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Metacarbonate Rocks (Calciphyres) of the Lapland–Kolvitsa Granulite Belt, Baltic Shield

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Abstract—Geological, petrochemical, and geochemical data are presented on metacarbonate rocks (calciphyres) of the Lapland–Kolvitsa granulite belt, Baltic Shield. The normative mineral composition of source rocks of the studied calciphyres was first reconstructed. High contents of some indicator elements (Fe, Mn, Cr, Co, P, Pb, and others) suggest that material supplied to the paleobasin was derived from diverse rocks (ultramafic, mafic, intermediate, and felsic). Contents and correlations of some trace elements (Sr, Li, F, Ba, and others) indicate that primary sediments formed under humid-semihumid paleoclimate in a fresh-water paleobasin (lagoon) characterized by occasional increase in salinity.

INTRODUCTION

It is known that Precambrian metacarbonate rocks bear important evidence on early sedimentation stages as well as emergence and evolution of life on the Earth. In addition, metacarbonate rocks often host lodes and occurrences of some mineral resources (Pb, Zn, P, and others). Hence, the study of Precambrian metacarbonate rocks is of great scientific and practical significance.

GENERAL INFORMATION

The Lapland–Kolvitsa granulite belt (LKGB) of the Baltic Shield represents an approximately 500-km-long arc-shaped structure, which is subdivided into two different-sized blocks: (1) Lapland block (Sal'nye Tundras, Tuadash Tundras, Lotta zone, Finnish Lapland, and Norwegian Lapland) and (2) small (~70 km) Kolvitsa Block (Kandalaksha and Kolvitsa Tundras) (Fig. 1). Rocks of the granulite complex underlie Caledonides of Polar Norway in the northwest and plunge beneath the Kandalaksha Bay of White Sea in the southeast.

By analogy with Saxonian granulites, high-grade Lapland metamorphic rocks were first described and termed as granulites by J. Jersnström in 1874. Subsequently, numerous works devoted to different issues of the geology of the granulite complex have been published in Russia and abroad. The list and review of these works have been reported in several monographs (Kozlov *et al.*, 1990; Vinogradov *et al.*, 1980; and others) and publications (Bibikova *et al.*, 1993; Ivliev, 1971; Mints *et al.*, 1994, 1996; and others). Despite the long history of study, the origin of rocks of the Lapland granulite complex remains a debatable issue. In recent years, most geologists (Bibikova *et al.*, 1993; Ivliev, 1977; Kozlov *et al.*, 1990; Mints *et al.*, 1994; 1996; and others) have suggested volcanosedimentary origin of the granulites. The granulite complex (~4 km) is subdivided into two sequences (Kozlov *et al.* 1990). The lower sequence consists of mafic granulites (garnet–plagioclase–pyroxene, plagioclase–pyroxene, and two-pyroxene crystalline schists) developed after metabasalts, metaandesites, and metadacites. The upper sequence mainly comprises metasedimentary felsic

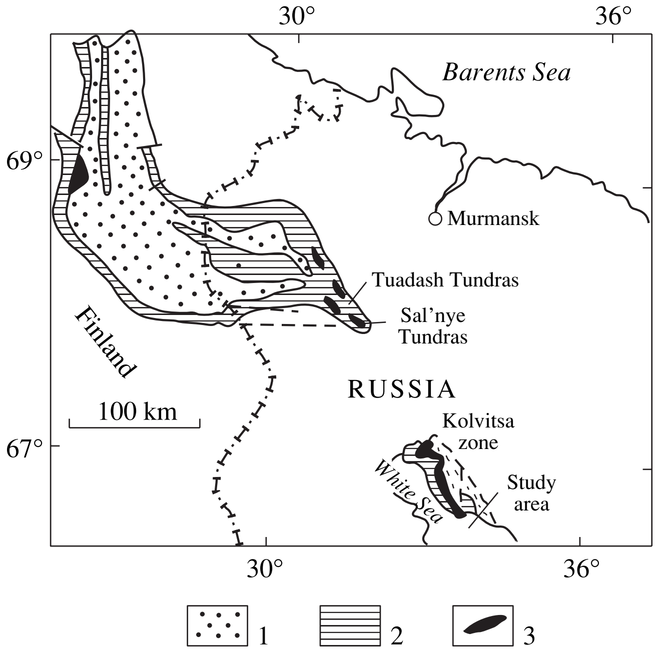

Fig. 1. Schematic location of the Lapland–Kolvitsa granulite belt of the Baltic Shield (Kozlov *et al.*, 1990). (1) Upper sequence, (2) lower sequence, (3) metagabbro–anorthosite massifs.

