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GEOCHEMISTRY

The REE Systematics of Upper Archean Sedimentary Assemblages in Central Karelia

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Geochemical composition of sedimentary assemblages is determined by the interaction of specifics of provenances, weathering conditions, mass transfer, sedimentation, metamorphism, and other factors. The role of geodynamic setting of provenances is crucial for the composition of sedimentary (mainly terrigenous) assemblages [1].Therefore, their chemistry is a reliable indicator of the paleogeodynamic setting [2–6].

Lithogeochemical studies of terrigenous associations of young (<2.9 Ga) greenstone structures of western Karelia (Kostomuksha and Hizovaara) [7, 8] provided new information on the evolution of the sedimentation regime and geodynamic setting of these structures. However, no lithogeochemical investigations have been carried out for the older greenstone domains of the Karelian Craton. We present new geochemical data on the REE systematics of sedimentary assemblages distinguished in the stratotype section of the Hautavaara–Koikary test site in the Upper Archean (3.05–2.85 Ga) Vedlozero–Segozero greenstone belt of central Karelia.

The greenstone belt located in the southeastern part of the Fennoscandian Shield extends over ~300 km in the N–S direction at a width of 50–60 km and consists of several local domains (Hautavaara, Koikary, Palaselga, Sovdozero, and others) [9, 10]. Geodynamic reconstructions [11] allowed us to distinguish magmatic systems related to the ancient (3.05–2.95 Ga) island arc [12], back-arc basin (3.05–2.95 Ga), and young (2.90–2.85 Ga) volcanic arc, which are consistent with formation of greenstone belt as convergent protoocean–protocontinent zone between microplates.

Based on lithogeochemical typification, sediments preserved in greenstone sequences, especially in the Hautavaara–Koikary test site, were subdivided into the following groups: volcanogenic group (redeposited tuffs, tuffites, BIF, graywackes, and tuffstones); terrigenous group (conglomerates, graywackes, arenites, arkoses, and siltstones); chemogenic (dolomites and silicites); and mixed group (chemogenic–terrigenous, volcanogenic–terrigenous, and other rocks). According to Pettijohn [1], the studied rocks can be classified as graywackes, arkoses, and, occasionally, lithic wackes (Fig. 1). The sedimentary assemblages are metamorphosed under greenschist to epidote–amphibolite facies. However, their primary structure and texture are retained.

Major and trace elements were analyzed by the XRF method on a Philips PW1480 device in the Analytical Laboratory of Geological Survey of Finland, Espoo. The maximum uncertainty was <6%. The REE concentrations were measured by the INAA method in the Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences, St. Petersburg (uncertainty <5%).

The typical composition of lithotypes is demonstrated in the table. Rock characteristics are listed on the basis of their geodynamic setting.

Intraformational sediments of the old island arc system marked by volcanic BADR series and subvolcanic adakites [12] are represented by a tuff–tuffite association, which experienced gravitational sedimentation and redeposition in the basins of intervolcanic depressions. The attenuation of explosive activity resulted in the alternation of tuffite, tuffstone, and silicite sequences. The upper portions of sections contain graphitic siltstones and silicites. The REE composition and distribution in fine tuffs and tuffites are similar to those in BADR series with insignificant LREE enrichment indicated by $(La/Sm)_n = 5.21 \pm 1.27$, $(Gd/Yb)_n = 1.94 \pm 0.25$, $(Ce/Yb)_n = 6.48 \pm 1.72$ (Fig. 2a).

Sedimentary assemblages restricted to the back-arc basin include komatiitic rocks (tuffs and tuffites), mafic (volcanogenic and volcanomictic) graywackes, silicites, and graphitic siltstones.

