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PECULIARITIES OF THE MINERAL COMPOSITION AND ORIGIN OF THE SIILLINJARVI CARBONATITES (FINLAND)

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The article presents the results of investigations of the Precambrian carbonatites (alvikites and beforcites) from the Siillinjarvi deposit (Finland). The carbonatites intruded into the older phlogopite-bearing rocks – syenites and glimmerytes. Dolomite and calcite are the main minerals of the carbonatites (more than 70 % of the total carbonatite volume). Apatite, tetraferriphlogopite and richterite are the secondary minerals. The accessory minerals are presented by strontianite, monazite, pyrochlore, baddeleyite, ilmenite, magnetite and pyrite. We established the stable chemical composition of the phlogopite. Take into consideration carbonates homogeneity and absence of their secondary phases we estimated crystallization temperature about 540 °C (according to the Talantsev's thermometer), and it is close to crystallization temperature of the coexisting carbonates according to isotopic calculations. Apatite of the deposit is rich in strontium and considerable variations of the strontium isotopes are characteristic. Isotopic composition of carbon and hydrogen from the Siillinjarvi carbonates are also variable, and often are not similar to the typical for young carbonatites.

Key words: carbonatite, igneous silicate rocks, apatite, tetraferriphlogopite, petrogenesis, isotopes of C, O, Sr, Siilinjarvi, Finland.

Carbonatites are relatively rare rocks composed mainly endogenic carbonates with some silicates and minor minerals of rare metals, REE, U and Th, etc. After first observations of carbonatites in the Fen complex, SE Norway [10], idea about their magmatic origin has been proposed. Since this recognition, a number of studies were performed on geology, mineralogy, origin and economic geology of carbonatites. Concentric and zonal shapes of the main carbonatite-bearing complexes are typical for their Phanerozoic varieties [3]. Paragenetic relationships of the ultrabasic rocks, alkaline rocks and carbonatites are indispensable conditions to establish real carbonatites in contrast to late carbonate veins, nests, and banded bodies, which are common inside zones of secondary alteration and hydrothermal halos. General similarity in mineral compositions and shapes carbonatites and late carbonates leaded to appearance a number of definitions to determine carbonatites, which combine different terms from magmatic up to metasomatic processes [1, 9, 12, 32]. Up to present time in the scientific literature we can meet harden discussions on the term "carbonatites", and there are about ten versions of the term [15, 16, 19, 21, 25, 26]. In addition to primary structural, geological, and petrographic criterions to establish real carbonatites [3, 25] now geologists use geochemical, isotope and petrologic evidences for these purposes. For example, due to fundamental isotopic investigations of carbonates from carbonatites [14] limits of oxygen and carbon isotope marks have been determined for typical carbonatites ("Oka box"). Besides clear evidence of carbonatite magmatic lavas from Oldoinyo Lengai, Tanzania [29] still now some geologists develop ideas on metasomatic origin of carbonatites, but another [23] note about success in investigation of relationship between carbonatite and kimberlite magmas. Different arguments on magmatic or metasomatic origin of carbonatites reflect real differences of mechanisms carbonatites formation from place to place in accordance to their evolution.

More complicated evidences we need to determine peculiarities of formation for the Precambrian carbonatites. Commonly they have linear shape, very often not all three rocks (ultrabasic, alkaline and carbonatites), which are typical for the Phanerozoic complexes, we can determine in association with carbonatites. Poorer specific for carbonatites rare metals mineralization, and wall rock alterations of the primary varieties are also problems for detection of the Precambrian carbonatites. Among the Precambrian carbonatites most old are the Siilliniarvi carbonatites, Eastern Finland [22, 28, 34, 40]. Since their discovery in 1950, they are examples of the Precambrian carbonatites due to old age and since 1979 – as a source of apatite and carbonate concentrates with some accompanies components for industry of Finland [28, 31, 37].