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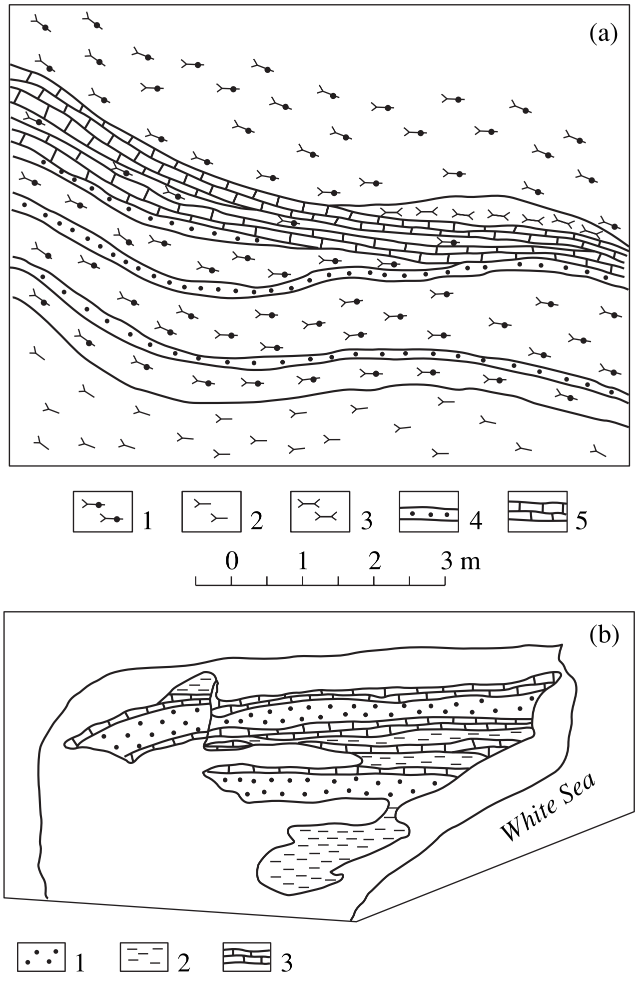

Fig. 2. Schematic geological map of the study areas in the Medvezhii and Kyzymshek islands. (a) Fragment of the Medvezhii Island area (Vinogradov *et al.*, 1980): (1) garnet–amphibole–diopside plagioschists, (2) garnet–two-pyroxene plagioschists, (3) plagioclase–hypersthene crystalline schists, (4) quartzites, (5) calciphyres. (b) Kyzymshek Island: (1) garnet–pyroxene plagioschists, (2) pyroxene–plagioclase crystalline schists, (3) calciphyres.

granulites (garnet–quartz–feldspar and sillimanite–garnet–quartz–feldspar rocks). Their abundance and thickness sharply increase to the west and reaches maximum in Finland (Fig. 1). Rocks of the LKGB overlie biotite–amphibole and kyanite–biotite–muscovite gneisses of the Korva Tundra and Karyaka Tundra formations in the central part of the belt and overlie gneisses and amphibolites of the Late Archean Belomorian Group in the east.

The metamorphic age of the rocks ranges between 1925 Ma (beginning of metamorphism) and 1870 Ma (cessation of metamorphism) (Bibikova *et al.*, 1993 and others). The protolith is supposed to be Early Proterozoic in age, although recent data indicate Pre-Proterozoic (Late Archean?) age of source rocks of the granulite complex (Mints *et al.*, 1996 and others).

The lower sequence of the granulite complex contains a small amount of metacarbonate rocks (calciphyres), which occur in the Kolvitsa zone and southeastern termination of the Lapland Block (Sal'nye and Tuadash Tundras) and are absent in the western areas (Lotta zone, Russia; Finnish and Norwegian Lapland areas).

This work is aimed at the petrochemical and geochemical study of metacarbonate rocks (calciphyres) mainly of the Kolvitsa zone at the reconstruction of their primary mineral composition and sedimentation conditions.

Metacarbonate rocks are most abundant in the Por'ya Bay area of the Kandalaksha Gulf (White Sea), where they are traced over 15 km within the Ploskaya Tundra sequence. The carbonate-bearing unit (80–100 m thick) was studied in the Medvezhii and Kyzymshek islands. It includes 5–10 m-thick horizons with calciphyre interbeds (from a few millimeters to 50–60 cm in thickness) intercalated with pyroxene, garnet–pyroxene, and other crystalline schists (Fig. 2). Individual beds of metacarbonate rocks are persistent in thickness and well traced over tens of meters along the strike.

