± 3.8	17.8 ± 8.4	3.4 ± 0.97	0.41 ± 0.20

includes volcanic ashes of the Lyamitsa, Verkhov, and Vaizitsa beds of the upper Vendian Ust-Pinega Formation in the southeastern Belomorian region. These ashes are identical in Ni/Cr and $(Ce/Yb)_{CN}$ ratios to the lower Sinian Liantnuo Formation (southern China) and the andesitic–rhyolitic tephra in the present-day island arcs of the Kamchatka type. Ash units of the Liantnuo Formation (South China Platform) are definitely related to the Banxi and Zhebao island-arc complexes (Yang *et al.,* 1999).

Beginning from a distance of 75–100 km from the eruption center, the volcanic glass prevails in silicic tephra as a result of eolian differentiation (Kir'yanov, 1983; Felitsyn and Kir'yanov, 1987). Therefore, the Ni/Cr and $(Ce/Yb)_{CN}$ ratios in the upper Vendian tephra presented in the table characterize the composition of andesitic and dacitic volcanic glasses (Borchwardt and Felitsyn, 1992; Felitsyn and Kir'yanov, 2002). The vitroclastic nature of ashes from the Bronnitsa Beds of the Podolian section was revealed by petrographic examination (Kopeliovich, 1965). The dispersed occurrence mode of major and rare elements (REE, Ni, Cr, and others) in ash particles of the distal tephra (Felitsyn *et al.*, 1990) is responsible for the lack of $(Ce/Yb)_{CN}$ and Ni/Cr variability during the eolian differentiation of tephra.

The ash particles, less than 50 μm in size, make up more than 60% of the bulk ash related to the Plinian-type explosions (Brazier *et al.*, 1983), suggesting an intense halmyrolysis of the volcanic ash and modification of its primary composition during the deposition in marine basins. Nevertheless, the relative Cr-depletion of the Vendian volcanics in the Podolian section cannot be accounted for the migration of Cr during the settling of ash particles in water, because the Cr concentration in the water-soluble fraction of ash material is not higher relative to the solid phase (Menyailov *et al.*, 1980). Moreover, solubility of the most abundant Cr^{3+} and Cr^{6+} compounds is minimal within a wide pH range (Bartlett and Kimble, 1976). The Ni/Cr ratio of the Bronnitsa volcanic ash does not depend on the analyzed material type (core or natural outcrop). Therefore, supergene processes probably played a negligible role in the distribution of Ni and Cr and their ratios in the studied volcanic rocks. According to the literature sources, the Ni and Cr contents in lower Vendian basalts from the Brest Basin are 54 and 50 ppm, respectively. The average Ni and Cr contents in the andesitic–dacitic tuffs are 16 and 7 ppm (Makhnach and Veretennikov, 1970); i.e., Ni/Cr > 1.0.

The absence of REE fractionation during diagenesis and alteration in the supergene zone is supported by numerous field observations (Fleet, 1984; Taylor and McLennan, 1985).

Thus, high values of the Ni/Cr and $(Ce/Yb)_{CN}$ ratios in various volcanic rocks from the flood basalt association of the Volhynia–Podolia region should be regarded as a primary geochemical signature of the early Vendian magmatism in the southwestern East European Platform.

