Continental Weathering in the Early Precambrian: Specific Features of Mineral Transformations and Composition of Supergene Solutions

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Abstract—The paper presents a detailed description of the geological structure, mineralogy, and chemical composition of the Archean weathering profile of granitoids in the Baltic Shield. Based on model calculations, the primary composition of granites in the substrate and weathering profile, as well as elemental composition of solutions draining the supergene profile, are determined. Model calculations for the Proterozoic weathering profile of analogous granitoids testify to the similarity of supergene alterations in the Early Precambrian. Mineral transformations during the weathering of granitoids are mainly expressed in the formation of minerals of new micas of the illite group against the background of large-scale decomposition of plagioclase. The composition of solutions in the hypergenesis zone of Precambrian weathering profiles sharply differs from the modern composition by lower contents of Ca^{2+} and K^+ and the higher content of Fe^{2+}. This is only possible under reducing conditions at high acidity of the diagenetic environment (pH < 6.5). The results obtained are essential for understanding the nature of unique Precambrian rocks (sedimentary iron ore rocks). The subordinate amount of carbonate sequences in Precambrian sedimentary sequences can be related to the specific composition of continental runoff primarily governed low-Ca supergene solutions.

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INTRODUCTION

Information pertaining to early geological history of the Earth is characterized by fragmentary nature because of the scarcity of ancient geological relicts and their significant structural–metamorphic transformations. It is rather difficult to interpret formation conditions of Early Precambrian sequences, because modern geodynamic reconstructions of ancient formations are commonly based on the comparative-actualistic analysis of the chemical composition of volcanic rocks without the consideration of specific features of exogenous processes.

Weathering profiles serve as the most reliable criterion of continental setting of lithogenesis in the Precambrian and other stages of the Earth's geological evolution. Precambrian weathering profiles played an essential role in the formation of the Earth's sedimentary cover. They were initial products of the exogenous differentiation of the primary mantle material and suppliers of highly mature terrigenous substance into sedimentary basins. Thus, the weathering profiles are sources of unique information concerning the composition and evolutionary changes in lithosphere, atmosphere, and hydrosphere.

At present, researchers have collected and analyzed a great body of data related to Early Precambrian weathering profiles that are weakly or intensely trans-formed by subsequent metamorphic processes. Despite the principle similarity of Precambrian and Phanerozoic weathering profiles owing to the similarity of major factors of weathering, they are characterized by several essential discrepancies. For example, based on the behavior of alkali and alkali earth elements, weathering profiles were divided into the pre-Mesozoic and younger groups (Mats and Popov, 1975). The young rocks are characterized by the loss of both Na_2O and K_2O. In the older rocks, only Na_2O is removed, while K_2O is accumulated. Drastic decrease in the K_2O content in platformal fine-grained terrigenous rocks coincided with the appearance of land plants (Vinogradov and Ronov, 1956; Ronov et al., 1990). Potassium is an essential nutrients, and its content is the plant ash can be as much as 10–15% (Sochava et al., 1994). Vascular plants have a strong influence on weathering, because modern supergene processes are significantly governed by organic acids and CO_2, which is formed during the decomposition of organic matter.

Weathering profiles have been reported from virtually all regions with ancient rock complexes. The Karelian granite–greenstone zone is among such regions characterized by the wide development of weathering profiles at all stratigraphic levels (Negrutsa, 1979; Heiskanen, 1990).

General stratigraphic scale			Age of boundaries, Ma	Region al scale (suprahorizons)	weathering profile
Proterozoic PR	Lower Proterozoic (Karelian) K	Upper Karelian K$_2$		Ludicovian	
			2100	Jatulian	Pre-Jatulian, Settlement of Girvas, Lake Okunevskoe, Lake Ahvenlampi (Table 1, nos. 2, 5, 7)
		Lower Karelian K$_1$	2300	Sariolian	Pre-Sariolian, Lake Vatulma, Lake Kosoe (Table 1, nos. 3, 4)
			2400	Sumian	Pre-Sumian, Kumsa structure (Table 1, no. 6)
			2500		
Archean AR	Upper Archean (Lopian) L	Upper Lopian L$_3$		Gimolian	Archean, Lake Voron'e (Table 1, no. 1)
		Middle Lopian L$_2$	2800		

Fig. 1. Position of weathered rock units of Karelia in the general stratigraphic scale of Lower Precambrian.

In Archean greenstone belts of northern Karelia, volcanic activity produced thick volcanosedimentary sections that are currently preserved in separate greenstone structures (Kostomuksha, Lekhta, Hizovaara, and others). Signs of intense chemical weathering of Archean rocks are observed in the majority of large greenstone structures. Arenites have been reported from the middle section of the Hizovaara structure (Kozhevnikov, 2000). Quartz–muscovite schists at the base of the Kostomuksha structure are considered redeposited rocks of the weathering profile (*Vulkanizm...*, 1981). In the Lekhta structure, supergene profile has been found at the contact of volcanics of the greenstone belt with gneissic granites of the basement (Matrenichev et al., 2005b).

Early Precambrian supracrustal complexes of the Lekhta synclinorium are composed of Late Archean (Lopian) and Paleoproterozoic (Sumian, Sariolian, and Jatulian) suprahorizons (Robonen et al., 1974). The northeastern part of the Lekhta structure (Lake Voron'e–Lake Pebozero) is composed of a virtually continuous stratigraphic succession from the Lopian supracrustal rocks to the Paleoproterozoic Jatulian rocks (Fig. 1). Supergene alterations are very well manifested at different stratigraphic levels of this structure (Negrutsa, 1979).

The majority of weathering profiles of the Lekhta structure demonstrate similar trends of chemical alterations (Table 1). The variation pattern of element concentrations in weathering profiles testifies to the similar geochemical specifics of their formation. When passing from initial rocks (hereafter, substrate) to weathered varieties, all profiles are enriched in Al_2O_3 and K_2O.

The accumulation of K_2O at the section top in the course of weathering is typical of rocks formed after both the granitic substrate and (or) basic volcanics, irrespective of the age of stratigraphic level and its paleoclimatic setting (Alfimova and Matrenichev, 2004). The concept of incomplete preservation of weathering profile due to the redeposition of the upper kaolinite zone is probably ill-founded, because similar degree of the erosion of different-age weathering profiles can hardly be explained from this point of view.

The aim of the present paper is to compare mineral and chemical transformations in the course of weathering of granitoids in the Archean and Early Proterozoic based on the study of rocks in the Lekhta structure (northern Karelia).

MATERIALS AND RESULTS

Weathering Profile at the Base of the Okhta Sequence (Upper Lopian)

Porphyric plagiogranites serve as the basement for Archean supracrustal rocks on the northern part of the Lekhta structure. On the northern shore of Lake Voron'e at the source of the Nizhnyaya Okhta River (Fig. 2), one can see direct contact between volcanics of the Okhta sequence (Matrenichev et al., 2005a) and plagiogranites via the weathering profile of granites (Table 1, no. 1; Fig. 1) (Matrenichev et al., 2005b).