Carbonate rocks typically serve as marking horizons and are distinguished by light color in aerial photographs. Relative to the harder rocks (quartzites, crystalline schists, and gneisses), which make up crests and cuesta, the carbonate rocks more rapidly erode and form depressions in the relief. Main indicator features of the carbonate-bearing bed of the granulite complex are depressions in relief, lighter color (with respect to the host crystalline schists) on the aerial photographs, and fine hatching (structural lines) reflecting the alternation of rocks with different physical properties (carbonate-free and carbonate-bearing varieties). Smoothed relief is typical of local areas with a significant thickness of metacarbonate interbeds. Thus, the studied carbonate-bearing bed is characterized by persistent continuation along the strike over many kilometers, constant thickness and composition, conformable bedding of compositionally different sheeted bodies involved in the folding, and fine intercalation of metacarbonate rocks with host crystalline schists that are almost rhythmically bedded. All these features suggest the primary sedimentary and volcanosedimentary origin of the metacarbonate rocks of.

Boudinage is typical of the carbonate-bearing rock unit. This process is developed in pyroxene schists and diopside rocks that are more rigid relative to the metacarbonate rocks. The lenslike shape of boudines gives the false impression of the formation of detached outliers owing to the introduction (metasomatism) of silicate material to carbonate substrate.

Metacarbonate rocks (calciphyres) of the granulite complex of the Baltic Shield are observed as light gray medium- to coarse-grained rocks, which often exhibit banded structure caused by the very fine layered distribution of colored minerals and granoblastic texture.

The calciphyres include dolomite, calcite, quartz, feldspars, diopside, olivine, and garnet with admixture of phlogopite inclusions, apatite, scapolite, and ore minerals. **Dolomite** typically forms equant untwinned grains. **Calcite** occurs as large polysynthetic-twinned irregular grains up to 4 mm across. **Diopside** accounts for up to 30–40% and occasionally forms large colorless grains with c : Ng = 40°, n_g-n_p = 0.032, and $2V = 64°$. It is replaced by tremolite and, more rarely, phlogopite. Rounded **olivine** grains are usually found as relicts among the reticulate serpentine and finely disseminated magnetite. They have high birefringence (n_g-n_p = 0.040, $2V = 84°$, and $n_g = 1.680$) and correspond to forsterite (Mg_2SiO_4) in composition. **Garnet** forms often well-shaped porphyroblasts up to 3–4 mm in size. **Phlogopite** is typically colorless or light brown and represented by large flakes (with inclusions of other minerals) or fine flakes developed after other minerals. In one sample (PB-17), we determined minor and accessory minerals (wt %): ilmenite 0.02, zircon 0.003, garnet 0.2, brown hornblende 0.1, pyrite 0.05, muscovite 0.2, chalcopyrite 0.0015, apatite 0.3, and titanite 0.5.

As mentioned above, the metacarbonate rocks (calciphyres) also occur in the Sal'nye Tundras region of the Lapland granulite complex (Table 1, samples CE-12 and CE-14). They are similar to the rocks described above; i.e., they also consist of calcite, dolomite, quartz, amphibole, and garnet. However, calciphyres of the Sal'nye Tundras region are characterized by the presence of (approximately 30 m thick and 1500 m long). According to (Ivliev, 1971), the above fact was confirmed by V.V. Lyubtsov (Kola Research Center, Apatity), I.N. Krylov and M.A. Semikhatov (Geological Institute, Moscow). In the bioherm base, calciphyre inliers are enveloped by stromatolitic buildups, which look like wide conjugate domal hillocks. In the middle and upper parts of the bioherm, the hillocks are smoothed and the bioherm acquires a slightly wavy surface. In terms of morphological features (predominance of low-angle wavy and plane layers intercalated with quartz beds), the stromatolites are similar to those reported from the Canadian Shield and Pechenga Group of the Kola Peninsula (Ivliev, 1971, 1977). According to our data, stromatolitic buildups are confined to the thickest areas of white calciphyres (Table 1, sample 1). In addition, these calciphyres and granulites are dominated by the garnet–quartz–feldspar assemblage and marked by graphite mineralization. For example, dark green calciphyres at the bottom and top of the stromatolite horizon contain from some flakes to 10 vol % graphite (Ivliev, 1971). Thus, the detection of traces of the vital activity of microorganisms (cyanobacteria) in the form of stromatolitic buildups and the carbon isotopic composition ($\delta^{13}C$ from –0.8‰ to –1.8‰), which corresponds to that of marine algae (Ivliev, 1977), suggest the biogenic nature of at least some part of the studied rocks.