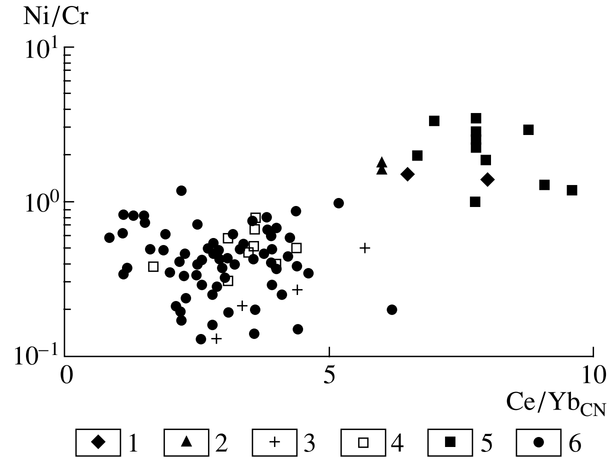

Fig. 1. Compositions of various volcanic rocks plotted on the Ni/Cr *vs.* $(Ce/Yb)_{CN}$ diagram. (1) Basalt from the lower Vendian Berestovets Formation; (2) volcanomictic sandstone from the lower Vendian Grushka Formation; (3) volcanic ash from the Liantnuo Formation (base of the Sinian System); (4) volcanic ash from the upper Vendian Lyamitsa, Verkhov, and Vaizitsa beds of the Ust-Pinega Formation in the southeastern Belomorian region (units I, II, and III); (5) volcanic ash from the Bronnitsa Beds (upper Vendian Yaryshev Formation, Podolia) and unit I of the Ust-Pinega Formation (Borehole Krasavino-2); (6) andesitic–rhyolitic tephra of recent eruptions in the Aleutian arc (Spurr, Ridout, Augustine, Katmai (Novarupta), Pavlof, and Fisher) and the Kuril–Kamchatka arc (Bezymyanny, Shiveluch, Opala, Khangar, Ebeko, Ksudach, Karymskii, Avacha, Alaid, and Gorelyi) (Felitsyn *et al.*, 1990; Melekestsev *et al.*, 1991; Kir'yanov and Felitsyn, 2000; and this work).

VENDIAN MAGMATISM AND COMPOSITION OF VOLCANIC ASHES IN THE EAST EUROPEAN PLATFORM

Volcanic ashes of the Ust-Pinega Formation (Belomorian section) are related to the Neoproterozoic volcanism in the Timan–Pechora Basin. This is suggested by variations in the spatial distribution of ash units and their mineral and elemental compositions (Aksenov, 1967; Aksenov and Volkova, 1969). The gabbro–monzonite and gabbro–syenite–granite complexes in the Kanin Peninsula and northern Timan areas have an age of 535–600 Ma (Kostyukhin and Stepanenko, 1987). They mark the paleosubduction zone at the boundary between the Izhma–Pechora and the Denisovka–Khoreiver megablocks (Belyakova and Stepanenko, 1991; Kostyuchenko, 1994). Explosive volcanism related to the island-arc system at the northeastern margin of the East European Platform delivered ashes with the typical island-arc $(Ce/Yb)_{CN}$ and Ni/Cr values to sedimentary basins in the northern Moscow Syneclise area, including the southeastern Belomorian region. As can be seen from Fig. 1, data points of volcanic ash from the Belomorian section are completely overlapped by the tephra field of the present-day volcanic eruptions in the Aleutian and Kuril–Kamchatka arcs.

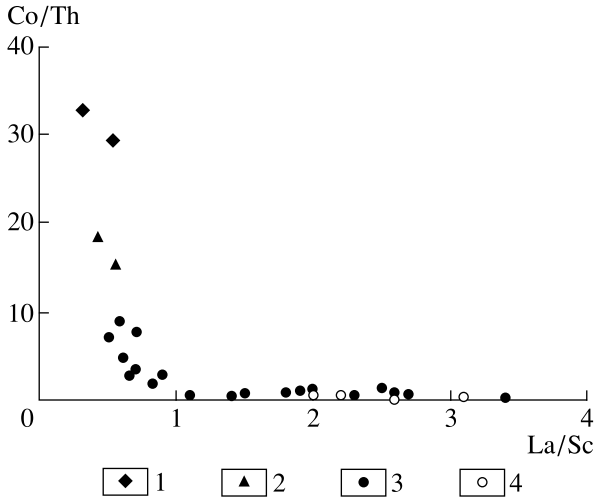

Fig. 2. Positions of Vendian volcanic and sedimentary rocks from the East European Platform plotted on the Co/Th *vs.* La/Sc diagram. (1) Basalt from the lower Vendian Berestovets Formation; (2) volcanomictic sandstone from the lower Vendian Grushka Formation; (3) fine-grained terrigenous rocks from the upper Vendian Yaryshev and Nagoryany formations in the Podolian reference region; (4) fine-grained terrigenous rocks from the basal portion of the upper Vendian Gdov Formation (Borehole Kostovo-13, 50 km northeast of St. Petersburg, depth 450–454 m) and the Pletenevka Formation (Borehole Gavrilov Yam-2, 50 km south of Yaroslavl, depth 2580–2588 m).