First idea on carbonatites origin evolved from transformation of limestone substratum and skarns [33, 35] up to modern points of view, which include mechanism of magma melting of the upper mantle [8, 29]. Basement of present models of carbonatite formation includes system of geological, mineralogical, and isotopic data [26, 27, 36, 38], and for the Precambrian carbonatites they are the only way to do conclusions on the carbonatites appearance.

To understand main peculiarities of the Siilliniarvi's carbonatites origin we compared its characteristics with other possible Precambrian carbonatites of Siberia and of the Ukrainian Shield [4, 5, 7, 39].

Geological setting and main rocks types. Geological ideas on main rocks groups and structure of the Siilinjarvi deposit varied since the first systematic reports [31]. To describe carbonate rocks of the Siilinjarvi deposit as carbonatites, K. Puustinen [31] used the Heinrich's definition [19] and pointed out for its purpose the association of ultramafic and alkaline rocks with carbonatites. This definition is close to opinion of A. Kukharenko and co-authors [3, 11] for the Phanerozoic carbonatites in close association with the ultrabasic and alkaline rocks, which are surrounding of fenites. But, in contrast to the Phanerozoic complexes with carbonatites, K. Puustinen [31] suggested glimmerites of the Siilinjarvi deposit as an analogous to the ultramafic rocks and indicated only sporadically development of fenites. In bigger scale at the scheme of distribution carbonatites and lamprophyres in the Fennoscandian Shield (Fig. 1) the Siilinjarvi carbonatites have been suggested as with no associated silicate rocks [37], and at the modern Yara's map of the deposit we can see wider development of the fenites and absence of syenite (Fig. 2).

According to proposed schemes [31, 34] glimmerites of the deposit as primary ultramafic phases were intruded into the host granitic gneisses and system of the sub-vertical carbonate veins is developed in several stages inside the glimmerites. The carbonate veins jointly form main carbonatite tabular body about 16 km long and up to 1.5 km wide. It was assumed early [31] that intrusion of glimmerite was followed by intrusion of syenites in the marginal zone of the glimmerite and the surrounding bedrock, but later the syenitic rocks as well as glimmerites were regarded by P. Herms [34] as fenitized host rocks. The radiometric age of the complex ranges from 2 000 up to 2 900 million years, and the oldest formation age of carbonatites was inferred from U/Pb investigations on zircons as 2.605±0.006 Ga [20, 22, 31, 34, 40].

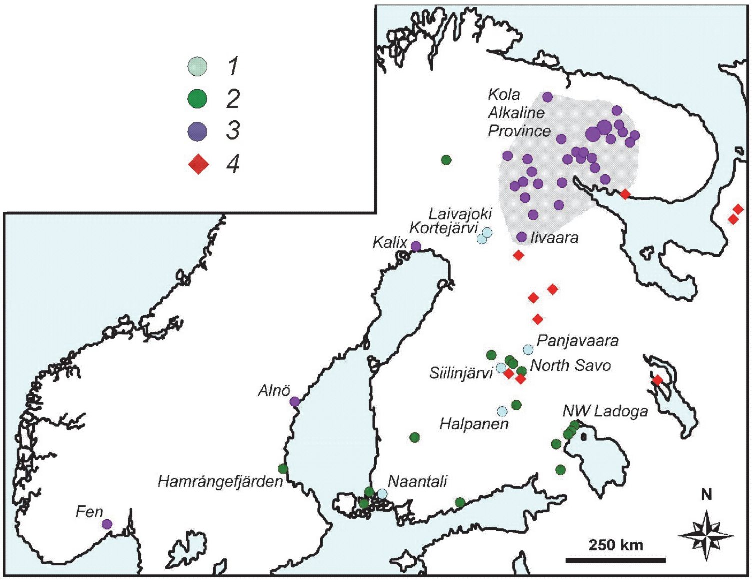

Fig. 1. The spatial distribution of carbonatites, lamprophyres and kimberlites in the Fennoscandian Shield [37]:

1 – carbonatites with no associated silicate rocks; *2* – shoshonitic lamprophyres with or without associated granitoids; *3* – ultramafic lamprophyres, carbonatites and associated alkaline silicate rocks; *4* – kimberlites of the first and second groups.