Tuffs and tuffites of komatiitic and basaltic compositions comprise beds from a few centimeters to a few meters in thickness. Their major element composition is similar to those of the corresponding lavas [10]: SiO_2 37–50 wt %, MgO 9–23 wt %, low Al_2O_3 content

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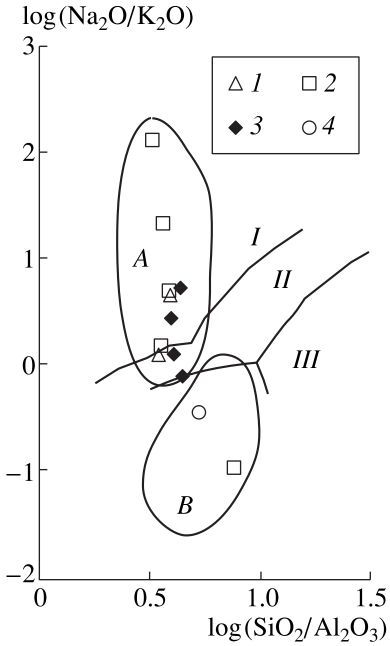

Fig. 1. The log (Na_2O/K_2O)–log(SiO_2/Al_2O_3) classification diagram [1] for volcanosedimentary and sedimentary rocks of the Vedlozero–Segozero greenstone belt. (*I*) Graywackes, (*II*) lithic wackes; (*III*) arkoses. Sedimentary rocks of the Vedlozero–Segozero greenstone belt (Chalka and Koikary structures): (*A*) graywacke assemblages, (*B*) arkoses [9]. (*1–4*) Numbers as in the table.

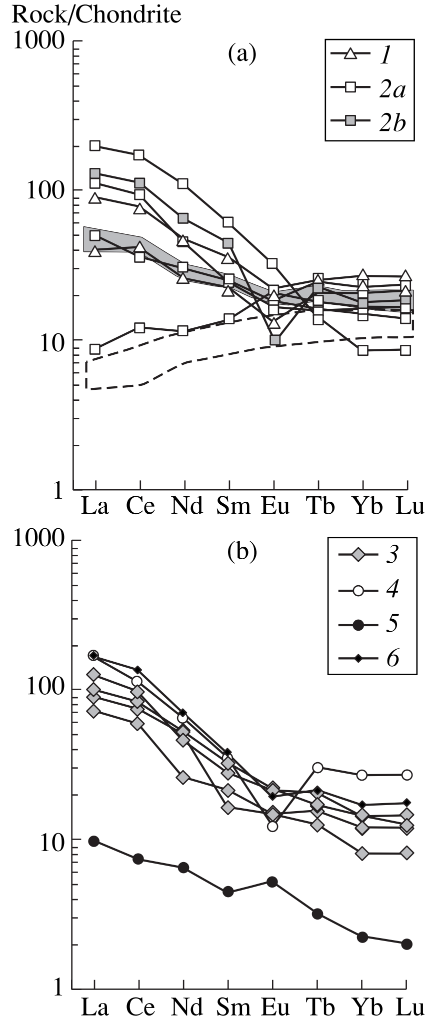

Fig. 2. C1 chondrite-normalized [13] REE patterns for volcanosedimentary and sedimentary rock associations of the Vedlozero–Segozero greenstone belt. (*1*) Andesite tuffites; (*2a*) mafic graywackes, (*2b*) interpillow silicite; (*3*) volcanosedimentary rocks (fine dacite tuff, feldspathic graywacke, siltstone); (*4*) cherty (chemogenic–terrigenous) arenite, (*5*) red dolomite; (*6*) Post-Archean Australian Shales (PAAS) [14]. Fig. 2a shows the typical composition of komatiitic basalt lavas from the Koikary structure [10] (light field) andesite lavas from the Chalka structure [12] (dark field).

(<8 wt %), and low alkali contents (Na_2O < 0.5 wt %, K_2O < 0.04 wt %). Contents of Cr (450–1200 ppm), Ni (120–700 ppm), trace elements, and REE are similar to those in komatiitic lavas (Fig. 2a). The rocks have a low CIA index [14] of 36.7 ± 16.05. Tuffites associate with volcanogenic mafic graywackes and replace them in the upper portion of the section.