Ash unit I from the lower part of the Ust-Pinega Formation (northeastern East European Platform) shows a notable compositional variation. The volcanic ash of the Lyamitsa Beds has typical island-arc values of the $(Ce/Yb)_{CN}$ and Ni/Cr ratios, whereas the respective values in the volcanic ash from Borehole Krasavino-2 located 600 km southeast of the White Sea are typical of the Vendian volcanics in the southwestern East European Platform (Table 1).

Volcanic ash from the lower part of the Ust-Pinega Formation in Borehole Krasavino-2 (samples 939-56A and 939-56B) makes up white smectite interlayers (1–2 mm). Aksenov and Volkova (1969) investigated thickness variation of ash interlayers in the Ust-Pinega sections of the Moscow Syneclise and suggested that the ash was supplied from the southwestern part of the platform during the formation of unit I in the northern and northeastern areas of the East European Platform.

Study of modern ash falls demonstrates that volcanic ash beds, a few millimeters thick, can extend over thousands of kilometers from the eruption center even in the case of a small volume of explosion products. The ash fall area of the Hekla Volcano eruption in Iceland (March 29, 1947) was 280000 km^2 (volume of andesitic tephra was 0.21 km^3). An air-fall ash bed, 2–3 mm thick and completely consisting of volcanic glass, extended over 3800 km from Hekla along the ash cloud trajectory in southern Finland (Thorarinsson, 1954). Thus, an active explosive volcanic center could exist in the southwestern framing of the East European Platform located ~2000 km away from the Mezen Basin, during the deposition of Ust-Pinega ash beds (1–5 mm) in the northern and northeastern areas of the platform. This assumption does not contradict data on the recent ash falls. It is quite probable that dozens of ash interbeds in unit I pelites of the northern Moscow Syneclise can contain the ash material from two sources (the volcanic province in the southwestern East European Platform and the island-arc volcanism zone in the Timan–Pechora region).

The comprehensive study of the flood basalt association in the Lvov–Kishinev and Brest basins (Makhnach and Veretennikov, 1970; Volovnik, 1990; Korenchuk, 1993) resulted in the discovery of numerous central-type volcanic edifices in the Ovadno–Ratno, Ratno–Khoteshov, Rovno, and Gorokhov zones. Although the spatial distribution of younger rocks of the Redkino Group in the Dniester Pericraton inherits the Volhynian structural pattern (Velikanov, 1985), there are no reasons to believe that the volcanic activity related to basaltic eruptions in the southwestern East European Platform terminated at the onset of the Redkino time. The occurrence of tephra material in the middle section of the Kalyus Beds (Nagoryany Formation), i.e., in the lower part of the Kotlin Horizon according to the modern stratigraphic schemes (Aseeva, 1993; Sokolov, 1997) was deduced from the mineralogical (Kopeliovich, 1965) and geochemical data (Felitsyn and Sochava, 1996).

The eruption centers could be situated within continental areas unaffected by the Redkino transgression. They are composed of flood basalts at margins of the late Vendian Volhynian–Podolian sedimentary basin (e.g., northeast of the Rovno–Kobrin line). The northward migration of volcanic centers during the early Vendian (Zinovenko, 1976; Garetskii and Zinovenko, 1994) assumes the existence of active volcanoes north of the Lvov–Kishinev Basin near the Mazur Ridge and Podlyassy–Brest Basin.