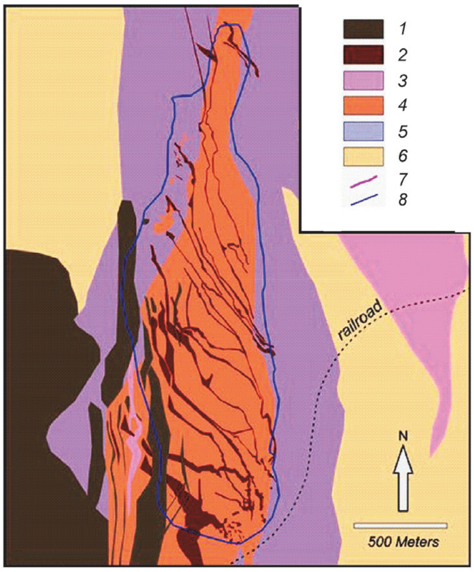

Fig. 2. Geological map of the Siilinjarvi carbonatite complex (the area of the main pit) [28].

1 – tonalite-diorite; *2* – diabase; *3* – granite; *4* – ore; *5* – fenite; *6* – gneiss; *7* – melasyenite dyke; *8* – current pit outline.

Mineral composition of the rocks. More than 25 minerals are established in the rocks of the Siillinjarvi deposit [28, 31, 37]. Besides dolomite and calcite (up to 70 % and more of total volume of the carbonatites), apatite, phlogopite, tetraferriphlogopite, richterite are common components of the rocks.

Sometimes white carbonatites (Fig. 3) contain rich in colourless apatite and silicates strips and nests more dark in colour. Phlogopite, richterite are main minerals of the glimmerites, and carbonates (less than 50 %) and apatite and zircon are minor phases [31].

Fig. 3. Contact of light carbonatite and carbonatite rich in tetraferryflogopite.

In contrast to small grains of apatite in carbonatites, in parts of dark and rich in tetraferriphlogopite glimmerites apatite grains are bigger in size and gray-green in color (Fig. 4). Strontianite, monazite, pyrochlore, baddeleyite, ilmenite, magnetite and pyrite are present as accessory minerals in the rocks [31]. Microcline with small amount of albite is minor minerals in the syenites, and absence of nepheline. Dark minerals are represented by aegirine-augite and actinolite. Some pegmatoid parts of syenites contain titanite rich in Nb. There is also information about finds of fergusonite and columbite [31].

Siilinjarvi carbonatite complex is one of the oldest carbonatite deposits in the world with in situ grade 4.2 % P_2O_5 with automated XRF/XRD for on-line analyses in the concentrator. Siilinjarvi Phosphate Mine currently owned and operated by Yara. Production of the apatite concentrates started in 1979 and has been in continuous operation since then firstly from the Sarkijarvi pit and from the Saarinen pit later (2012).

Carbonates. According to observations with thin sections dolomite and calcite varieties of the carbonatites of the Siillinjarvi deposit are developed independently. We did not found any substitutions between calcites and dolomites in the carbonatites, and we assumed that chemical compositions of the carbonates reflect its primary phases.

Fig. 4. Apatite crystal surrounding by tetraferryflogopite rose.

Chemical compositions of the carbonates (Table 1) are relatively homogenous, and at the compositional diagram (Fig. 5) we can see two isolated fields – one of the pure calcites, and second – of dolomites. Taking into consideration homogeneity of the carbonates and absence of secondary phases, we calculated its crystallization temperature with the Talantsev's geothermometer [6] approximately under 540 °C. It is close to the crystallization temperatures obtained by calculations after isotopic data for the coexisting carbonates [13].

Tetraferriphlogopite. During investigations of the tetraferriphlogopite of the Siillinjarvi deposit in thin sections, we found its high homogeneity. Its chemical compositions (Table 2) are relatively stable and at the compositional diagram (Fig. 6), the tetraferriphlogopites form compact and isolated field. Obtained data confirm previous conclusions [30, 31] about absence of alteration of the primary phlogopite.

