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GEOCHEMISTRY

Age and Isotopic Geochemical Characteristics of Archean Carbonatites and Alkaline Rocks of the Baltic Shield

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Occurrences of Archean alkaline rocks are insignificant. Only a few complexes in the Canadian Shield (Superior Province), Greenland, Australia (Yilgarn Block), and South Africa are known to date [1]. They are composed of alkali and nepheline syenites, foidolites, carbonatites, peralkaline granites, lamprophyres, and potassic volcanic rocks. The age of the oldest alkaline rocks is estimated at ~2.7 Ga. The Neoproterozoic and Phanerozoic alkaline rocks occur in three main geodynamic settings: (1) continental rifts, (2) oceanic islands, and (3) subduction zones (peralkaline granites in back-arc zones). The Early Precambrian alkaline rocks formed at hotspots of the oceanic crust and are unknown in continental rifts. Therefore, the geodynamic setting of the Archean alkaline rocks is interpreted as a subduction-related environment and the depleted mantle is thought to be their source. The Late Archean subduction-related alkaline complexes presumably formed at the final stages of the evolution of greenstone belts, while the depleted source is accounted for by the absence of metasomatic processes in the Archean mantle [1].

High concentrations of Sr and REE, which are typical of alkaline rocks, make it possible to neglect contamination in the course of later superimposed processes and consider the primary isotope ratios as true characteristics of the mantle. This is very important for understanding the oldest (Archean) processes of lithosphere formation, because the initial geodynamic setting and role of mantle–crust interaction are often masked by numerous superimposed processes.

In this communication, we present new geochronological data obtained with U–Pb (zircon and baddeleyite) and Sm–Nd (glimmerite and minerals) methods, as well as isotopic–geochemical (Nd, Sr) data on the oldest alkaline rocks and carbonatites of the Baltic Shield.

The Siilinjärvi carbonatite complex of eastern Finland is related to the margin of the Archean Karelian Craton. The rock massif is a steep dikelike body about 16 km long and up to 1.5 km wide at the surface [2]. This massif intrudes the Archean granite gneiss and consists of glimmerite (mainly composed of phlogopite), phlogopite carbonatite, calcite carbonatite, and their apatite-rich varieties (up to 10% apatite). All rocks are characterized by a massive structure and medium- to coarse-grained texture. The first and major intrusive phase is represented by phlogopite-rich and phlogopite-bearing rocks with occasional richterite (up to 10%). Barite, strontianite, monazite, pyrochlore, magnetite, ilmenite, pyrite, baddeleyite, and zircon are accessory minerals. The melasyenite dike (4 km long and 20–30 m thick) is the youngest intrusive phase. The host rocks are fenitized over a distance of 1 km from carbonatites and fit alkali syenites in composition.

The Sakharijok massif of alkaline rocks is located in the western sector of the Keivy Terrane, Kola Peninsula. The terrane is mainly composed of Late Archean mafic-to-felsic metavolcanic and metasedimentary rocks that overlie the oldest tonalite–trondhjemite–granodiorite (TTG) basement of the Central Kola Block. Interformational intrusive bodies of peralkaline granite are also present. According to the geochronological data, the oldest basement of the Central Kola Block was formed during several stages of the Neoarchean endogenic activity and has an isotopic age of 3.0–2.7 Ga [3]. The felsic metavolcanics of the Keivy Terrane, which completed the extrusive succession, represent orogenic rocks with a U–Pb zircon age of 2871 ± 15 Ma [4]. The anorogenic Keivy peralkaline granite and granosyenite formed 2.68–2.65 Ga ago [5]. The Sakharijok massif occurs in the western sector of the West Keivy Complex of peralkaline granites. This is a fissure-type intrusion composed of alkali gabbroids (essexites), nepheline syenites, and alkali syenites [6].