The Co/Th–La/Sc diagram (Fig. 2) shows compositions of fine-grained terrigenous rocks of the Yaryshev and Nagoryany formations in the Podolian reference sections of the southwestern East Russian Platform. The hyperbolic arrangement of data points is consistent with a model of the simple two-component mixing. According to this model, basalts of the Berestovets Formation (Co/Th ≈ 35; La/Sc ≈ 0.30) and crystalline basement rocks of the East European Platform (Co/Th ≈ 0.45; La/Sc 3.4) are end members of upper Vendian mudstones from Podolia. The Upper Vendian fine-grained terrigenous sequence, which includes lower parts of the Gdov Formation (northwestern Moscow Syneclise) or the Pletenevka Formation (central Moscow Syneclise), is characterized by Co/Th = 0.45–0.71 and La/Sc = 2.0–3.1. Intraplatform sources of clastic materials dominated during the deposition of the upper Vendian basal section in the above territories (Sochava *et al.*, 1992). Therefore, the Co/Th (up to 9.0) and La/Sc (up to 0.6) values in the fine-grained terrigenous rocks show that the basic volcanics occurred in the provenance during the deposition of mudstones of the upper part of the Redkino and the lower part of the Kotlin horizons. McLennan and Taylor (1984) demonstrated that the Co/Th and La/Sc ratios can be applied to verify the two-component model of mixing during the deposition of fine-grained terrigenous sediments even for high-grade metamorphic complexes.

It is reasonable to suggest that volcanic ashes with elevated Ni/Cr and Ce/Yb ratios in the southwestern East European Platform are genetically related to flood basalts having the same geochemical signature. This suggestion does not contradict the elemental composition of Vendian volcanics described in the present communication, the distribution of volcanic ashes in the Redkino section, and the lithofacies reconstructions of sedimentation in the early and late Vendian of the Podolian reference district.

Basalts with high Ce/Yb values are typical of the flood basalt provinces (Lightfoot *et al.*, 1990). Such basalts form as a result of the partial melting of mantle peridotite in the garnet stability region (Wooden *et al.*, 1993) and the consequent high Ce/Yb values in the magma. Magmatic evolution of continental olivine tholeiites and picrites, which are regarded as parental magmas for flood basalt complexes, is characterized by fractionation within the transitional magma chambers. According to the experimental data, the olivine tholeiite magma is subjected to fractionation at 12–20 kbar (depth 35–70 km) under conditions of a restricted crystallization of olivine as a result of drastically expanded pyroxene crystallization field (Wyllie, 1979). Consequently, the derivative melts are enriched in Ni and depleted in Cr, because the olivine–melt partition coefficient (K_P) for Ni is much higher than the pyroxene–melt partition coefficient. The opposite trend is typical of Cr (Rollinson, 1993). It is evident that a deeper (70–100 km) fractionation of the picritic magma also may yield the basaltic magma with high Ce/Yb and Ni/Cr ratios.

Our recent data show that the ε_{Nd} (550 Ma) value is +4.8 ($^{147}Sm/^{144}Nd$ = 0.12144; $^{143}Nd/^{144}Nd_{meas}$ = 0.512614 ± 9; Sm = 8.4 ppm; Nd = 41.7 ppm) for the lower Vendian basalt from the Brest Basin (Borehole Kobrin, depth 231 m) and +3.5 ($^{147}Sm/^{144}Nd$ = 0.12557; $^{143}Nd/^{144}Nd_{meas}$ = 0.512559 ± 14; Sm = 10.2 ppm; Nd = 49.3 ppm) for basalts from the Ovadno–Ratno volcanic field (Borehole Ratno, depth 541 m). These $\varepsilon_{Nd}[t]$ values are rather typical of flood basalt provinces, indicating an insignificant depletion of the mantle source and a virtual lack of crustal contamination in transitional magma chambers.

The subsequent fractionation and ultimate formation of andesitic and dacitic melts are largely controlled by pyroxene and amphibole. Taking into consideration the partition coefficient of the melts and mineral phases (Rollinson, 1993), such fractionation results in the increase of Ce/Yb and Ni/Cr ratios in the final differentiates. Inheritance of geochemical signature of parental magma by acid melts has been reliably established by the study of elemental compositions of alkaline volcanics of the Kuril–Kamchatka arc (Popolitov and Volynets, 1981).