Apatite. In the Siillinjarvi deposit the mineral occurs mainly as irregular grains up to a few millimetres in carbonatites and glimmerites. Sometimes apatite grains up to a few centimetres with vague crystallographic forms are present in glimmerites surrounding by aggregates of tetraferriphlogopite (See Fig. 2).

Main peculiarities of chemical composition of apatite from the Siillinjarvi deposit are deficiency of phosphorus and high strontium concentration (Table 3) [31]. Last is typical for apatite from the Phanerozoic alkaline rocks (up to 5.5 % SrO in Murun and Khibiny massifs) and carbonatites.

At the binary diagram (Fig. 7), which reflects strontium and calcium isomorphic substitutions, high strontium concentrations in apatite from the Precambrian linear carbonatites of Ukraine [5, 39] and apatite poor in strontium from the Precambrian carbonate-bearing rocks [17] are shown.

Table 1

Chemical composition and formula coefficients of carbonates from Siilinjarvi deposit

Com-po-nents	Number of the analysis										
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*
MgO	0.52	0.38	0.59	17.48	17.46	17.35	17.72	17.34	17.82	1.55	1.66
CaO	55.02	56.84	54.26	31.15	30.34	32.40	30.63	29.87	32.66	52.84	51.30
MnO	0.19	0.65	0.29	0.74	0.12	0.51	0.30	0.39	0.37	0	0.63
FeO	0.76	0.59	0.68	3.85	3.02	3.36	3.17	2.83	3.25	0.63	0.25
NiO	0.49	0	0.64	0	0	0	0	0.20	0	0.46	0.39
SrO	1.52	0.63	0.75	0.74	0	1.34	0.50	0.52	0.73	1.64	1.17
∑	58.49	59.09	57.21	53.96	50.94	54.96	52.32	51.15	54.83	57.12	55.40
Ca	0.95	0.97	0.96	1.05	1.06	1.07	1.05	1.05	1.08	0.93	0.93
Mg	0.01	0.01	0.01	0.82	0.85	0.80	0.85	0.85	0.82	0.04	0.04
Mn	0.00	0.01	0.00	0.02	0.00	0.01	0.01	0.01	0.01	0.00	0.01
Fe^{2+}	0.01	0.01	0.01	0.10	0.08	0.09	0.08	0.08	0.08	0.01	0.00
Sr	0.01	0.01	0.01	0.01	0.00	0.02	0.01	0.01	0.01	0.02	0.01
Ni	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01
∑	1	1	1	2	2	2	2	2	2	1	1

Table 2

Chemical composition and formula coefficients of tetraferryflogopite from Siilinjarvi deposit

Components	Number of the analysis				
	1	*2*	*3*	*4*	*5*
SiO_2	40.22	39.98	40.44	40.54	40.54
Al_2O_3	6.69	6.83	6.26	6.73	6.88
TiO_2	0.22	0.42	0.17	0.39	0.34
FeO	6.80	9.00	7.00	6.80	7.20
Fe_2O_3	6.88	4.85	6.79	7.56	6.54
MgO	22.61	21.85	22.78	23.23	23.06
MnO	0.20	0.36	0	0.37	0.40
CaO	0.03	0.08	0.01	0.14	0
Na_2O	0	0	0	0	0.15
K_2O	10.93	10.96	10.74	10.87	11.32
∑	94.58	94.33	94.19	96.63	96.43
Si	3.01	3.23	3.04	2.98	2.99
Al	0.59	0.65	0.55	0.58	0.60
Ti^{4+}	0.01	0.03	0.01	0.02	0.02
Fe^{3+}	0.39	0.29	0.38	0.42	0.36
∑	4.00	4.19	3.98	4.00	3.97
Fe^{2+}	0.43	0.61	0.44	0.42	0.44
Mg	2.52	2.63	2.55	2.54	2.53
Mn^{2+}	0.01	0.02	0.00	0.02	0.02
∑	2.96	3.26	2.99	2.98	3.00
Ca	0.00	0.01	0.00	0.01	0.00
Na	0.00	0.00	0.00	0.00	0.02
K	1.04	1.13	1.03	1.02	1.06
∑	1.05	1.13	1.03	1.03	1.09