The plagiogranites are medium-grained leucocratic homogeneous rocks with schistosity emphasized by biotite. They contain sporadic xenoliths of fine-grained biotite schists 5–25 cm in size. The presence of relicts of initial magmatic structures testifies to the primary

Table 1. Variation of chemical composition of rocks during the formation of Early Precambrian weathering profiles of Karelia

No.	Location, age, and source	Substrate	$K(SiO_2)$	$K(Al_2O_3)$	$K(CaO)$	$K(Na_2O)$	$K(K_2O)$
1	Lake Voron'e, base of the Okhta sequence, pre-upper Lopian	granite	−0.37	11.19	−63.51	−75.68	132.84
2	Lake Okunevskoe, lower Jatulian (Negrutsa, 1979)	granite	−8.97	57.31	−79.84	−97.92	341.72
3	Lake Vatulma, pre-Sariolian (Negrutsa, 1979)	quartz porphyry	−1.54	21.15	−76.36	−49.18	30.83
4	Lake Kosoe, pre-Sariolian (Negrutsa, 1979)	quartz porphyry	−23.20	23.26	1008.70	−87.88	28.91
5	Settlement of Girvas, pre-Jatulian (*Putevoditel'* ..., 1998)	basaltic andesite	−5.90	53.74	−92.12	−96.31	616.00
6	Kumsa structure, pre-Sumian (Korosov, 1991)	granite	−8.85	37.19	100.00	−75.00	45.83
7	Lake Ahfenlambi, central Karelia, pre-Jatulian (Heiskanen, 1990)	granite	−14.19	20.64	−18.33	−94.55	98.97

Note: Variation of chemical composition is shown as coefficient K(el), % = [(Kel. wp − Kel. sub)/Kel. sub] × 100, where Kel. wp is the element concentration in weathering profile and Kel. sub is the element concentration in initial unaltered rock (substrate).

hypabyssal nature of bedding of these rocks. Their microscopic study reveals relicts of relatively large (4–6 mm) porphyric phenocrysts of plagioclase corresponding to oligoclase no. 20–25 with an immature zonality, while the groundmass contains numerous small (0.5–1 mm) and intensely zonal crystals of plagioclase (oligoclase no. 15–20). The groundmass structure in relicts of the initial plagioclase-dominated rock have hypidiomorphic texture. In some places, large porphyric crystals of zonal plagioclase contain poikilitic inclusions of the fine-grained euhedral microcline. Metamorphic alterations are expressed in the formation of a fine-grained granoblastic quartz–feldspar aggre-

gate associated with biotite (<10%). Signs of replacement by microcline or other chemical alterations of rocks are absent (Table 2).

Gneissic granites and tuffs of komatiitic basalts of the Kivirista Formation are separated by a metamorphosed weathering profile of granites. At present, the weathering profile represents a muscovite schist interlayer with the muscovite content considerably increasing toward the contact with amphibolites (up to 50 vol %). The thickness of muscovite-rich schists, which appreciably differ from the gneissic granites, varies from 1.5 to 2.5 m along the strike. The contact is gradual with plagiogranites and sharp with amphibolites (without
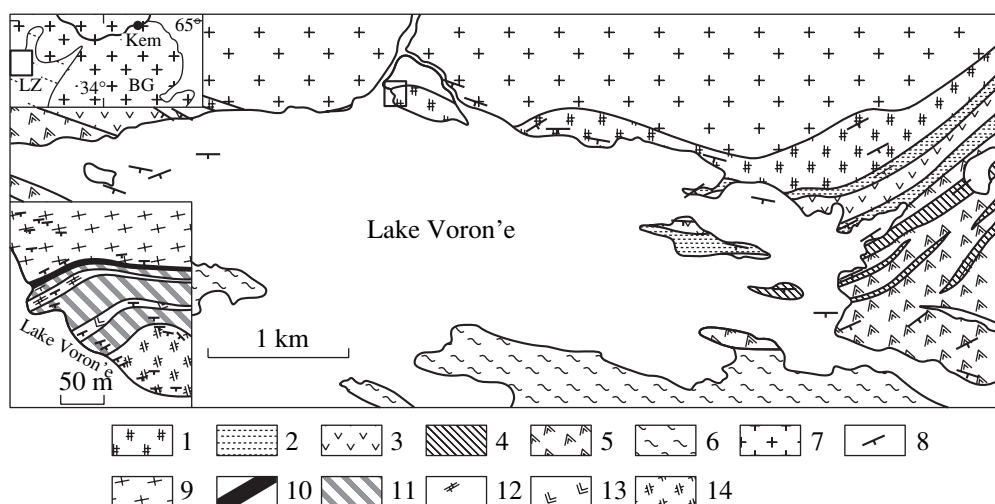

Fig. 2. Schematic geological structure of the northeastern flank of the Lekhta synclinorium zone. (1–8) Okhta Group: (1) Okhta sequence: (1) lavas and tuffs of komatiitic basalts and komatiites, (2) tuffs and tuffites of basalts, (3) lavas of aphyric pillow basalts, (4) lavas and tuffs of plagioporphyritic basaltic andesites, (5) lavas and tuffs of andesites along with tuffs and tuffites of dacites; (6) rocks of the Pebozero Group; (7) granitoids of the Belomorian zone; (8) dip and strike. Inset shows geological scheme of the contact between gneissic granites of the basement and volcanic rocks of the Okhta sequence: (9) gneissic granites, (10) weathering profile formed after gneissic granites, (11) komatiitic basalts, (12) melanocratic komatiitic basalts, (13) plagioporphyritic komatiitic basalts, (14) komatiitic tuffs. (LZ) Lekhta zone, (BG) Belomorian granites.

Table 2. Chemical composition of Archean gneissic granites and their weathering profiles, wt %

Sample	499a	10401c	10401	500b	10401d	10401f	500a	10401e	10401b
No.	1	2	3	4	5	6	7	8	9
SiO_2	70.70	69.69	70.81	71.89	72.53	73.36	71.74	70.41	69.43
TiO_2	0.31	0.25	0.21	0.20	0.20	0.23	0.23	0.25	0.27
Al_2O_3	14.46	15.18	14.17	14.91	14.06	15.12	15.99	17.10	15.06
Fe_2O_3	2.88	2.37	2.20	2.12	2.03	1.94	2.47	2.22	2.90
MnO	0.05	0.05	0.05	0.03	0.04	0.01	0.01	0.03	0.04
MgO	1.22	0.89	0.88	0.60	0.85	0.88	0.91	1.08	1.18
CaO	2.57	2.99	2.88	2.12	2.73	0.60	0.87	0.40	2.45
Na_2O	4.38	4.45	4.58	4.71	4.36	1.72	0.92	0.89	1.47
K_2O	2.09	2.30	1.84	2.17	1.65	3.87	4.68	5.14	4.22
P_2O_5	0.10	0.07	0.06	0.06	0.06	0.08	0.08	0.07	0.07
L.O.I.	0.83	1.30	1.80	0.88	1.10	2.00	1.60	2.20	2.40
Total	99.56	99.54	99.48	99.69	99.61	99.81	99.50	99.79	99.49
Rb	41	55	49	37	44	93	96	95	90
Sr	183	110	115	107	112	63	31	46	77
Y	–	12	17	11	14	14	–	11	12
Zr	100	88	100	90	96	115	71	88	106

Note: Major oxide contents were determined by the RFA method in the Sevmorgeo laboratory. Trace element contents (ppm) were determined by A.A. Kol'tsov at the Institute of Precambrian Geology and Geochronology, St. Petersburg. (1–5) Gneissic granites; (6–9) weathering profile; (–) not detected.

metasomatic alterations of metavolcanics). In general, the weathering profile is characterized by relict lenticular banding manifested in the appearance of plagioclase- or quartz-rich interlayers among the relatively homogeneous quartz–plagioclase matrix. The muscovite content is virtually similar in compositionally different interlayers (Fig. 3). Relicts of the initial rock (substrate) contain intensely zonal plagioclase. The plagioclase grains mainly represent granular fragments of the primary larger crystals. Fragments of large plagioclase crystals with obscure zonality are subordinate. Muscovite is commonly developed as elongate aggregates along schistosity cracks. One can also see episodic relicts of the initial laminated structure with muscovite emphasizing the primary distribution of clay minerals (Fig. 4).