EVIDENCE FOR THE CHEMICAL WEATHERING OF ROCKS IN THE VENDIAN SECTION OF THE EAST EUROPEAN PLATFORM

Upper Vendian fine-grained terrigenous rocks of the East European Platform are characterized by extremely low Ca and CO_2 contents (Ronov *et al.*, 1990; Sochava *et al.*, 1992). The nature of this geochemical anomaly of Vendian rocks remains ambiguous. Weathered rocks of the eastern Ukrainian Shield served as a source of clastic material for the phosphorite-bearing Nagoryany Formation of Podolia. The weathering proceeded under tropical humid conditions at $T \sim 25°C$ and pH ~5.5 (Korenchuk, 1993). The kaolinite content in mudstones from the Kalyus Beds (Nagoryany Formation) is as much as 20 wt % even in the <0.6 μm fraction (Mel'nikov *et al.*, 1990), indicating the intense chemical weathering in a warm and humid environment, peneplanation of land, and slow sedimentation. The *in situ* kaolinite weathering crust and its erosion products have been found in the upper part of the Mezen Formation (the southeastern Belomorian region) and the Nepeitsino Formation (the central Moscow Syneclise) (Borchwardt and Felitsyn, 1992), i.e., at stratigraphic levels with upper Vendian phosphorite-bearing units (Felitsyn, 2002b). The distribution of indices characterizing the pelitic material maturity [(Na/(Na + K), Ti/Al, and Mg/Al] through the section has shown that clayey materials from the upper part of the Redkino and the lower part of the Kotlin horizons reached the highest maturity. The Baltic and Ukrainian shields, as well as Voronezh and Volga–Kama massifs, were the sources of clastic material (Sochava *et al.*, 1992; Aksenov, 1998).

Data on Ca, Sr, and P distribution in the upper Vendian–Lower Cambrian stratigraphic subdivisions of the East European Platform completely corroborate the intense chemical weathering of the provenance since the Nagoryany time. Fine-grained sediments of the upper part of the Redkino Horizon and the overlying Kotlin Horizon are extremely depleted in Ca, Sr, and P (Table 2) against the background of their low concentrations in the Vendian mudstones relative to the PAAS and East European Platform (RPSC) shale samples.

The calculated CO_2 amount needed to transform rocks from the Ukrainian and Baltic cratons into phosphorite-bearing shales of the Nagoryany Formation and their stratigraphic analogs in other areas of the platform is 2.0–2.5 mmol/g (Felitsyn, 2002b). This value substantially exceeds the CO_2 amount consumed for the formation of Neoproterozoic and Phanerozoic mud-

Table 2. Ca, Sr, and P contents in upper Vendian–Lower Cambrian mudstones of the East European Platform and the composite shale samples

Element	Redkino Horizon	Phosphorite-bearing level at the roof of the Redkino Horizon and base of the Kotlin Horizon	Kotlin Horizon	Lower Cambrian Lontova Horizon	PAAS (Taylor and McLennan, 1985)	RPSC (Migdisov *et al.*, 1994)
Ca, wt %	0.46 (525)	0.26 (28)	0.26 (539)	0.33 (156)	0.94	4.4
Sr, ppm	128 (439)	70 (88)	79 (514)	93 (132)	200	–
P, ppm	410 (591)	230 (156)	280 (761)	330 (185)	700	490

Note: Numerals in parentheses are numbers of determinations.

stones (1.6 and 1.3 mmol/g, respectively) in the East European Platform (Holland, 1984). The Ca and Sr mobility in the course of continental weathering is maximal in comparison with other alkali earth elements. The depletion of residual products in these elements is controlled by the breakdown of plagioclase and K-feldspar even at the early stage of weathering (Nesbitt *et al.*, 1980). Thus, depletion of the Kotlin mudstones in alkali earth elements relative to the PAAS carbonate-free shale (by two to three times) and the RPSC shale (by 10 to 15 times) is most likely caused by an intense chemical weathering. The depletion in phosphorus also indicates chemical weathering in the acid environment. Phosphorus is contained in sedimentary and igneous rocks mainly as minerals of the apatite group. Their stability under weathering is controlled by the pH value of meteoric water, quantity of sediments, and temperature (McKelvey, 1973). Hydroxylapatite is unstable at pH < 4.0. The solubility of calcium phosphates is one to two orders of magnitude higher at pH = 5.0–6.0 than that at pH = 7.0–8.0 (Brown, 1973). The influence of arid or humid weathering character on phosphorus mobility during the weathering of basic volcanic rocks has been discussed in (Felitsyn, 2002a). Similar patterns of the Ca and P distribution in pelitic rocks of the East European Platform in the Riphean–Cambrian shales and minimal concentrations of these elements in the Vendian section (Ronov *et al.*, 1990; Felitsyn, 2002b) confirm the significant role of calcium phosphate as a source of Ca and P in terrigenous rocks.