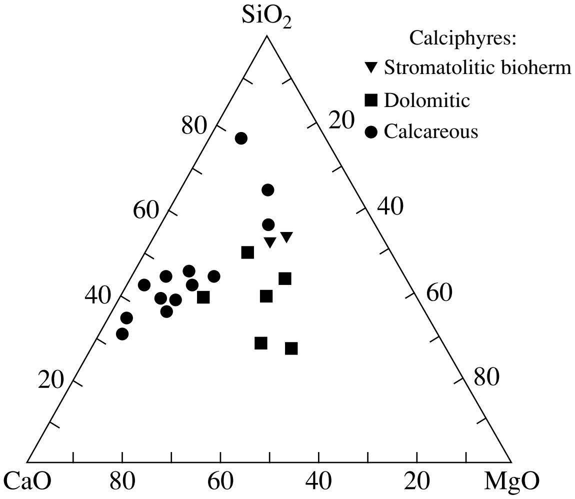

Fig. 3. The SiO_2–CaO–MgO diagram for calciphyres of the granulite complex.

Metacarbonate rocks (diopside calciphyres) in the Tuadash Tundras west of the Sal'nye Tundras also make up extended beds and lenslike bodies with the same minerals that are present in the calciphyres from other regions of the granulite complex (Kolvitsa zone and Sal'nye Tundras).

Metacarbonate rocks (marbles and calciphyres) are more abundant in some other Precambrian terrains. For example, metacarbonate rocks account for 3–10% of the Upper Archean Khapchan Group in the Anabar Shield and approximately 25% of the entire metasedimentary succession of the Aldan Shield. Metacarbonate rocks are also abundant in the Ukrainian Shield, southern and western areas of the Transbaikal region (Slyudyanka and Ol'khon groups), the Pamirs (Goran Group), and some other regions of the Earth (Khristoforova, 1990; Makrygina *et al.*, 1994; Vinogradov, 1975; Zlobin, 1988; and others).

MAJOR ELEMENT COMPOSITION

In terms of CaO and MgO contents and their ratios, the studied metacarbonates are subdivided into two groups that can be named as dolomitic and calcareous (calcitic) calciphyres. In terms of silicate admixture, they are subdivided into the silicate–carbonate (CO_2 20–30%) and carbonate–silicate ($CO_2 < 20\%$) rocks (Table 1, Fig. 3). With respect to the dolomite coefficient (M = MgO/CaO + MgO, wt %) (Zlobin, 1988), they range from the dolomitic limestone to dolomite and scarce magnesian dolomite ($M > 0.42$) (Table 1). In the MA'K diagram (Predovskii, 1980), data points of most calciphyres are plotted in the field of volcanosedimentary facies (Fig. 4).

Lithochemical calculations of normative mineral composition using the MINLITH program (Rosen *et al.*, 1999) showed that primary sediments could be composed of the sandy–carbonate material. The clastic component mainly consisted of quartz with less abun-