Volcanogenic mafic graywackes (VMG) are dark green fine-grained (silt- and sand-sized) bedded rocks with 2- to 3-cm-thick laminae and 25- to 30-m-thick beds. The rocks are characterized by low contents of SiO_2 (45.79 ± 1.66 wt %), TiO_2 (0.3–0.5 wt %), and alkalis (Na_2O 0.74 ± 0.38 wt %, K_2O < 0.3 wt %) and a high MgO content (9–12 wt %). The Cr and Ni contents reach 784 and 338 ppm, respectively. The rocks are characterized by LREE-enriched patterns ($(La/Sm)_n$ = 1.88) with unfractionated HREE ($(Gd/Yb)_n$ = 1.12), which are similar to those for basaltic komatiites. The Zr/Y ratio is higher (3.12–4.41) relative to komatiites (2.83 ± 0.38). The CIA index (40–60) suggests an insignificant provenance weathering. The VMGs are developed in the Koikary structure (Rebo and Janish lakes) and the upper member of the Louhivaara Formation of the Hautavaara structure.

Volcanomictic mafic graywackes (VG) are recognized based on the appearance of plagioclase clasts or their intergrowths embedded in a matrix of the following composition: plagioclase (5–20%), chlorite (60–70%), titanite (3–5%), magnetite (1–2%), carbonate (0–5%), epidote (0–2%), and rare amphibole. They associate with siltstone or lithic graywacke (with basaltic fragments) lenses, komatiitic tuffite beds, and silicite lenses. Occasionally, they contain fine-grained quartz, in addition to plagioclase. The total thickness of the VG bed is 150–170 m. These rocks have a variegated chemical composition with high contents of SiO_2 (up to 56–64 wt %), Na_2O (0.4–5.3 wt %), MgO (5–10 wt %), and significant contents of FeO_{tot} (4–6 wt %), Cr < (30–70) and Ni < (10–50 ppm). Other parameters are as follows: Zr/Y ~ 10; CIA 54.52 ± 4.15; $(La/Sm)_n$ = 3.50 ± 1.16; $(Ce/Yb)_n$ 1.62–6.53. The REE pattern remains similar in the series. Model calculations show that LREE

Table 1. Composition of Late Archean volcanosedimentary and sedimentary rock lithotypes of the Vedlozero–Segozero greenstone belt (oxides in wt %, elements in ppm)