It is not easy to extrapolate data on the modern chemical weathering to acid leaching in the Precambrian, because products of the higher plant breakdown are the main sources of organic acids at the present time. The absence of such plants in provenances defined many specific features of sedimentation in the pre-Devonian time (Sochava *et al.*, 1994). Nonetheless, the presence of pre-Devonian kaolinite zones clearly demonstrates that the acid leaching predated the diversification of land vegetation.

The existence of interrelation of ash layers with flood basalts at the southwestern margin of the East European Platform (in the present-day coordinates) suggests the supply of a considerable amount of volcanic acid-forming substances into the provenance up to the terminal Nagoryany time. Second in importance to CO_2 is sulfur dioxide of the dry volcanic gas. The amount of SO_2 released during volcanic eruptions is estimated as ~15×10^{12} g/yr (Lambert *et al.*, 1988). The quantity of sulfur dioxide emitted by some individual eruptions can exceed its supply from all of the rest volcanoes of the Earth over a year. During the Pinatubo Volcano eruption in 1991, the SO_2 emission amounted to 17×10^{12} g (Keppler, 1999). In the process of the Great Tolbachik fissure eruption in 1975, the acid-forming substance emission reached ~1×10^{12} g over 2.5 months The pH value of atmospheric water was 2.0–4.1 near cones of the northern vent and 3.1 near the southern vent (Menyailov *et al.*, 1980). Calculations of acidity of atmospheric water during the anthropogenic SO_2 emission have shown that the pH value of atmospheric water at a distance of 600 km from the source amounts to 3.8 if the SO_2 concentration above the source area is equal to 50 μg/m^3 (quite realistic figure for a region with active volcanism) and the transportation velocity is equal to 20 km/h. The main contribution to acidification of sediments is made by the sulfuric acid (Izrael *et al.*, 1989). It is quite evident that the atmospheric water with such pH values can leach alkali earth elements and phosphorus in the process of plagioclase and apatite decomposition.

The sulfur dioxide in atmosphere is oxidized to H_2SO_4 with a lifetime of ~50 h under the modern temperate climatic conditions. The latter is mainly neutralized by the biochemical ammonia (Izrael *et al.*, 1989). Since vascular plants—the main source of the present-day organic matter and its degradation products in the continental soil layer (Kodina and Galimov, 1984)—were absent in the Vendian, volcanic acids probably existed over a prolonged time in the Vendian atmosphere. Hence, the impact of volcanic acids on the geochemistry of the pre-Devonian continental weathering could be more efficient in comparison with the later time when organic matter biodegradation became the source of neutralizing agents.

THE EAST EUROPEAN PLATFORM AS A SOURCE OF SOLUBLE PHOSPHORUS COMPOUNDS IN THE LATE VENDIAN BASINS

The volume of upper Vendian terrigenous rocks in the East European Platform is ~1 mln km^3 (Ronov *et al.*, 1990; Aksenov, 1998) with an average P content of 300 ppm (Felitsyn, 2002b and this work). The phosphorus deficit in the upper Vendian sedimentary cover relative to the PAAS samples is (5.0–10.5) $\times 10^{17}$ g. This value exceeds the identified phosphorus reserve (~4.0 $\times 10^{15}$ g) in the Vendian–Cambrian pellet phosphorites (Yanshin and Zharkov, 1986). Since the upper Vendian shales of the East European Platform bear indications of the acid leaching, the contribution of the soluble phosphorus compounds to the bulk phosphorus flow from the East European Platform was presumably increased in the 7- to 10-Ma- long late Vendian time. The concentration of orthophosphates in the present-day rivers in various climatic belts ranges from 9 to 12 μg/l and the maximal rate of soluble phosphate runoff in rivers of the humid tropical belt is as much as 10^4 g km^{-2} yr^{-1}. This estimate is 1.0–1.5 orders of magnitude higher than the phosphorus runoff with subarctic rivers (Meybeck, 1982).