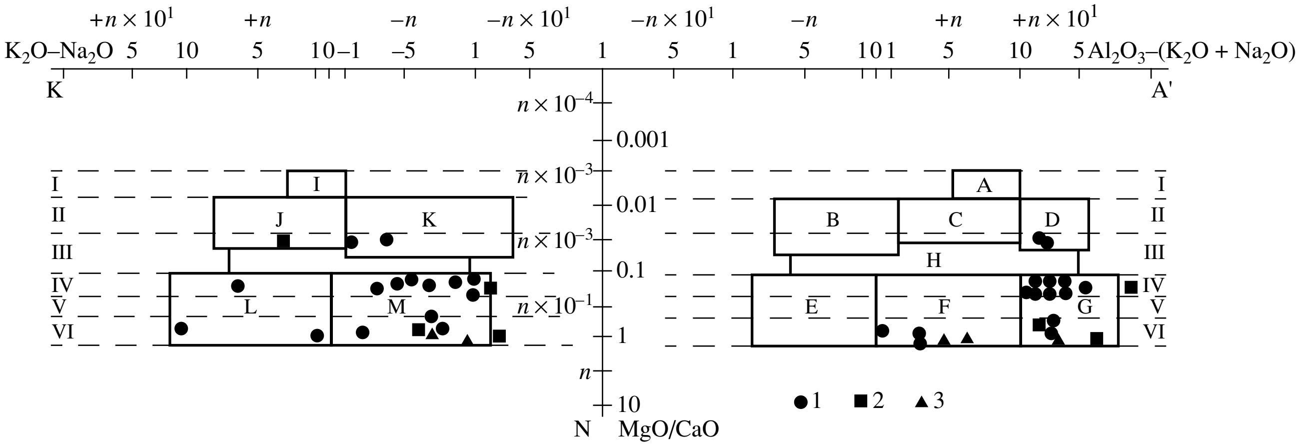

Fig. 4. The MA'K diagram (Predovskii, 1980) for calciphyres of the granulite complex. (1) Dolomitic and calcareous calciphyres (original data); (2) calciphyres of the Kolvitsa zone (Kozlov *et al.*, 1999); (3) pyroxene calciphyres of stromatolitic bioherm (Ivliev, 1971). Subdivisions with respect to relations between Mg and Ca contents: (I) limestones with the minimal Mg content, (II) normal limestones; (III) low-Mg limestones, (IV) dolomitic limestones, (V) calcareous limestones, (VI) dolomites. (A, I) Limestones of stable sedimentation zones with the minimal content of Mg and silicate admixture; (C, J) normal limestones; (D, J) clayey and pure limestones; (B, K) limestones of individual volcanosedimentary facies and calcareous tuffs; (N, H) low-Mg limestones ranging from rocks containing the terrigenous clayey admixture to rocks from the distal volcanosedimentary facies); (I, F, G in combination with L) dolomitic limestones, calcareous dolomites, and dolomites in the terrigenous–sedimentary facies); (I, F, G in combination with M) the same rocks but within the volcanosedimentary facies.

dant felsic plagioclase and subordinate K-feldspar (Table 2). The pelitic component could include a small amount of hydromica and chlorite and compositionally corresponded to normative montmorillonite characterized by the absence of kaolinite and smectite (Table 2). In contrast, the carbonate component included calcite and dolomite (Table 2).

Thus, primary carbonate rocks of the granulite complex were characterized by the maximal development of the carbonate–sandy (silty) composition. This is supported by the clustering of all data points in the clay–carbonate field (marls) of the ternary (carbonate–pelite–sand) diagram (Fig. 5). The same situation is observed in the feldspar–pelite–quartz diagram (modified after Pettijohn), where data points are plotted in the graywacke, subgraywacke, and quartzose sandstone fields and only approach the pelite field (Fig. 6).

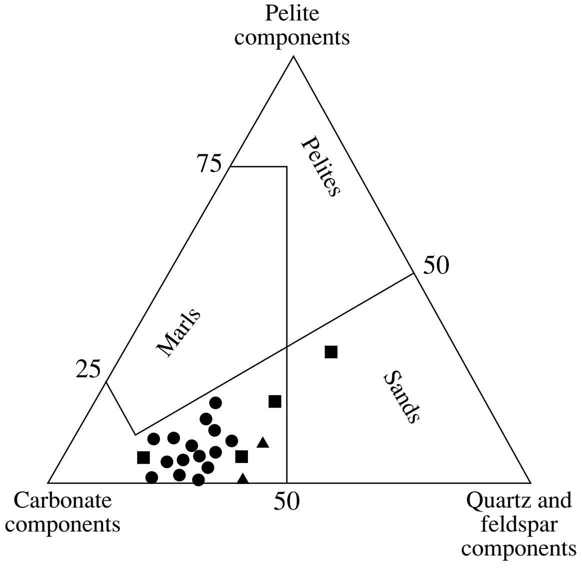

Fig. 5. The carbonate–pelite–quartz–feldspar diagram for the normative mineral composition of metacarbonate rocks of the granulite complex. Symbols are shown in Fig. 4.

All of the studied metacarbonate rocks are characterized by the occasionally significant predominance of FeO over Fe_2O_3, increase of several major oxides (SiO_2, Al_2O_3, Na_2O, and K_2O), and decrease of CaO and MgO owing to the introduction of terrigenous and volcanogenic–terrigenous material into the carbonate rocks.

GEOCHEMICAL FEATURES OF CALCIPHYRES

The study of the minor and rare composition (hereafter, trace element composition) of calciphyres (Table 3) showed that some **iron group** elements (Cr, Ti, Co, V, and Sc) well correlate with SiO_2 and Al_2O_3 (Fig. 7), indicating their delivery with the terrigenous and volcanogenic–terrigenous admixture. Ni also correlates with the total Fe. High contents of iron group elements, as well as Cu and Ba, in Sample M-509 (Tables 1, 3) may be explained by the significant delivery of silicate material to the primary sediments. Despite a small number of determinations of Mo, Pb, Zr, and Rb (Table 3), the results show their relation with felsic–intermediate material that was introduced into the sedimentary paleobasin. The observed positive Rb–K_2O correlation (Fig. 8) is typical of Phanerozoic sedimentary rocks and was undisturbed by the granulite-facies metamorphism.