Component	1		2					3				4	
	101-2	104-1	10-2	27-C	29-1C	29-2C	28-2C	28-3C	5718-9C	26-C	30-C	57-C	52-C
	Chalka		Koikary									El'mus	
SiO_2	57.40	59.94	50.34	56.10	43.26	53.68	79.56	61.72	67.90	65.82	67.16	76.36	7.72
TiO_2	0.86	0.64	0.88	0.67	1.69	0.77	0.05	0.74	0.65	0.51	0.48	0.09	0.04
Al_2O_3	16.64	15.26	15.15	14.54	12.01	15.22	10.61	15.20	15.56	16.64	15.11	12.42	1.45
Fe_2O_3	1.41	1.56	1.83	0.87	3.05	0.86	0.45	1.40	1.13	1.03	0.70	1.14	5.07
FeO	6.11	4.88	10.34	8.19	15.94	5.45	0.57	4.52	3.01	4.02	4.59	0.28	0.57
MnO	0.130	0.14	0.16	0.142	0.238	0.159	0.022	0.077	0.066	0.051	0.060	0.025	0.651
MgO	4.77	4.94	8.44	8.98	7.19	5.86	0.50	4.00	1.74	2.36	3.18	0.87	17.93
CaO	6.17	7.86	2.23	1.14	6.43	5.00	0.28	2.28	0.71	0.57	0.57	0.43	25.31
Na_2O	2.56	3.02	3.47	1.99	0.43	2.71	0.61	3.19	5.73	4.12	1.84	0.08	0.08
K_2O	2.00	0.65	0.03	0.41	0.02	1.81	6.61	2.54	1.05	1.50	2.34	6.81	0.22
P_2O_5	0.04	0.01	0.18	0.08	0.10	0.21	0.02	0.24	0.23	0.10	0.13	0.02	0.01
H_2O	0.08	0.09	6.78	0.16	0.20	0.10	0.04	0.10	0.14	0.09	0.12	0.10	0.08
L.O.I.	1.62	1.15	50.34	6.33	9.53	7.86	0.70	3.98	1.73	2.77	3.67	1.36	40.68
Total	99.81	100.14	99.91	99.60	100.09	99.69	100.02	99.99	99.65	99.58	99.95	99.99	99.81
Cr	541	236	240	784	31	295	122	33	29	145	196	33	21
Ni	184	368	160	338	13	107	24	26	14	32	41	26	16
Co	39.5	58.2	63	59	65	25	<1	<1	10	14.9	16.9	<1	7.8
V	232	188	240	276	850	134	<15	<15	115	123	123	<15	47
Pb	3	8	15	17	19	126	5	15	9	9	17	15	7
Rb	40	21	20	9	3	36	101	127	35	2	54	127	2
Ba	248	196	153	120	124	265	1129	1186	546	327	429	1186	80
Sr	148	258	64	61	53	79	22	7	171	20	25	7	40
Nb	7	8	4	2	3	10	11	14	9	8	8	14	2
Zr	152	146	63	71	62	190	122	191	224	65	93	191	5
Y	34	38	26.1	22	27	32	28	40	27	10	17	40	5
Th	2.5	2.9	3.6	3.3	0.75	6.3	12.7	7.4	7.3	3.8	9.1	14.3	0.90
La	9.5	21.4	1.87	47.1	12.0	26.4	29.5	23.1	29.2	16.7	21.3	39.2	2.3
Ce	25.4	47.2	6.7	105.1	21.7	57.1	67.5	50.1	58.7	35.7	44.2	67.7	4.5
Nd	11.8	21.8	4.93	51.2	13.8	20.8	28.5	23.4	21.7	11.9	24.1	29.7	3.0
Sm	3.35	5.37	1.88	9.22	3.72	3.71	6.44	4.84	4.16	3.19	2.45	5.11	0.69
Eu	0.74	1.23	1.09	1.84	1.02	0.93	0.56	1.23	1.20	0.85	0.83	0.7	0.3
Tb	0.77	0.92	0.61	0.51	0.90	0.58	0.77	0.74	0.62	0.46	0.57	1.09	0.12
Yb	3.52	4.41	2.50	1.43	3.72	2.43	2.87	2.42	2.37	1.36	2.01	4.47	0.38
Lu	0.52	0.66	0.38	0.21	0.57	0.34	0.44	0.36	0.31	0.20	0.30	0.66	0.05
U	0.6	0.6	0.4	0.5	0.5	0.67	2.3	1.9	1.1	1.0	0.5	1.3	0.5
Sc	37.6	31.1	20.3	34.1	52.7	19.4	3.21	16.5	10.5	15.5	20.0	5.18	1.63
Hf	3.1	2.8	1.8	1.9	1.9	4.1	4.3	4.7	5.4	3.6	3.3	6.0	0.5
Ta	0.39	0.44	0.21	0.17	0.14	0.50	0.79	0.64	0.53	0.25	0.48	0.80	0.028
Cs	4.27	1.66	0.8	0.5	0.5	2.4	3.3	5.2	0.53	2.4	2.0	4.3	0.5

Note: Sedimentary lithotype formation site: (1) island arc (3.05–2.95 Ga), (2) back-arc basin (3.0–2.95 Ga), (3, 4) young volcanic arc (2.9–2.85 Ga). (Samples 101-2 and 104-1) psammitic andesite tuffite; (10-2, 27-C) volcanogenic mafic graywacke; (29-1C) volcanomictic mafic graywacke; (29-2C) siltstone graywacke; (28-2C) interpillow silicite; (28-3C) andesidacite tuff; (5718-9C) fine dacite tuff; (26-C) feldspathic graywacke; (30-C) siltstone; (57-C) cherty arenite (chemogenic–terrigenous); (52-C) red dolomite.

enrichment is related to the input (10–25%) of chemogenic silica (Fig. 2a).

The mafic graywackes were derived from disintegration products of komatiitic–basaltic lavas, their pyroclastics, and internal sediments (tuffites, silicites, and graphitic siltstones) with the addition of andesite volcanoclastic rocks upward the section. Sediments precipitated in a quiet hydrodynamic environment of the sea basin with weakly rugged floor and regressive sedimentation.