The confinement of phosphorus deposition epochs to intense chemical weathering periods was known long ago (Zanin, 1984; Kholodov and Paul, 1993; and others). These authors suggested that processes of phosphate formation and weathering were geologically contemporaneous because of a short residence time of phosphorus in the modern oceans (~10^4 yr, according to Ruttenberg, 1993)). Fölmi (1995) established that the rate of phosphorus burial together with biogenic and terrigenous sediments (including deep-water sediments) increased during the warming and intense continental weathering over the last 160 Ma. Our results show that the phosphorus cycle was also governed by continental weathering in the late Precambrian.

The contribution of external sources of clastic material to the upper Vendian sedimentary cover of the East European Platform was appreciable since the late Redkino time and during the major part of the Kotlin time (Sochava *et al.*, 1992). Therefore, the weathered material could be supplied into the sedimentary basins from both the platform basement inliers and the folded framework (Bekker, 1988). Epiplatformal basins of the East European Platform in the Kotlin time were much more freshened. This is indicated by lithological and mineralogical indicators in sediments of the Podolian reference district (Aseeva, 1993), as well as the central (Afanas'eva *et al.*, 1995) and northwestern (Pirrus, 1989) parts of the Moscow Syneclise. The precipitation of phosphates and carbonates in such basins is unlikely. Therefore, elements mobilized by weathering as soluble compounds should be supplied into the marine basins that surrounded the Baltica Plate.

According to the paleontological (Gubanov, 2002) and isotopic-geochemical data (Felitsyn and Gubanov, 2002), marine basins dividing the Rodinia fragments in the late Precambrian and Early Cambrian were probably narrow straits rather than vast oceanic water areas. Increase in the phosphorus flow as a result of the chemical weathering in the East European Platform in the late Vendian should substantially affect the hydrochemistry of these basins and increase the bioproductivity of littoral zones and phosphorus deposition. Variations of the phosphorus cycle near the Precambrian–Cambrian boundary were supposed in (Braiser, 1992). Such variations was traditionally attributed to the oceanic phosphorus reservoir—water mixing in the stratified ocean (Cook and Shergold, 1984), dynamic upwelling (Baturin, 1999), and so on. The phosphorus depletion of the Vendian sedimentary cover of the East European Platform suggests that the continental chemical weathering could be responsible for changes in the late Precambrian phosphorus cycle and the Vendian Baltica continent could serve as an important source of phosphorus for the late Precambrian basins.

CONCLUSIONS

The relationship of explosive volcanism, which supplied a considerable amount of pyroclastic material into the upper Vendian sedimentary basins in the East European Platform, with trap volcanism in the southwestern area of the platform (in the present-day coordinates) explains the occurrence of volcanic ash in the Podolian reference district. This conclusion is consistent with the late Precambrian regional geodynamics. The Ni/Cr and $(Ce/Yb)_{CN}$ ratios in the bulk of tephra in three volcanosedimentary units of the Ust-Pinega Formation in the northeastern area of the platform are similar to the respective values in silicic tephra from active island arcs of the Kamchatka type. This volcanic ash is most likely related to the latest Precambrian subduction at the northeastern margin of the East European Platform. The role of trap volcanism as a source of pyroclastics was apparently crucial. The ash with geochemical signature typical of the Berestovets basalts occurs in upper Vendian sections in the northeastern part of the platform (in the present-day coordinates).

Active volcanic zones simultaneously existed in the southwestern and northeastern areas (in the present-day coordinates) until the early Kotlin time. Therefore, the drastic depletion of the fine-grained terrigenous rocks in Ca, Sr, and P, which are most mobile under acid leaching conditions, is caused by the impact of volcanic acid-forming substances.

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