Table 1. Chemical composition of calciphyres from the granulite complex, wt %

Ordinal no.	Sample no.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	S_{tot}	CO_2	L.O.I.	Total	M
Calciphyres of the Kolvitsa zone (Kozlov *et al.*, 1990)																	
1	283 B	20.09	0.04	2.65	0.98	2.76	0.36	1.91	41.61	0.11	0.50	–	–	–	–	–	0.0414
2	M-514	48.98	0.40	9.85	2.31	9.24	0.26	9.65	13.54	1.97	0.85	–	–	–	–	–	0.4116
3	M-740	51.62	0.17	3.77	0.83	5.45	0.28	14.14	21.15	0.60	0.62	–	–	–	–	–	0.3984
4	M-509	57.33	0.50	12.70	3.65	4.72	0.21	2.48	12.66	1.84	0.98	–	–	–	–	–	0.1520
Pyroxene calciphyres of stromatolitic bioherm (Ivliev, 1971)																	
5	1	51.47	0.17	3.88	0.59	1.76	0.086	17.14	19.52	0.82	0.36	0.13	–	2.14	0.72	99.70	0.4664
6	543	54.56	0.04	0.93	0.27	1.10	0.10	17.57	24.14	0.28	0.04	0.06	–	0.37	–	100.12	0.4211
Dolomitic calciphyres (original data)																	
7	PB-1	18.90	0.098	0.82	1.42	1.89	0.19	18.92	20.90	0.11	0.30	0.002	0.26	29.33	4.08	100.34	0.4743
8	PB-3	21.74	0.16	1.22	1.52	2.30	0.16	17.20	28.30	0.08	1.02	0.01	–	23.30	24.21	99.86	0.3750
9	CE-12	34.66	0.20	1.70	0.31	2.73	0.20	16.64	24.80	0.60	0.40	0.24	–	–	17.25	99.50	0.4000
10	143^{zh}	35.96	0.14	2.64	1.43	2.16	0.22	16.78	20.75	0.20	0.15	0.09	0.10	16.83	1.97	99.60	0.4467
11	PZ-55	36.74	0.25	4.27	0.54	4.07	0.34	10.75	20.26	0.61	0.44	0.11	0.14	21.90	0.94	100.36	0.3447
Calcareous calciphyres (original data)																	
12	PZ-63	22.93	0.18	2.70	0.32	3.27	0.37	1.65	42.61	0.26	0.02	0.21	–	23.85	1.19	99.56	0.0373
13	PB-17	25.70	0.25	3.81	0.80	3.95	0.46	4.64	36.45	0.94	0.23	0.18	–	20.20	22.14	100.61	0.1118
14	PZ-59	26.94	0.22	3.23	0.94	3.42	0.41	5.74	38.30	0.24	0.04	0.18	0.10	19.70	–	99.36	0.1301
15	143^{z}	27.76	0.14	3.42	1.83	2.41	0.43	5.97	36.78	0.60	0.08	0.14	0.12	19.73	0.32	99.97	0.1392
16	CE-14	29.85	0.27	2.40	0.28	1.65	0.10	9.00	32.60	0.22	0.90	0.27	–	–	21.89	–	0.2127
17	PZ-43	31.44	0.34	5.11	1.33	3.61	0.37	3.35	35.87	0.47	0.20	0.19	0.10	16.87	0.31	99.56	0.0845
18	PB-16	32.53	0.18	2.91	0.58	2.18	0.27	1.65	40.99	0.27	0.28	0.18	–	20.20	22.14	100.61	0.0373
19	143^{l}	34.50	0.26	5.09	2.70	3.12	0.50	6.12	33.13	0.46	0.08	–	0.10	13.28	0.79	100.03	0.1555
20	PE-23	34.64	0.28	5.76	2.80	3.95	0.53	6.72	34.00	0.24	0.05	0.16	–	10.80	10.70	100.31	0.1648
21	PZ-73	35.74	0.16	3.72	0.16	3.74	0.31	8.56	30.74	0.93	0.16	0.11	0.20	14.53	0.49	99.56	0.2172

Notes: (–) Data are absent. Analyses were performed in the chemical–analytical laboratory of the All-Russia Research Institute of Mineral Resources (Z.I. Belousova, V.R. Balasina, and V.M. Lur'e, analysts). M = MgO/CaO + MgO (wt %) is the dolomite coefficient (Zlobin, 1988).