Accessory Minerals in Weathering Profiles

Specific assemblage and ratio of accessory minerals is an essential diagnostic sign of weathering profiles. Zircon is one of the most characteristic relict primary minerals among end products of the weathering profile decomposition (Koryakin, 1975). Owing to stability in the course of physical and chemical weathering, this mineral is retained and gradually accumulated in the newly forming crustal sequence, while large masses of mobile components are removed.

The study of heavy mineral assemblages in artifact panned samples taken in the weathering profile extending from unaltered plagiogranites to the contact with the overlying volcanics revealed that the content of iron hydroxides is 20–25 times higher than that in granitoids. In gneissic granites, iron hydroxides represent secondary minerals (products of the alteration of sulfides). In the weathering profile, iron hydroxides occur as flattened structureless grains and fragments with traces of corrosion and dissolution. In the weathering profile, contents of apatite and zircon are 2–2.5 and 8–10 times higher, respectively, relative to the substrate.

Zircon, the major and constant accessory, can be divided into four morphological types (Fig. 5). The major type is represented by transparent well-faceted pale pink crystals of the hyacinth habitus with the coefficient of elongation ranging from 1 : 2 to 1 : 6. Grains with dissolution signs (grooves and pits) on the faces are sporadic. Zircons from the weathering profile are generally analogous to those in gneissic granites. However, the first variety contains many crystals with dissolution signs, cracks, and haziness (up to the point of opacity). The appearance of traces of corrosion and dissolution in zircons from the weathering profile was reported first in (Chaika et al., 1985). Some zircon crystals from the weathering profile show the typical fine dissemination of newly formed monocrystals on faces and the overgrowth by the newly formed zircon
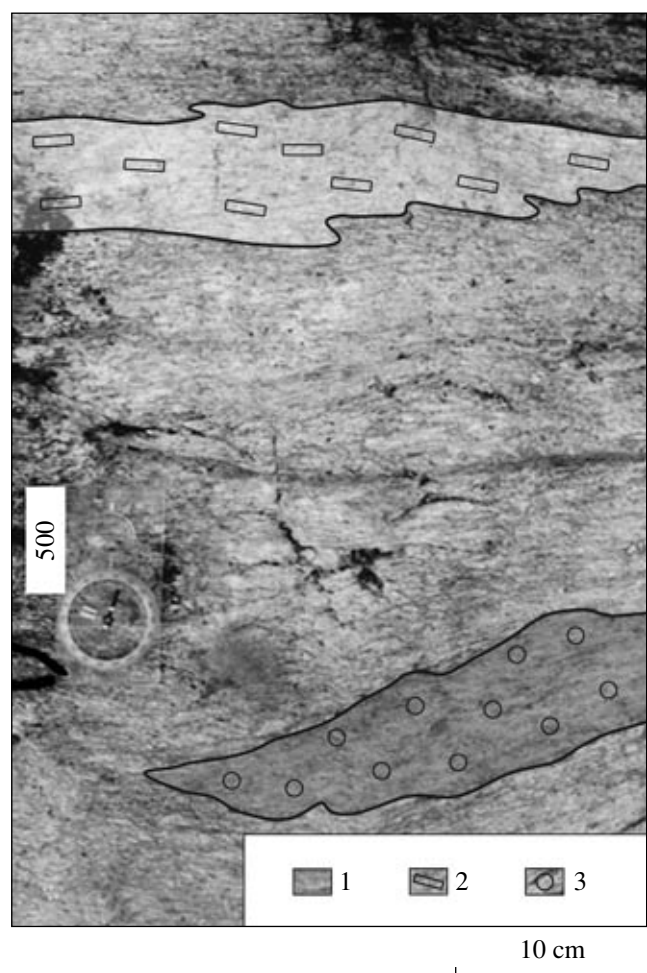
Fig. 3. Relicts of lenticular banding in the weathering profile (drawing based on photograph). (1) Quartz–feldspar matrix; (2) feldspar matrix; (3) quartz matrix.

(Fig. 5). Edges and, particularly, apices of prisms are strongly smoothed. The grain surface is intensely corroded, dull, and, therefore, translucent.

The U–Pb zircon age of gneissic granites is 2795 ± 19 Ma (Matrenichev et al., 2005a). The $t(^{207}Pb/^{206}Pb)$ value estimated for one zircon variety from the weathering profile is similar to the zircon age in the gneissic granites. The coincidence of zircon ages in the gneissic plagiogranite and weathering profile indicates their syncontemporaneous timing. Andesites from the upper portion of the Okhta sequence have an age of 2807 ± 3 Ma (Matrenichev et al., 2005a). Thus, the weathering profile formed in less than 8 Ma.

Chemical Alteration of Plagiogranites during Weathering

Regularities in the compositional variation of plagiogranites in the course of hypergenesis and weathering at the base of the Okhta sequence is typical of Precambrian weathering profiles (Golovenok, 1975). We

analyzed the distribution of major and trace elements across the weathering profile (from the unaltered gneissic granites to products of weathering profile). In terms of the degree of mobility, both major and trace elements can be divided into three groups (Fig. 6); (1) Na_2O, CaO, and Sr are evacuated from supergene rocks; (2) SiO_2, Al_2O_3, TiO_2, FeO, MgO, Y, Nb, and Zr are relatively inert; and (3) K_2O and Rb are accumulated in the weathering profile. The loss of Na_2O, CaO, and Sr suggests that plagioclase was primarily dissolved during the formation of the weathering profile. The gain of K_2O and Rb indicates that these elements entered the newly formed hydromicas and accumulated in the weathering profile. Elements of the second group (Tables 2, 3) behave similarly relative to the most mobile elements (Fig. 6).