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Table 1. Isotopic U--Pb data on baddeleyite (bd) and zircon from carbonatites and syenites of the Siilinj'arvi and Sakharijok massifs

Sample	Charge, mg	Content, ppm		Pb isotopic composition[1]			Isotope ratios and age, Ma[2]					Rho
		Pb_{tot}	U	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{208}Pb$	$^{207}Pb/^{235}U$	%	$^{206}Pb/^{238}Pb$	%	$^{207}Pb/^{206}Pb$	
Carbonatite, Siilinj'arvi massif												
1[2] (bd)	1.20	5.8	11.6	1720	5.670	7.319	10.432	1.5	0.4386	1.0	2550 ± 18	0.73
2[2]	0.50	4.4	8.6	1420	5.483	5.364	10.314	5.0	0.4305	3.0	2594 ± 60	0.71
3[3]	0.25	4.3	7.0	220	4.308	2.529	9.688	10.0	0.3993	6.0	2615 ± 60	0.73
4[3]	0.45	1.2	33.6	690	5.124	4.167	1.016	3.0	0.0922	1.5	2629 ± 30	0.71
1[4]	1.70	5.3	9.0	780	5.209	5.127	11.710	1.0	0.4835	0.8	2612 ± 12	0.80
2[4]	0.65	3.1	5.7	624	5.178	5.086	10.650	3.4	0.4474	2.6	2583 ± 33	0.83
3[4]	1.00	4.3	8.1	530	5.090	4.898	9.959	2.5	0.4192	1.6	2580 ± 27	0.77
4[4]	0.90	6.1	15.1	378	4.778	4.030	7.145	1.7	0.3034	0.9	2612 ± 21	0.73
Nepheline syenite, Sakharijok massif												
1[5]	0.55	28.9	86.3	552	7.246	6.542	4.5780		0.2918		1862	0.64
2[5]	0.50	28.8	76.3	953	6.900	6.931	6.0490		0.3341		2115	0.70
3[5]	0.40	27.2	72.8	114	4.724	3.086	3.4000		0.2600		1458	0.48
4[5]	0.50	27.6	68.2	615	6.611	5.506	6.4525		0.3437		2098	0.85
Alkali syenite, Sakharijok massif												
1	0.20	586.1	1008.5	4593	5.5464	5.3622	12.060		0.4925		2631	0.94
2	0.85	64.9	113.5	5262	5.5567	5.9061	12.018		0.4907		2631	0.95
3	1.25	52.1	93.8	3643	5.5715	6.9134	11.781		0.4852		2617	0.94
4	1.20	9.1	15.5	1056	6.1515	1.9501	8.2846		0.3994		2351	0.91

Note: ([1]) All ratios are corrected for procedure blank (0.2 ng Pb and 0.04 ng U) and for mass discrimination (0.12 ± 0.04%).

([2]) Correction for admixture of common lead is determined for age according to Stacey–Kramers model [10].

([3]) Correction for isotopic composition of microcline is introduced: $^{206}Pb/^{204}Pb = 16.49 \pm 0.02$; $^{207}Pb/^{204}Pb = 15.17 \pm 0.03$; $^{208}Pb/^{204}Pb = 35.17 \pm 0.10$.

([4]) Correction for isotopic composition of microcline is introduced: $^{206}Pb/^{204}Pb = 19.804 \pm 0.01$; $^{207}Pb/^{204}Pb = 16.206 \pm 0.02$; $^{208}Pb/^{204}Pb = 36.14 \pm 0.24$.

([5]) Correction for isotopic composition of syenite (WR) is introduced: $^{206}Pb/^{204}Pb = 14.77$; $^{207}Pb/^{204}Pb = 15.00$; $^{208}Pb/^{204}Pb = 33.84$ [7].

The alkaline magma intruded as >7-km-long steep dikelike bodies along vertical faults between peralkaline granites and diorite gneisses. The massif is as wide as 1.5–2.0 km in its northern part. Alkali syenites occur in the western and southwestern sectors of the massif, while nepheline syenites occupy its eastern sector and host large (up to 80 × 200 m^2) essexite blocks. Nepheline syenites alter metasomatically the enclosing peralkaline granites, alkali syenites, and essexites to form fenite aureoles and pegmatite veins.