Table 2. Normative mineral composition of calciphyres from the Lapland granulite complex

Components of primary rocks		Calciphyres																			
		Kolvitsa zone				bioherm		dolomitic					calcareous								
Mineral groups	Minerals	283-B	M-514	M-740	M-509	1	543	PB-1	PB-3	CE-12	143^{zh}	PZ-55	PZ-63	PB-17	PZ-59	143^{z}	CE-14	PZ-43	PE-16	143^{1}	PE-23
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Clastic	Quartz	14.98	24.03	33.45	29.67	32.69	37.94	13.41	14.91	24.23	28.25	27.29	16.92	15.58	19.27	18.51	21.79	20.55	24.07	22.62	21.93
	Plagioclase	1.09	15.55	4.38	14.12	5.96	2.11	1.18	0.44	4.79	1.53	5.43	2.12	7.76	2.00	5.01	1.54	3.62	2.01	3.44	1.91
	Orthoclase	–	–	–	–	–	–	1.04	5.23	1.64	–	–	–	–	–	–	2.67	–	–	–	–
	Total	16.07	39.58	37.83	43.79	38.65	40.05	15.63	20.58	30.66	29.78	32.72	19.04	23.34	21.27	23.52	26.00	24.17	26.08	26.06	23.84
Pelite	Kaolinite	–	–	–	–	–	0.56	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	Hydromica	3.55	5.67	3.40	7.68	2.38	–	0.89	–	0.27	0.99	3.10	–	1.34	–	0.65	3.07	1.34	1.95	0.64	0.30
	Montmorillonite	–	–	–	7.77	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	Chlorite	3.71	11.28	1.57	16.82	2.67	–	–	–	–	5.62	5.55	9.96	4.97	9.31	6.21	–	15.56	6.08	14.13	18.31
	Serpentine	–	–	–	–	4.11	0.40	9.06	–	-	0.43	–	–	–	–	–	–	–	–	–	–
	Total	7.26	16.95	4.97	32.27	9.16	0.96	9.95	–	0.27	7.04	8.65	9.96	6.31	9.31	6.86	3.07	16.90	8.03	14.77	18.61
Oxide	Goethite	–	–	–	–	1.80	1.09	3.25	–	1.17	2.92	–	–	–	–	–	–	–	–	–	–
	Pyrolusite	–	–	–	–	0.07	0.07	0.27	–	0.21	0.23	–	–	–	–	–	–	–	–	–	–
	Total	–	–	–	–	1.87	1.16	3.52	–	1.38	3.15	–	–	–	–	–	–	–	–	–	–
Carbonate	Calcite	64.32	–	–	18.26	–	–	–	2.31	–	–	7.42	68.72	45.40	48.26	43.71	29.32	56.03	61.42	41.35	42.30
	Dolomite	5.16	26.85	46.75	-	49.92	57.81	70.33	67.35	62.90	59.43	39.66	0.44	14.38	13.70	17.43	36.13	1.25	1.76	10.90	9.00
	Ankerite	6.60	11.21	6.39	4.90	–	–	–	9.42	4.31	–	10.21	0.78	9.31	6.21	7.24	4.54	0.38	1.80	5.82	5.05
	Siderite	–	4.69	3.58	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	Rhodochrosite	0.55	0.38	0.35	0.32	–	–	–	0.20	–	–	0.54	0.53	0.71	0.59	0.60	0.11	0.52	0.40	0.68	0.66
	Total	76.63	43.13	57.07	23.48	49.92	57.81	70.33	79.28	67.21	59.43	57.82	70.47	69.80	68.76	68.98	70.10	58.18	65.38	58.75	57.01
Minerals of Ti, P, and others		0.04	0.34	0.13	0.46	0.40	0.03	0.57	0.14	0.48	0.60	0.80	0.53	0.55	0.66	0.64	0.83	0.75	0.51	0.42	0.54

Notes: (–)Absent. Ordinal numbers are as in Table 1. Inferred source rocks: (1) clayey–sandy–calcareous, (2) clayey–sandy–carbonate, (3) quartz–carbonate, (4) carbonate–clayey-sandy, (5) clayey–sandy–dolomite, (6) sandy dolomites, (7) clayey–sandy dolomites, (8) sandy dolomites, (9) sandy dolomites, (10) clayey–sandy dolomites, (11) clayey–sandy–carbonate, (12) clayey–sandy–calcareous, (13–15) clayey–sandy–carbonate (essentially calcareous), (16) sandy–carbonates, (17) clayey–sandy–carbonate (essentially calcareous), (18) clayey–sandy–calcareous, (19) clayey–sandy–carbonate (essentially calcareous), (20) clayey–sandy–carbonate (essentially calcareous). Calciphyres are calculated for the normative mineral composition following the method given in (Rosen *et al.*, 1999).