It is obvious that the modern composition of minerals and their quantitative ratios in granitoids and weathering products differ from those in the primary rocks, because the substrate was transformed by metamorphism. Therefore, we calculated primary ratios of minerals in plagiogranites and the Archean weathering profile in order to obtain the quantitative estimate of the degree of supergene alterations (Table 3). The calculations were based on minerals from the modern granitoids and metasedimentary rocks (Table 3). Model calculations of the mineral composition of granites were based on quartz, plagioclase, K-feldspar, muscovite, and biotite. Calculations of the mineral composition of the weathering profile were based on quartz, plagioclase, K-feldspar, illite, smectite, and hematite. Although hematite is present in the heavy fraction of gneissic granites, the content of this mineral is insignificant to influence the calculated ratios of the major minerals in the initial gneissic granite. Volumetric ratios of dissolved components of the rock were defined as the compositional discrepancy between the granite and weathering profile (Tables 4, 5). Calculations were based on the model of supergene alterations with the following assumptions: (a) micas (biotite and muscovite), which are decomposed and transformed into illite and smectites, are the least stable mineral phases in the weathering profile; (b) plagioclase is dissolved without the formation of new mineral phases (potassium delivered to the solution participates in the formation of illite). We calculated two versions of compositional transformations of granites in the course of weathering. In the first version, the amount of potassium in the solution is minimal. The whole amount of potassium evacuated from granite minerals (biotite, muscovite, K-feldspar, and plagioclase) is captured by the newly formed hydromicas. This version corresponds to the minimal degree of decomposition of the granitic substrate (65%). The second version assumes the maximal quantity of K-feldspar decomposition in the granite. In this case, potassium needed for the formation of illite and smectites is accumulated in the weathering profile, while the excess K is transferred to the solution and
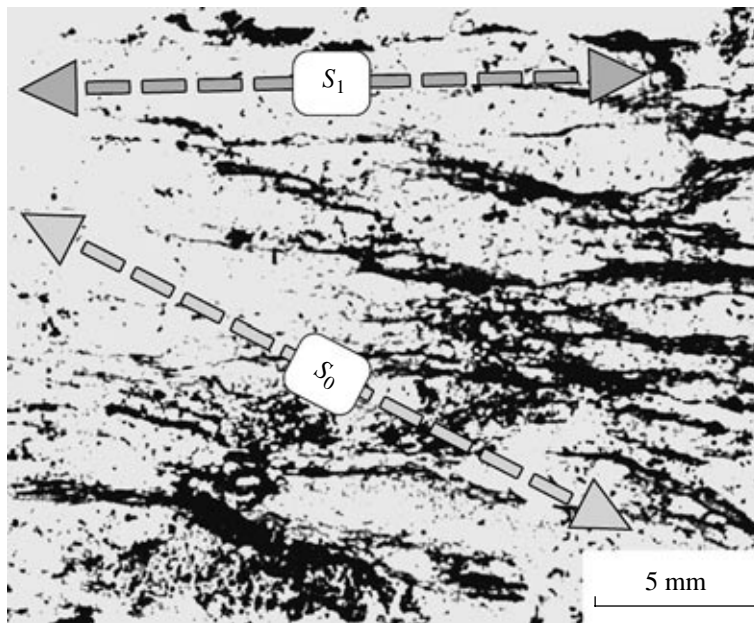
Fig. 4. Relicts of the primary laminated structure in the weathering profile. Photomicrograph of thin section showing muscovite (black) and quartz–feldspar aggregate (white). (S_0) Plane of primary bedding of clay minerals; (S_1) schistosity plane.
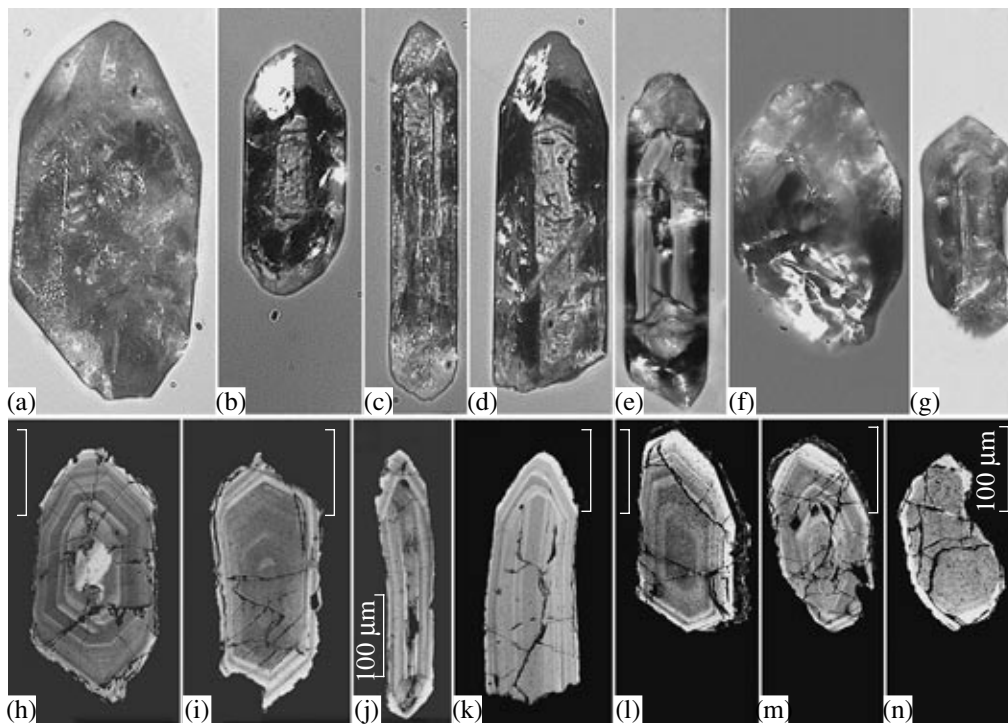

Fig. 5. Microimages of accessory zircon from gneissic granites: (a–g) optical microscope without analyzer; (h–n) reflected electron image. (a–d, h–k) zircon from gneissic granites; (e–g, l–n), zircon from weathering profile at the base of the Okhta sequence.

evaluated from the residual weathering profile. The degree of substrate breakdown in this case is 68% (Table 5). Discrepancies between the two calculated versions are less significant than the assumptions accepted in mineralogical calculations. Therefore, the further calculations were based on average contents of the major and trace elements in the water-free residue of the supergene solution (Table 5).

We calculated the amount of newly formed illite and smectite based on the following assumptions: 1 mole of
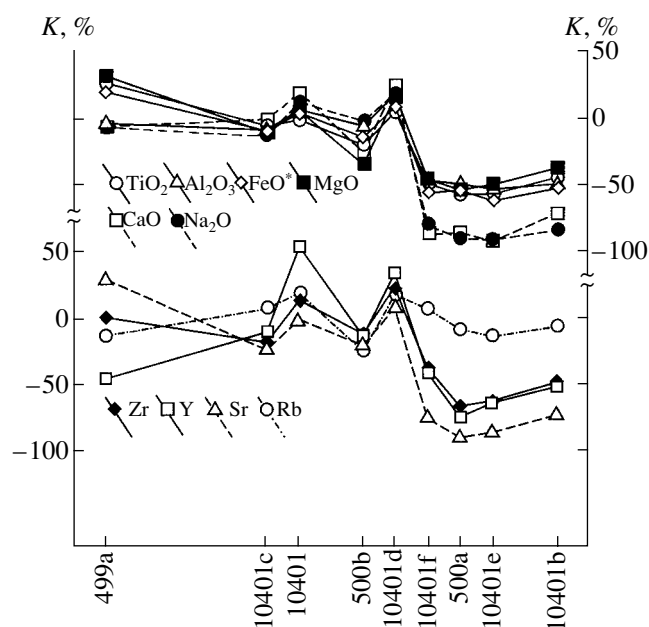
Fig. 6. Major and trace element distribution patterns across the weathering profile extending from unaltered gneissic granites (sample 499a) to the contact with amphibolites of the Okhta sequence. Recalculations are based on (Nesbitt et al., 1980). $K = [(El_s/K_2O_s) - (El_{sub}/K_2O_{sub})]/(El_{sub}/K_2O_{sub}) \times 100$, where El_s and El_{sub} are concentrations of elements in the sample and gneissic granite, respectively; K_2O_s and K_{sub} are concentrations of K_2O in the sample and gneissic granite, respectively. The distance between samples 499a and 10401b is 8 m.