Alkali syenite is a medium- to coarse-grained rock with distinct lineation of dark-colored minerals. The massive variety is subordinate. The rock has a stable composition: albite (40–50%), microcline (25–30%), lepidomelane (10–15%), and ferrohastingsite (5–10%). Zircon, allanite, fluorite, and magnetite are accessory minerals. Nepheline syenite is a medium- and coarse-grained rock of trachytoid (most abundant) and porphyritic textures. The trachytoid nepheline syenite is composed of albite (30–40%), microcline (20–25%), nepheline (20–25%), aegirine (10–20%), and lepidomelane (10–15%). Porphyritic syenite is largely composed of albite, microcline, and nepheline in approximately equal amounts. Large poikiloblasts or idioblasts of ferrohastingsite (up to 20%) are typical. Zircon, fluorite, calcite, and britholite are accessory minerals of nepheline syenite. Essexite is a massive medium-grained rock composed of omphacite (30–60%), phlogopite (10–50%), plagioclase (up to 30%), nepheline (up to 5%), and calcite (1–3%). Some varieties contain amphibole of the hastingsite–pargasite series (up to 5%). Magnetite, apatite, and fluorite are accessory minerals.

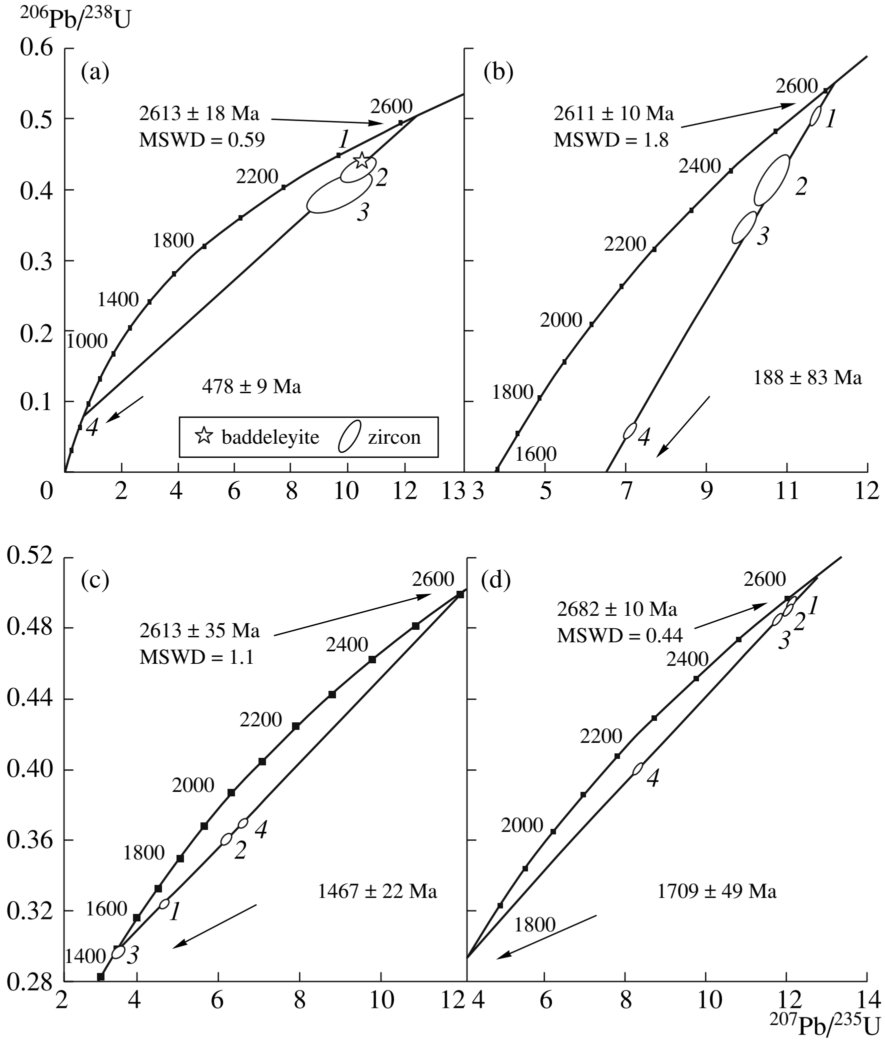

Fig. 1. U–Pb diagram with concordia. (a, b) Zircon and baddeleyite from carbonatite of the Siilinjärvi massif; (c, d) zircon from nepheline syenite and alkali syenite of the Sakharijok massif.