Sediments representing erosion products of continental margin are marked in the Vedlozero–Segozero greenstone belt (Hautovaara structure) by shelf deposits and coastal-marine turbidites. They are represented by an up to 300-m-thick sequence of alternating fine-, medium-, and coarse-grained arenites, subarkosic arenites, intraformational conglomerates, tuffstones, and arkoses with basal sediments (conglomerates) at the base.

Arenite–arkosic assemblages are characterized by coarse bedding (beds are up to tens of meters thick), which is caused by variations in the composition and grain size distribution of sediments, and fine lamination inside the beds. The rocks exhibit direct and inverse rhythmicity corresponding to the short-term variations in the transgressive–regressive cycles. A thick bed of homogenous unstratified arkoses marks the contribution of new provenances (granitoid massifs).

Arenites are varigrained sandstones with quartz prevailing in the clastic part and acid plagioclase dominating in the sericite–quartz–albite matrix. The rocks are characterized by high contents of SiO_2 (up to 72–76 wt %) and TiO_2 (0.23 ± 0.24 wt %), a low MgO content (0.6–1.1 wt %), and wide variations of FeO (1.5–2.5 wt %), Na_2O (0.5–2.8 wt %), and K_2O (3.5–4.5 wt %). The maximum Cr and Ni contents are 185 and 204 ppm, respectively. Other parameters are as follows: Cr/Ni 2.01 ± 1.74, Cr/V 0.54 ± 0.19, Zr/Y 12.55 ± 1.63 (15.8 ± 2.9 in TTG) and CIA ~ 63.

Arkosic arenites are characterized by the following composition: SiO_2 61–69 wt %, Na_2O 3.70 ± 1.46 wt %, K_2O 1.6–4.6 wt %, MgO 0.86 ± 0.08 wt %, Cr <145 ppm, Ni <10 ppm, Cr/Ni 16.10 ± 0.64, Cr/V 5.58 ± 1.20, Zr/Y ~4, and CIA 54.56 ± 2.12.

Volcanic arc (2.9–2.85 Ga) marked by CMA-type andesidacites associates with volcanosedimentary rocks (tuffites, tuffstones, and silicites) and chemogenic–terrigenous rocks (cherty arenites). Fine tuffs and tuffites correspond compositionally to Na-andesidacite lavas.

The intense silica accumulation (formation of silicites) in the Koikary and Hautavaara structures is coeval to the deposition of the fine-grained acid pyroclastics. They are characterized by horizontal and lenslike bedding, as well as concretion and gel sediment textures. The highest thickness of silicites (0.5–25 m) was found in the Janish (Koikary) and El'mus paleovolcanoes, where they precipitated in the crater likes and active fumarole fields. Depending on the admixture of two- or

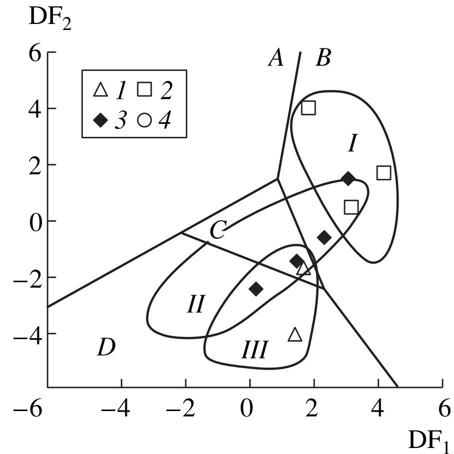

Fig. 3. The Bhatia discrimination diagram [2] reflecting the geodynamic setting of sedimentary assemblages. Fields: (*A*) passive continental margins, (*B*) oceanic settings; (*C*) continental island arcs, (*D*) active continental margins

three-valent iron, silicites vary in color from white and greenish to pink, red, and black. Their chemical composition is as follows (oxides in wt %): SiO_2 76–82, FeO_{tot} 0.1–1.3, MgO <0.8, CaO <0.4, $(La/Sm)_n$ <2–14, and $(Ce/Yb)_n$ <2–35 (Fig. 2b).