mica (biotite and muscovite) produces 1.32 moles of clay minerals; 1 mole of plagioclase, 0.064 moles of illite and smectite; and 1 mole of K-feldspar, 2.01 moles of clay minerals in the weathering profile.

Coefficients for recalculation were based on the K_2O content in the initial and final mineral phases and the volumetric ratio between unit cells of minerals.

Composition of Solutions

Based on model results of mineral transformations in the hypergenesis zone, we calculated the chemical composition of the anhydrous residue of solution draining the supergene profile (Table 6).

If the chemical composition of dry residue is available, one should estimate the amount of solvent in order to determine the concentration of elements in solution. The amount of solvent can be determined based on the solubility of the least soluble components in the rock.

The modern concept of dissolution of silicates and aluminosilicates in the hypergenesis zone assumes the incongruent style of process (Mason, 1966; Garrels and McKenzie, 1971). Alkali and alkali earth elements located in polyhedra with 8, 10, and 12 apices are the first elements to be evacuated in the course of decomposition. Al and Si are introduced to the solution at the last stage of dissolution. Therefore, solubility of silica and alumina plays an important role in the calculation of the quantity of solvent. In acidic weathering responsible for the transformation of gneissic granites, the solubility of alumina varies in a wide range depending on pH, Eh, and other characteristics of the diagenetic environment (Mason, 1966; Garrels and Mckenzie, 1971; Bushinskii, 1971), while variation of the solubility of silica is insignificant. In solutions equilibrated with illite and montmorillonite, the solubility of silica is 60 mg/l (Garrels and Mckenzie, 1971), which is proba-

Table 3. Chemical composition of the Archean weathering profile, granite, and minerals used in model calculations, wt %

Oxides	Minerals of granite				Newly formed in the WP			Average granite	WP 10401e
	kfs	pl	bt	mu	il	hem	sm		
SiO$_2$	64.20	62.98	35.61	48.50	48.25	0.00	44.39	72.33	70.41
TiO$_2$	0.00	0.00	3.77	1.23	0.22	0.00	0.09	0.24	0.25
Al$_2$O$_3$	19.70	23.06	15.35	35.56	31.47	0.00	5.97	14.80	17.10
FeO	0.10	0.22	22.10	1.98	2.90	100.00	29.79	2.36	2.00
MnO	0.00	0.00	0.36	0.00	0.04	0.00	0.00	0.04	0.03
MgO	0.00	0.04	12.05	1.51	1.68	0.00	1.03	0.90	1.08
CaO	0.31	4.52	1.62	0.00	0.30	0.00	2.74	2.70	0.40
Na$_2$O	2.28	8.78	0.67	1.13	0.68	0.00	0.00	4.57	0.89
K$_2$O	13.41	0.40	8.46	10.08	8.48	0.00	0.00	2.04	5.14
L.O.I.	0.00	0.00	4.88	4.75	5.99	0.00	15.99	1.42	2.70

Note: (kfs) K-feldspar; (pl) plagioclase; (bt) biotite; (mu) muscovite; (il) illite; (hem) hematite; (sm) smectite; (WP) weathering profile. Average granite composition is based on 5 analyses.

bly the most reliable estimate of silica solubility in the weathering zone. If we accept this solubility of silica, the quantity of solvent required for the alteration of 1 kg of substrate is 7.9×10^3 l. The Al_2O_3 concentration calculated for this quantity of solution is equal to 12 mg/l, which fits the middle interval of Al_2O_3 contents in aqueous extracts from soils (1.5–23.0 mg/l) (Bushinskii, 1971). Calculations of concentrations of the major cations in solution were based on the composition of solid residual and the calculated quantity of solvent (Table 7).

Weathering profile at the Base of the Segozero Sequence (Lower Jatulian) In order to define constraints of supergene alterations in the Early Proterozoic, we calculated mineral transformations for the weathering profile at the base of the Segozero sequence (Table 1, no. 2). Choice of this profile for calculations was dictated by the fact that rocks similar to granitoids at the base of the Okhta sequence are subject to supergene alterations in this area (Negrutsa, 1979). The mineral composition of the weathering profile at the base of the Segozero sequence was calculated by a method similar to that used for calculating the composition of the hypergenesis zone at the base of the Okhta sequence. Initial data used for calculations were represented by the chemical compositions of unaltered rock, weathering profile, and minerals from the modern analogues (Table 8). The mineral composition of granite was calculated on the basis of quartz, K-feldspar, plagioclase, apatite, biotite, and muscovite. Quartz, feldspar, hematite, illite, and smectite were used for calculating the composition of weathered horizon (Tables 8, 9). The calculations were based on the following two model concepts:

(i) The K content in the solution is minimal. Illite and smectites are formed during the decomposition of biotite and muscovite. K-feldspar is not dissolved. This version corresponds to 93% destruction of the initial rock.

(ii) Not only micas are decomposed, but also K-feldspar is dissolved. The degree of substrate decomposition is as high as 96% (Table 10). Plagioclase is completely dissolved (this mineral is lacking in the weathering profile). Calcium released in this process is used for the formation of smectite. Quantitative ratios of illite and smectite formed in the weathering profile, on the one hand, and the dissolving minerals of granite, on the other hand, were calculated by the same method used for modeling the composition of solution draining the weathering profile at the base of the Okhta sequence.

Composition of Solutions

The quantity of solvent and concentrations of the major cations were calculated by the method used for calculating the solution composition in the weathering profile at the base of the Okhta sequence. The quantity of solvent needed for the transformation of 1 kg of substrate is equal to 11.7×10^3 l. The concentration of alumina is estimated at 9 mg/l. Concentrations of other elements in the solution (based on the quantity of solvent) and the chemical composition of solid residual are given in Table 7.

Table 4. Calculated mineral composition of granite and the Archean weathering profile, vol %

Minerals	Granite	WP
quartz	32.58	38.75
K-feldspar	6.26	10.60
plagioclase	50.20	4.70
hematite	–	0.31
micas	10.97	45.64
	(biotite 9.28, muscovite 1.69)	(illite 43.36, smectite 2.28)
Total	100	100

Note: (Granite) mineral composition of the substrate; (WP) mineral composition of the weathering profile; (–) absent.