Representative samples more than 20 kg in weight were taken from all the above rocks for U–Pb dating and Nd–Sr isotopic geochemical study. The extracted minerals and rocks were processed using the standard technique applied at the Laboratory of Geochronology and Isotope Geochemistry of the Geological Institute, Kola Scientific Center, Russian Academy of Sciences [7]. The isotopic compositions of U, Pb, Nd, and Sr were measured on MI-1201-T and Finnigan-MAT 262 (RPQ) mass spectrometers. The coordinates of points and parameters of isochrons were calculated with software packages [8, 9]. The correction for admixture of common lead was introduced according to the model [10], and the commonly accepted constants of decay [11] were used. The results of U–Pb dating are shown in Table 1 and Fig. 1.

The age of the Siilinjärvi Complex was estimated previously at 2.58 Ga [1] and 2.61 Ga [12]. The newly obtained U–Pb ages of zircon and baddeleyite from carbonatite (Fig. 1a) and a large (2 cm) zircon crystal from pegmatoid body (Fig. 1b) are 2613 ± 18 and 2611 ± 10 Ma, respectively. These values specify the timing of rock formation.

The U–Pb zircon age of nepheline syenites from the Sakharijok massif is 2613 ± 35 Ma (Fig. 1c). This dating coincides within error limits with the age of carbonatites and suggests a single Neoarchean magmatic pulse of the formation of alkaline nepheline rocks and carbonatites of the Baltic Shield. The U–Pb zircon age of alkali syenites from the Sakharijok massif is 2682 ± 10 Ma (Fig. 1d), i.e., much older than the age of nepheline syenite. At the same time, this age falls within an interval obtained for peralkaline granites of the Keivy Complex. Thus, the alkali syenites may be regarded as the early intrusive phase of an peralkaline granite complex.

Representative samples of all rock varieties in the massif were taken for the Sm–Nd isotope investigation. The mineral fractions of apatite, richterite, and phlogopite were separated from glimmerite sample BTS-04/2

Table 2. Nd and Sr isotopic compositions of rock and minerals from the Siilinj'arvi and Sakharijok massifs

Sample	Massif, rock, mineral	Sm	Nd	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	$\varepsilon_{Nd}(2610)$
		ppm				
S-04/1	Siil, Cb	31.353	211.568	0.089583	0.510775 ± 19	–0.4
S-04/2	The same	29.152	197.254	0.089341	0.510741 ± 21	–1.0
S-04/6	Siil, Gm	13.348	89.951	0.089703	0.510778 ± 25	–0.4
S-04/9	The same	7.226	48.499	0.090067	0.510743 ± 12	–1.2
S-04/10	"	8.095	54.764	0.089357	0.510753 ± 11	–0.7
BTS-04/2	"	29.152	197.254	0.089341	0.510803 ± 21	0.4
The same	Siil, Rch	1.921	14.062	0.082595	0.510690 ± 13	
"	Siil, Ap	231.494	1575.333	0.088832	0.510791 ± 11	
"	Siil, Phl	0.096	0.604	0.096240	0.510925 ± 21	
Fm-8	Sakh, Es	1.35	6.78	0.120321	0.511172 ± 12	–3.0
Cx M-18	Sakh, Ns	25.84	156.89	0.099565	0.510917 ± 4	–1.0
Skh-20-10	The same	51.41	266.25	0.116700	0.511283 ± 16	0.4
Skh-20-245	"	51.47	315.96	0.098400	0.510930 ± 8	–0.3