Dolomites formed as lenses during coastal salinization and have the following composition (in wt %): CaO 22–28, MgO 14–19, MnO 0.7–0.9, SiO_2 <15, Na_2O <0.17, and K_2O <0.53. The L.O.I. value is extremely high (32–43 wt %). The Fe_2O_3 content is two to four times higher than the FeO content. The REE distribution is characterized by a low (background) level and distinct LREE enrichment ($(La/Sm)_n$ = 2.15, $(Ce/Yb)_n$ = 3.26) (Fig. 2b).

The terrigenous sequence of graywackes, arenites, and graphitic siltstones formed after the termination of volcanic activity. Terrigenous graywackes compose a lateral series closely associated with coarse-clastic sediments (conglomerates) in the proximal facies and siltstones associated with chemogenic deposits in the distal facies.

Lithic graywackes (LG) are green coarse-bedded rocks with small fragments of dacites, basalts, and plagioclase grains, as well as rounded quartz in a fine-grained plagioclase–muscovite–chlorite–carbonate–epidote–quartz matrix. These rocks occur in the northern part of the Koikary structure and demonstrate a wide compositional variation (oxides in wt %): MgO < 3.5, FeO < 4, SiO_2 68.30 ± 4.31, TiO_2 0.41 ± 0.33. Cr <100 ppm, Ni < 300 ppm, and CIA 44–73. The REE chemistry in LGs can be correctly characterized for fine-grained varieties. They have LREE-rich patterns ($(La/Sm)_n$ = 3.30) with fractionated HREE ($(Ce/Yb)_n$ = 20.36).

Feldspathic graywackes (FG) are green fine-grained massive rocks which occasionally contain interbeds of quartz–sericite schists (metasiltstones). The mineral composition is as follows (wt %): plagioclase 25–40, quartz 0–10, chlorite 5–25, muscovite 15–40, carbonate 0–5, titanite 0–5, and magnetite 0–5. The FGs were found in the upper portions of the Kivilampi Formation of the Koikary structure and the upper portion of the Louhivaara Formation in the Hautavaara structure, as well as in the Pokrovskoe, Luzma, and Korbozero structures. In terms of geochemical composition, they are divided into high-Mg (MgO 4–12 wt %, Cr 840 ppm, Ni 600 ppm) and low-Mg (MgO 1–4 wt %) groups, thus marking the contrasting provenances. The REE pattern is insignificantly enriched in LREEs ($(La/Sm)_n$ = 2.08, $(Ce/Yb)_n$ = 1.62). The CIA value ranges from 50 to 78.

Quartz–feldspathic graywackes (QFG) are greenish gray fine-grained sandstones and siltstones with rhythmic bedding. The rhythm is 2–3 cm thick. Individual grains of albite and quartz are embedded in a fine-grained muscovite–chlorite–albite–quartz matrix. These rocks have the following features: SiO_2 56.51 ± 4.25 wt %, $(La/Sm)_n$ 3.38, $(Ce/Yb)_n$ 7.32), and CIA 30–83.

The REE patterns of terrigenous graywacke assemblages of the Hautavaara–Koikary test site are similar to the PAAS version [14] (Fig. 2b). They are typical of the Archean granite–greenstone terranes [14, 15]. Data points of sedimentary assemblages in the Bhatia factor diagram (Fig. 3) (according to the method of DF1 and DF2 calculation described in [3]) are distinctly discriminated between protooceanic and protocontinental rocks, supporting our geodynamic classification of sedimentary rocks.

In addition to the characteristics of magmatic associations, lithogeochemical characteristics of sedimentary assemblages (trace element and REE distribution patterns) described above are an important tool for paleogeodynamic reconstructions within Archean greenstone belts. The association of geodynamically contrasting sedimentary assemblages with different sedimentary histories supports the existence of convergent regimes in Archean (3.05–2.85 Ga ago). The geological evolution of the Vedlozero–Segozero greenstone belt involved early accretionary and late collisional stages, which were responsible for the formation of the recent stratotectonic section characterized by the lateral absence of individual rock associations.

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