Table 5. Amount of major minerals transferred to solution during the formation of the Archean weathering profile, vol %

Minerals	Solution		
	1	2	3
quartz	15.16	17.69	16.43
K-feldspar	1.49	2.19	1.84
plagioclase	48.09	48.40	48.24
Total	64.74	68.28	66.51

Note: Degree of substrate decomposition: (1) minimal, (2) maximal, (3) average values used for the calculation of the solution composition.

Table 6. Amount of elements removed from rocks during the weathering of 1 kg of granite, g

Component	Weathering profile at the base of the Okhta Group, upper Lopian	Weathering profile at the base of the Segozero Group, lower Jatulian
SiO_2	472.0	702.6
Al_2O_3	93.8	106.1
FeO	15.2	35.9
MnO	0.3	0.50
MgO	9.6	12.3
CaO	24.0	43.4
Na_2O	44.9	28.1
K_2O	1.7	13.00
Total	665.1	947.6

Table 7. Concentrations of major cations in supergene solutions of pre-Kemurian and Phanerozoic weathering profiles, mg/l

Compo-nent	1	2	Average chemical composition of groundwaters in the hypergenesis zone (Shvartsev, 1998)				
			tropical and sub-tropical zones	permafrost zones	temperate climate	highlands	average
Fe^{2+}	1.50	2.21	0.25	0.33	0.69	0.43	0.42
Mn^{2+}	0.03	0.03	0.04	0.01	0.06	0.02	0.03
Mg^{2+}	0.74	0.59	8.07	5.56	16.50	14.50	11.20
Ca^{2+}	2.18	2.66	16.60	16.80	38.30	37.80	27.40
Na^+	4.24	1.78	10.90	6.64	23.80	13.80	13.80
K^+	0.29	0.87	2.25	0.83	2.74	1.55	1.84
Total	8.99	8.15	38.11	30.17	82.09	68.10	54.70

Note: (1) Weathering profile at the base of the Okhta Group (upper Lopian); (2) weathering profile at the base of the Segozero Group (lower Jatulian).

Table 8. Chemical composition of the pre-Jatulian weathering profile, granite, and minerals used in model calculations, wt %

Oxides	Minerals of granite					Newly formed in the WP			Granite (Negrutsa, 1979)	WP (Negrutsa, 1979)
	ap	kfs	pl	bt	mu	il	sm	hem		
SiO_2	0.21	64.20	62.65	35.61	48.50	50.12	40.56	0.00	74.04	64.27
TiO_2	0.00	0.00	0.05	3.77	1.23	0.50	0.00	0.00	0.52	0.36
Al_2O_3	0.19	19.70	23.85	15.35	35.56	25.13	10.17	0.00	11.95	17.93
FeO	0.16	0.10	0.53	22.10	1.98	6.13	8.14	100.00	3.91	3.06
MnO	0.03	0.00	0.01	0.36	0.00	0.03	0.24	0.00	0.12	0.11
MgO	0.04	0.00	0.23	12.05	1.51	3.93	20.76	0.00	1.43	2.78
CaO	54.03	0.31	4.74	1.62	0.00	0.35	1.94	0.00	3.91	0.75
Na_2O	0.06	2.28	7.47	0.67	1.13	0.05	0.25	0.00	2.53	0.05
K_2O	0.06	13.41	0.47	8.46	10.08	6.93	0.32	0.00	1.59	6.69
L.O.I.	45.22	0.00	0.00	4.88	4.53	6.82	17.61	0.00	0.00	3.99

Note: (ap) Apatite. See Table 3 for abbreviations of other minerals.

Table 9. Calculated mineral composition of granite and the pre-Jatulian weathering profile, vol %

Minerals	Granite (Negrutsa, 1979)	WP (Negrutsa, 1979)
Quartz	44.62	22.14
K-Feldspar	2.28	24.28
Plagioclase	35.35	–
Apatite	2.49	–
Hematite	–	0.16
Micas	15.26	53.42
	(biotite 14.65, muscovite 0.61)	(illite 50.38, smectite 3.04)
Total	100.00	100.00

Note: (Granite) mineral composition of the substrate; (WP) mineral composition of the weathering profile; (–) absent.

DISCUSSION

Mineral transformations in the course of weathering of plagiogranites of the Lekhta structure during both Archean and Proterozoic times were mainly characterized by the preferential decomposition of plagioclase and the formation of hydromicas of the illite group with a minor admixture of smectite.

Transformations of the chemical composition of granitoids of the Lekhta structure were marked by the following essential features. Despite discrepancies in the degree of chemical disintegration of rocks in the course of weathering, both the Archean weathering profile and the Proterozoic profile of supergene alterations were characterized by the gain of K and Al, on the one hand, and the simultaneous loss of Na and Ca (Tables 3, 8; Fig. 7). Results of model calculations indicate that Late Archean and Early Proterozoic weathering conditions in the Baltic Shield were similar. However, they

differed from conditions of the formation of Phanerozoic supergene profiles.

Weathering profile at the base of the Okhta sequence formed during the 65–68% decomposition of the granite substrate, which required the consumption of no less than 7.9×10^3 l of solution per 1 kg of initial rock. During the formation of the pre-Segozero weathering profile, 93–96% of substrate was weathered under the chemical impact of 11.7×10^3 l of solution per 1 kg of initial rock. The degree of substrate destruction and the quantity of solution required for the formation of the Proterozoic profile are much higher than those for the Archean profile. This fact suggests that the Proterozoic weathering profile formed over a longer period relative to the Proterozoic profile.

In general, solutions from Archean and Proterozoic hypergenesis zones have similar compositions (Table 7, Fig. 7). The major cations are represented by Na^+ and Fe^{2+} (4.24 and 2.2 mg/l, respectively). The Proterozoic solutions are distinguished by a lower Na content and higher K content.

Comparison of calculated concentrations of alkali and alkali earth elements in solutions in Precambrian weathering profiles with their concentrations in modern solutions of the hypergenesis zone revealed several discrepancies (Table 7, Fig. 8).

The calculated solubility of Al_2O_3 in ancient supergene solutions is close to the values obtained in direct measurements of the content of soluble alumina in aqueous extracts from soils (Bushinskii, 1971). Such values correspond to conditions of low Al_2O_3 solubility (pH = 4–9) rather than the possible maximal ones (Mason, 1966). The Archean and Proterozoic supergene profiles were formed in similar environments. Discrepancies in the solubility of alumina in solutions could be provoked by minor variations in physicochemical constraints of hypergenesis.
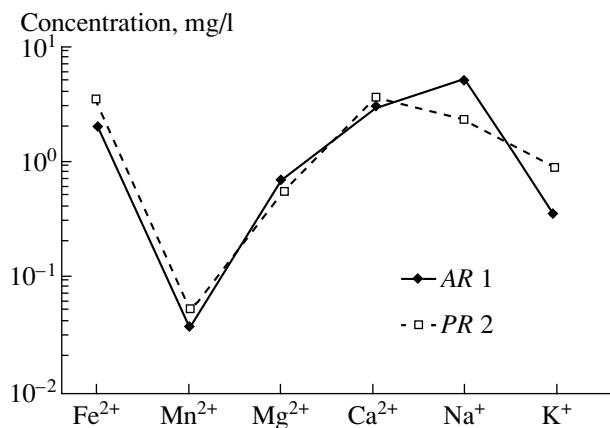
Table 10. Amount of major minerals transferred to solution during the formation of the pre-Jatulian weathering profile, vol %

Minerals	Solution		
	1	2	3
Quartz	42.54	43.00	42.77
K-Feldspar	0.00	0.50	0.25
Plagioclase	35.06	35.12	35.09
Apatite	2.49	2.49	2.49
Biotite	12.84	14.34	13.59
Muscovite	0.54	0.60	0.57
Total	93.47	96.04	94.76

Note: Degree of substrate decomposition: (1) minimal, (2) maximal, (3) average values used for the calculation of the solution composition.