Sample	Massif, rock, mineral	Rb	Sr	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	$\varepsilon_{Sr}(2610)$
		ppm				
S-04/1	Siil, Cb	0.203	9218.4	0.000065	0.70177 ± 15	6
S-04/2	The same	62.049	8196.1	0.022548	0.70237 ± 20	2
S-04/6	Siil, Gm	282.844	1911.8	0.440664	0.71996 ± 7	28
S-04/9	The same	301.746	523.0	1.719464	0.76611 ± 11	–3
S-04/10	"	331.46	633.2	1.561215	0.76387 ± 10	51
Fm-8	Sakh, Es	120.9	355.4	1.0136	0.74754 ± 14	110
Cx M-18	Sakh, Ns	561.6	67.2	24.8891	1.79779 ± 38	2200
Skh-20-10	The same	484.0	22.4	64.3488	3.5437 ± 39	5800
Skh-20-245	"	791.3	69.3	34.0500	2.15626 ± 59	2400

Note: Average values (2σ) for standards during the measurement period: La Jolla 0.511833 ± 6 (11) and JiNd1 0.512072 ± 2 (44). Massifs: (Siil) Siilinj'arvi; (Sakh) Sakharijok. Rocks: (Cb) carbonatite; (Gm) glimmerite; (Es) essexite; (Ns) nepheline syenite. Minerals: (Rch) richterite; (Ap) apatite; (Phl) phlogopite.

(total weight 15 kg) of the Siilinjärvi massif. The results of Sm–Nd measurements are presented in Table 2. The isochron for minerals and whole-rock sample yielded 2615 ± 57 Ma (Fig. 2), which coincides within the error limits with U–Pb age of carbonatite.

The studied rocks from the Siilinjärvi and Sakharijok massifs are characterized by high Nd contents (50–300 ppm). Therefore, we can neglect the possible contamination of the Sm–Nd isotopic system with crustal material (Nd content in rocks of TTG complex is up to 20 ppm). Carbonatites and glimmerites of the Siilinjärvi massif are characterized by an $\varepsilon_{Nd}(T)$ value ranging from –0.4 to –1.2. These isotopic data fit the true parameters of the mantle source, because the Sm–Nd isotopic system was not disturbed in the course of the subsequent processes. This is confirmed by the concordance of the U–Pb and Sm–Nd ages. The variations of $\varepsilon_{Sr}(T)$ are wider (from –2.7 to +50.5) and are probably related to the magma fractionation. Thus, our isotopic–geochemical data indicate that the primary magma of carbonatites and glimmerites was related to a moderately enriched mantle source (Fig. 3).

The Sm–Nd isotopic system of alkaline rocks in the Sakharijok massif is distinguished by a wider range of $\varepsilon_{Nd}(T)$ values (from +0.4 to –3.0) in consistence with a high grade of metamorphism of the majority of rock varieties. The variation of $\varepsilon_{Sr}(T)$ from +100 to +5800 is explained by long-term magma fractionation. However, it should be noted that data points of the least metamorphosed and fractionated varieties of rocks (alkali gab-

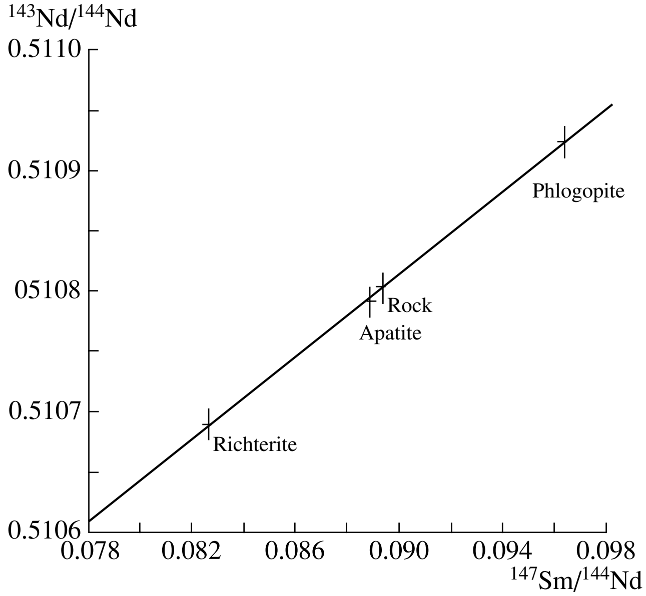

Fig. 2. Sm–Nd isochron for glimmerite and minerals from the Siilinjärvi massif. $T = 2615 \pm 57$ Ma; $\varepsilon_{Nd}(T) = +0.4 \pm 0.2$; MSWD = 0.37.