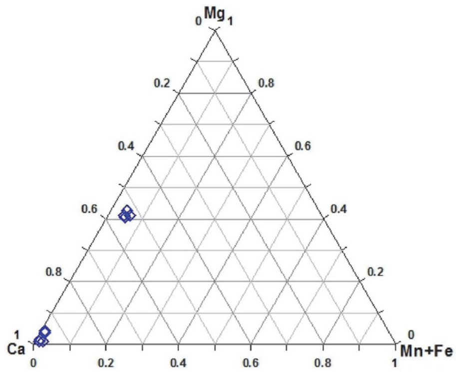

Fig. 5 Variations of the Siilinjarvi's carbonates compositions on the diagram Ca–Mg–(Mn^{2+}+Fe^{2+}).

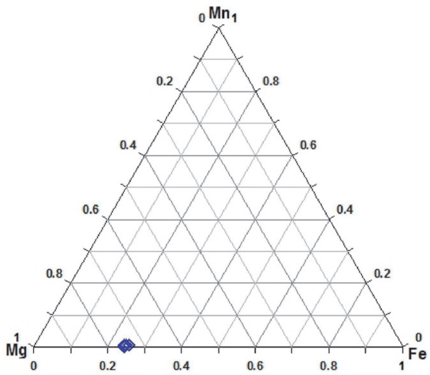

Fig. 6. Variations of the Siilinjarvi's tetraferryflogopites compositions on the diagram Mg–Mn–Fe.

Table 3

Chemical composition and formula coefficients of apatite from Siilinjarvi deposit

Components	Number of the analysis			
	1	*2*	*3*	*4*
P_2O_5	38.11	37.06	37.56	38.31
CaO	56.40	55.23	55.12	56.22
K_2O	0	0.37	0.10	0.11
MnO	0.27	0	0	0
MgO	0.22	0	0	0
FeO	0.13	0	0	0
∑	95.14	92.66	92.79	94.64
P_2O_5	2.96	2.96	2.98	2.98
Ca	5.54	5.58	5.54	5.54
Mn	0.02	0.00	0.00	0.00
Mg	0.03	0.00	0.00	0.00
Fe	0.01	0.00	0.00	0.00
K	0.00	0.04	0.01	0.01
∑	5.60	5.63	5.55	5.55

Isotopic compositions of Sr in apatite of the Siillinjarvi deposit are variable [13, 34] and are close to the crust marks in apatite from the glimmerites and the Precambrian metasedimentary carbonate rocks [2, 17, 24]. At the same time the lowest Sr isotope ratios of apatites and carbonates from the Siilinjarvi carbonatites (0.70137) are in the range of bulk silicate Earth and higher than those from Canadian carbonatites of similar ages [20, 34].

System investigations of the geology, mineralogy and petrology of the Siillinjarvi deposit [20, 28, 31, 40] has been shown, on one hand, the presence of carbonatites in the Fennoscandian Shield Archean rocks, which are characteristic for more young, Phanerozoic complexes, and on the other hand – their diversity by linear form, reduced and specific in composition ultramafic and alkaline rocks, common for ultrabasic-alcaline complexs with carbonatites, poor in minerals with rare metals and REE specialization or its absence, etc.

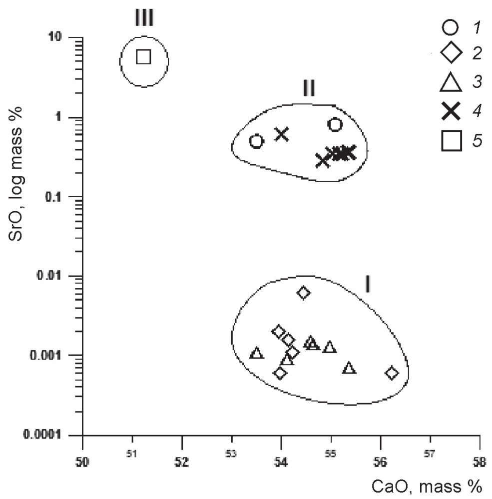

Fig. 7. Variations of apatite compositions on the diagram CaO–SrO:

1 – from calcite carbonatites of the Behim-Chokrak (Chernihiv zone, Pre-Azov region, Ukraine); *2* – from the Precambrian Mg-skarn; *3* – from the Precambrian apatite bearing carbonate rocks; *4* – from kimberlites; *5* – from alkaline metasomatic rocks of the Murun massif (North-Western Aldan, Siberia). Fields of the apatite of similar chemical composition: I – from the Precambrian Mg-skarns and apatite bearing carbonate rocks; II – from kimberlites and calcite carbonatites of the Behim-Chokrak; III – from alkaline metasomatic rocks of the Murun massif.

Exploration and mining for some decades of the Siillinjarvi deposit in open pits promoted in news data about the deposit [28, 37], but final decision on origin of the carbonatites and associated rocks are still far.

Modern data on peculiarities of geological and structural position as well as chemical and mineralogical compositions of the rocks and minerals of the Siillinjarvi deposit can be used as special etalon for the Precambrian linear carbonatites to estimate evolution of Precambrian endogenous formations. There is similarity of the Siillinjarvi deposit and other Precambrian deposits [5, 7, 39] by linear shape of the main carbonatite bodies, but there is not direct analogous in composition and transformation of the primary rocks of the deposits. Glimmerites are regarded as products of alteration of ultramafic initial rocks, but there is a big homogeneity among tetraferriphlogopite grains. The silicate rocks of the Siillinjarvi deposit have close chemical compositions to typical relatively fresh ultramafic rocks, but we cannot retrace all line of transformations in the glimmerites. Similar peculiarity is characteristic of the carbonates.

Minerals of rare metals and REE, characteristic of the Phanerozoic carbonatites, have been found only in small amounts or are absent at all. Besides high strontium concentration in apatite another strontium minerals typical for carbonatites are very rare in the Siillinjarvi deposit.

Isotopic compositions of carbon and oxygen in carbonates of the Siillinjarvi deposit are also heterogeneous and deflected from typical for limits of young carbonatite [14]. Relatively high data for isotopically heavy carbon ($\delta^{13}C = -3.7$ ‰, PDB) from the carbonatites are close to characteristics which we found in carbonates formed in near surface conditions [18].

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ОСОБЛИВОСТІ МІНЕРАЛЬНОГО СКЛАДУ ТА ПОХОДЖЕННЯ КАРБОНАТИТІВ СІІЛІНЬЯРВІ (ФІНЛЯНДІЯ)

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Висвітлено результати дослідження докембрійських карбонатитів (альвікіти і бефорсити) родовища Сііліньярві (Фінляндія). Карбонатити вкорінені в давніші флогопітові породи – сієніти і глімерити. Головними мінералами є доломіт і кальцит (становлять понад 70 % від загального об'єму карбонатитів); серед другорядних виявлено апатит, тетраферифлогопіт і рихтерит, серед акцесорних – стронціаніт, монацит, пірохлор, баделеїт, ільменіт, магнетит, пірит. Визначено однорідний хімічний склад флогопіту. На підставі однорідності карбонатів і відсутності їхніх вторинних фаз з'ясовано температуру їхньої кристалізації (за геотермометром А. Таланцева) – 540 °C, що близько до температури кристалізації карбонатів, що співіснують, за ізотопними значеннями. Досліджений апатит збагачений стронцієм за значних варіацій співвідношення ізотопів стронцію. Ізотопний склад вуглецю й кисню в карбонатах родовища Сііліньярві також неоднорідний і часто не відповідає типовому для карбонатів із карбонатитів.

Ключові слова: карбонатити, магматичні силікатні породи, апатит, тетраферифлогопіт, петрогенезис, ізотопи C, O, Sr, Сііліньярві, Фінляндія.