The Ca^{2+} distribution shows an opposite pattern (Fig. 8). The concentration of Ca^{2+} ions in solutions of Early Precambrian leaching zones is much lower than that in any modern solutions, irrespective of climatic zones and geomorphological provinces. The low Ca^{2+} concentration was probably related to the following fact: calculations of the composition of solutions for the Precambrian weathering profiles were based on the assumption that carbonate-bearing sedimentary rocks are absent in the leaching zone. However, the modern solutions of hypergenesis zones drain such rocks as well (Ronov et al., 1990). Thus, calcium was mainly delivered to ancient solutions as a result of the decomposition of plagioclase. In the Early Precambrian, sedi-
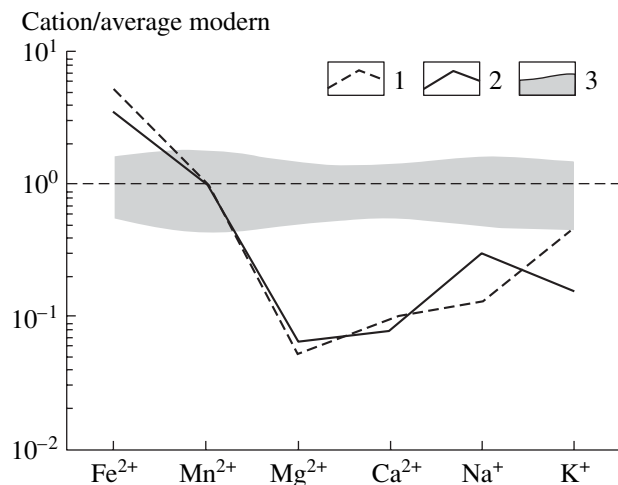
Fig. 7. Concentrations of the major cations in Early Precambrian solutions draining supergene profiles. (1) Solution draining the Archean profile; (2) solution draining the Proterozoic profile.

Fig. 8. Ratios of major cations in solutions of Precambrian and modern weathering horizons. The vertical axis shows concentrations of the major cations in the solution normalized to average values for the modern waters in hypergenesis zone (Shvartsev, 1998). (1) Solution draining the Archean supergene profile; (2) solution draining the Proterozoic weathering profile; (3) groundwaters in modern hypergenesis zones.

mentary rocks were primarily represented by graywackes with a minor content of carbonate sequences, probably, as a result of the lower (relative to the modern value) content of Ca in supergene solutions that govern the share of Ca in the continental runoff.

The lower concentration of Na in solutions from the pre-Segozero weathering profile can be related to the low content of this element in the disintegrated granite (Table 8). In Archean granitoids, the Na content is high as the average Na content in granites (Tables 2, 3).

Concentrations of K in solutions of the Archean and Proterozoic hypergenesis zones could be lower than those in the modern solutions because of the absence of subaerial vegetation and the accumulation of K-bearing clay minerals (illite and smectite) in ancient residual products of weathering zones.

Results of model calculations show that the Fe content in Precambrian solutions is considerably higher than that in the modern ones. Concentrations of Fe in water solutions can be high only under highly acid ($pH < 6.5$) reducing conditions when iron migrates as Fe^{2+} ion (Garrels and McKenzie, 1971). Thus, the high concentration of Fe in ancient solutions indicates a reducing character of atmosphere in the Early Precambrian. Similar conclusions concerning the Early Precambrian atmosphere were presented by Schidlowski (1975), Holland (1984), and other researchers. Solutions draining the hypergenesis zone govern relationships between the major components of continental runoff. Hence, high concentrations of Fe in these solutions testify to the high Fe content in the Early Precambrian seawater. This conclusion is consistent with the following well-known fact: the majority of sedimentary iron ore formations formed at early stages (up to 2 Ga) of the Earth's geological history (Holland, 1984).

Based on the observed thickness of the Archean weathering profile and model calculation data on the degree of substrate decomposition, we estimated the rate of weathering. The weathering profile has an average thickness of 2 m. Given that the calculated degree of substrate disintegration is 65–68%, the above fact testifies to chemical decomposition (without the consideration of products of physical weathering) of a granite bed slightly more than 6 m thick. Taking into consideration measurement errors, discrepancy of isotope ages of gneissic granites of the basement and volcanics of the Okhta sequence suggests that the weathering profile was completed in less than 8 Ma. Thus, basement granitoids of Archean greenstone belts underwent the continental weathering at the minimal rate of 0.8 mm/ka.

Modern estimates of the rate of chemical weathering of granitoids show a wide variation range. The lowest rate ($1 mm/10^5$ yr) is typical of the polar climate (Porter, 1975), while the value for the European temperate zone is as much as 1 m/100 yr (Zuener, 1958). Based on the estimate of the modern rate (5–10 mm/5 ka) of chemical weathering of granites in arid climate

(Kukal, 1983), the weathering profile at the base of the Okhta sequence can be formed in 3–6 Ma.

Thus, the Archean supergene profile could be formed in 3–8 Ma at the weathering rate of 1–2 mm/ka.

CONCLUSIONS

In the Archean and Proterozoic, mineral transformations during the weathering of plagiogranites of the Lekhta structure were primarily expressed in the decomposition of plagioclase and the formation of hydromicas of the illite group with a minor admixture of smectites.

The Lekhta weathering profile formed as a result of the decomposition of the granite substrate (65% in the Archean profile and 95% in the Proterozoic profile) with the consumption of solution equal to 7.9×10^3 and 11.7×10^3 l, respectively, per 1 kg of initial rock. The higher degree of rock transformation in the Proterozoic weathering profile can suggest its formation over a longer period, relative to the Archean profile.

The K content in solutions of Archean and Proterozoic hypergenesis zones are lower than those in solutions draining the modern hypergenesis zone. This feature can be related to the accumulation of K-bearing clay minerals (illite and smectite) in ancient residual products of weathering zones.

The concentration of Ca^{2+} ions in solutions of Early Precambrian leaching zones is considerably lower than that in any modern solutions. Calcium in ancient solutions was primarily derived from the decomposition of plagioclase. Thus, the scarcity of carbonate sequences in sedimentary sections can be related to the specific composition of continental runoff that was mainly governed by the low-Ca supergene solutions.

The Fe content in the calculated Precambrian solutions is significantly higher than that in modern solutions. Concentrations of Fe in water solutions can be high only under highly acid ($pH < 6.5$) reducing conditions. Thus, high concentrations of Fe in ancient solutions, relative to the modern ones, indicate a reducing character of atmosphere in the Early Precambrian.