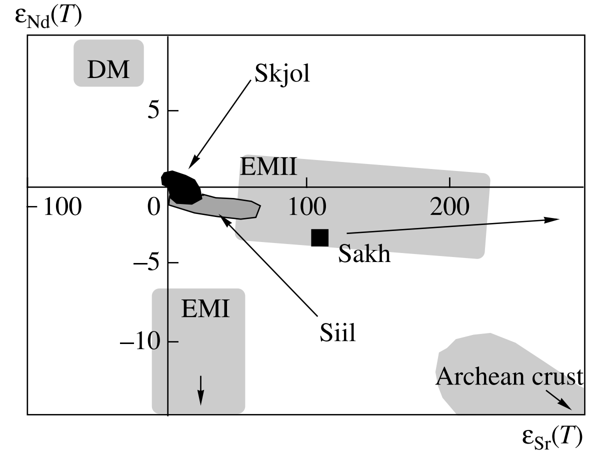

Fig. 3. $\varepsilon_{Sr}(T)$–$\varepsilon_{Nd}(T)$ diagram for Archean alkaline rocks of the Baltic and Greenland shields. (Sakh) Trend for alkaline rocks of the Sakharijok massif (alkali gabbro (essexite) is designated by box); (Siil) Siilinjärvi carbonatite complex; (Skjold) Skjoldungen alkaline province.

bro or essexite) fall into the field of reservoir EM II in the $\varepsilon_{Sr}(T)$–$\varepsilon_{Nd}(T)$ diagram (Fig. 3). As is supposed, this reservoir was formed by metasomatic enrichment of the mantle during the percolation of fluids from the subducted oceanic crustal rocks and sediments. In contrast to the other Archean alkaline rocks, syenites of the Sakharijok massif are enriched in HFSE (Zr up to 3000 ppm, Nb 200–600 ppm, Ta 10–20 ppm, Y 10–500 ppm, total REE 0.1–0.3 wt %, and Rb 400–900 ppm) and characterized by relatively low Y/Nb and Yb/Ta ratios (<1.2). This is also typical of derivatives of the enriched mantle.

Thus, the geochemical characteristics of nepheline syenite of the Sakharijok massif match properties of fractionation products of alkali basalts from oceanic islands (OIB-type magmas). It should be noted that the nearly coeval peralkaline granites of the Keivy Complex are classed with typical A-granites formed in the within-plate setting [13].

Among all known Archean alkaline complexes, the Skjoldungen alkaline province of eastern Greenland (pyroxenite, hornblendite, monzonite, foidolite, and carbonatite) dated at 2.70–2.66 Ga [14] is closest to the studied rocks in terms of isotopic geochemical features. The comparative analysis of the Archean alkaline rocks of the Baltic and Greenland shields [15] has shown their common genetic and geodynamic evolution in the course of development of the Neoarchean plume with parameters of the enriched mantle (2.70–2.66 Ga: the initial stage of the plume evolution, near-chondritic and slightly enriched mantle source, parental magma of shoshonitic type; 2.65–2.61 Ga: the final stage, enriched source, parental magma of OIB-type).

Thus, the U–Pb datings of zircon and baddeleyite, as well as the Sm–Nd age of rock-forming minerals of carbonatites and alkaline rocks from the Siilinjärvi and Sakharijok massifs in the Baltic Shield, reliably corroborate their Archean age. The Nd and Sr isotopic systems suggest the formation of alkaline rocks from an enriched mantle source that is unique for the Archean.

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