The Archean supergene profile formed in 3–8 Ma at a rate of 1–2 mm/ka.

Results obtained in our work can play an important role in understanding the compositional evolution of atmosphere and the carbonate sedimentation in the Earth's history. They can also foster the study of mechanisms of the formation of unique sedimentary iron ore formations in the Precambrian.

REFERENCES

Alfimova, N.A. and Matrenichev, V.A., Accumulation of Potassium in the Archean Weathering Crust: Specifics of Continental Weathering at Early Stages of the Earth's Geological History, Abstracts of Papers *Mezhdunarodnaya nauchnaya konferentsiya "Gliny i glinistye mineraly"* (Int. Scientific Conference on Clays and Clay Minerals), Voronezh: Voronezh. Gos. Univ., 2004, pp. 11–13.

Bushinskii, G.I., *Geologiya boksitov* (Geology of Bauxites), Moscow: Nedra, 1971.

Chaika, V.M., Gorshkova, E.B., and Kazak, A.P., Zircon Dating Technique for Precambrian Sedimentary Geology, in *Tsirkon v porodakh dokembriya i fanerozoya* (Zircon in Precambrian and Phanerozoic Rocks), Moscow: Nauka, 1985, pp. 3–14.

Garrels, R. and Mackenzie, F., *Evolution of Sedimentary Rocks,* New York: Norton, 1971. Translated under the title *Evolyutsiya osadochnykh gornykh porod*, Moscow: Mir, 1974.

Golovenok, V.K., Precambrian Weathering Crusts, Their Specific Features, and Lithogeochemical Analysis Techniques, in *Dokembriiskie kory vyvetrivaniya* (Precambrian Weathering Crusts), Moscow: Nauka, 1975, pp. 16–27.

Kheiskanen, K.I., *Paleogeografiya Baltiiskogo shchita v Karel'skoe vremya* (Karelian Paleogeography of the Baltic Shield), Petrozavodsk: Karel. Nauchn. Tsentr Ross. Akad. Nauk, 1990.

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

Korosov, V.I., *Geologiya doyatuliiskogo proterozoya vostochnoi chasti Baltiiskogo shchita (sumii, sariolii)* (Geology of the Pre-Jatulian Proterozoic in the Eastern Baltic Shield: Sumian, Sariolian), Petrozavodsk: Karel. Nauchn. Tsentr Ross. Akad. Nauk, 1991.

Koryakin, A.S., Diagnostic Criteria of the Metamorphosed Weathering Crust), in *Dokembriiskie kory vyvetrivaniya* (Precambrian Weathering Crusts), Moscow: Nauka, 1975, pp. 28–34.

Kozhevnikov, V.N., *Arkheiskie zelenokamennye poyasa karel'skogo kratona, kak akkretsionye orogeny* (Archean Greenstone Belts of the Karelian Craton as Accretionary Orogens), Petrozavodsk: Karel. Nauchn. Tsentr Ross. Akad. Nauk, 2000.

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

Mason, B., *Principles of Geochemistry,* London, 1966 (3rd ed.). Translated under the title *Osnovy geokhimii*, Moscow: Nauka, 1971.

Matrenichev, V.A, Alfimova, N.A., Levchenkov, O.A., et al., Lopian Complex of the Lekhta Structure (Northern Karelia). Isotopic Dating, Stratigraphy, and Interrelations with the Basement, *Materialy soveshchaniya "Geologiya i geodinamika arkheya"* (Proceedings of the Conference on Archean Geology and Geodynamics), St. Petersburg, 2005a, pp. 21–23.

Matrenichev, V.A., Pinkova, L.O., Levchenkov, O.A., et al., The Most Ancient Weathering Crust of Granites on the Baltic Shield, *Dokl. Akad. Nauk*, 2005b, vol. 400, no. 1, pp. 83–87 [*Dokl. Earth Sci.* (Engl. Transl.), vol. 400, no. 1, pp. 62–66].

Mats, V.D. and Popov, Yu.G., Some Features of Evolution of the Chemical Weathering Crust of Granites, in *Dokembriiskie kory vyvetrivaniya* (Precambrian Weathering Crusts), Moscow: Nauka, 1975, pp. 104–116.

Negrutsa, T.F., *Paleogeografiya i litogenez rannego proterozoya oblasti sochleneniya karelid i belomorid* (Early Proterozoic Paleogeography and Lithogenesis of the Karelide–Belomoride Junction Zone), Leningrad: Leningr. Gos. Univ., 1979.

Nesbitt, N.N., Markovics, G., and Price, R.C., Chemical Processes Affecting Alkalies and Alkaline Earths during Continental Weathering, *Geochim. Cosmochim. Acta*, 1980, vol. 44, pp. 1659–1666.

Porter, S.C., Weathering Rinds as a Relative-Age Criterion: Application to Subdivision of Glacial Deposits in the Cascade Range, *Geology*, 1975, vol. 3, pp. 101–103.

Putevoditel' geologicheskikh ekskursii Mezhdunarodnogo simpoziuma "Paleoklimaty i evolyutsiya paleogeograficheskikh obstanovok v geologicheskoi istorii Zemli" (Guidebook for Geological Excursions of the Int. Symposium on Paleoclimates and Evolution of Paleogeographic Environments in the Earth's Geologic History), Petrozavodsk: Karel. Nauchn. Tsentr Ross. Akad. Nauk, 1998.

Robonen, V.I., Korosov, V.I., and Eliseev, M.A., Stratigraphy and Tectonics of Volcanogenic Complexes in the Pebozero Region (Eastern Karelia), in *Problemy geologii nizhnego proterozoya Karelii* (Problems of Lower Proterozoic Geology of Karelia), Petrozavodsk: Karel. Nauchn. Tsentr Akad. Nauk SSSR, 1974.

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

Schidlowski, M., Archean Atmosphere and Evolution of Oxygen Reserves of the Earth, in *The Early History of the Earth,* Windley, B., Ed., London: Wiley, 1975. Translated under the title *Rannyaya istoriya Zemli*, Moscow: Mir, 1980.

Shvartsev, S.L., *Gidrogeokhimiya zony gipergeneza* (Hydrogeochemistry of the Hypergenesis Zone), Moscow: Nedra, 1998.

Sochava, A.V., Podkovyrov, V.N., and Felitsyn, S.B., Late Precambrian Evolution of the Composition of Terrigenous Rocks, *Stratigr. Geol. Korrelyatsiya,* 1994, vol. 2, no. 4, pp. 3–21.

Trendall, A.F. and Blockley, J.G., Precambrian Iron-Formation, in *Developments in Precambrian Geology*, 2004, vol. 12, pp. 403–421.

Vinogradov, A.P. and Ronov, A.B., Composition of Sedimentary Rocks in the Russian Platform and Its Tectonic Evolution, *Geokhimiya*, 1956, no. 6, pp. 3–24.

Vulkanizm arkheiskikh zelenokamennykh poyasov Karelii (Volcanism of Archean Greenstone Belts), Leningrad: Nauka, 1981.

Zuener, E., *Dating the Past. An Introduction to Geochronology*, London: Methuen, 1958.