The **boron content** in the studied rocks is significantly less (17 ppm in dolomitic and 12.1 ppm in calcareous calciphyres) than that in the Phanerozoic sedimentary rocks of the Russian Plate (61 ppm in carbonate sediments and 86 ppm in silty–sandy sediments) (Ronov and Migdisov, 1996). However, according to other determinations (Ovchinnikov, 1990; Yudovich, 1980; and others), the B content in the Phanerozoic sedimentary rocks is slightly lesser (18–20 ppm in carbonates and 35 ppm in sandstones). This content is only insignificantly higher than that in the studied calciphyres.

The **Ba content** in the studied calciphyres (Table 3) occasionally significantly exceeds the content in the Phanerozoic carbonate rocks and ranges from 63 to 120 ppm (Condie *et al.*, 1991; Ronov and Migdisov, 1996; Yudovich, 1980). The studied metacarbonate rocks show a relatively regular Ba distribution in different types: 100–360 ppm (average 198 ppm) in dolomitic rocks and 100–380 ppm (average 214 ppm) in calcareous rocks. One can suggest that primary sediments derived Ba mainly from the silicate (terrigenous and volcanogenic–terrigenous) material. This is confirmed by the Ba–(SiO_2 + Al_2O_3) correlation (Fig. 9).

The **Sc content** in calciphyres of the granulite complex (10–32 ppm, average 22.2 ppm for 13 samples) is closer to the content in the mafic rocks (clarke 30 ppm) rather than that in the Phanerozoic sedimentary rocks (9 ppm in sandstones and 2.2 ppm in carbonate rocks). The Sc content in felsic granulites (essentially, garnet–quartz–feldspar rocks) of the granulite complex shows variation range similar to that in the calciphyres (3–35 ppm, average 15.8 ppm). Similar value of 14 ppm (average from six analyses) for felsic granulites was obtained by other authors (Mints *et al.*, 1994). Thus, the Sc content in metacarbonate rocks (calciphyres) is higher than that in silicate rocks and felsic granulites. This is likely to be a characteristic feature of rocks of the studied complex. For example, metacarbonate rocks of the Khapchan Group (Anabar Shield) are characterized by a different Sc distribution. The Sc content in garnet gneisses and granulites (2–35 ppm, average 14.3 ppm) is similar to the average Sc content and variation in granulites of the Baltic Shield, whereas metacarbonate rocks have lower Sc contents (2–15 ppm, average 6.8 ppm for 12 samples).

Thus, the data presented above indicate that the material delivered to metacarbonate sediments of the granulite complex of the Baltic Shield was enriched in Sc relative to the essentially sandy rocks, felsic granulites, and carbonate sediments of the Khapchan Group (Anabar Shield).

Manganese is the characteristic element of carbonate rocks. In the studied rocks, its content varies from 0.08 to 0.41% (Table 3), which is universally higher than that in the Phanerozoic carbonate rocks (0.04–0.07%) (Ronov and Migdisov, 1996 and others). The Mn content in calcareous varieties of the studied

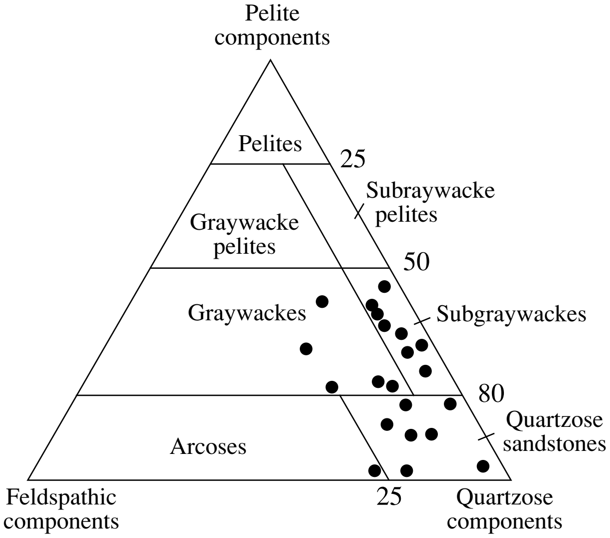

Fig. 6. The Pettijohn (feldspar–pelite–quartz–feldspar) diagram for the primary silicate composition of calciphyres from the granulite complex.

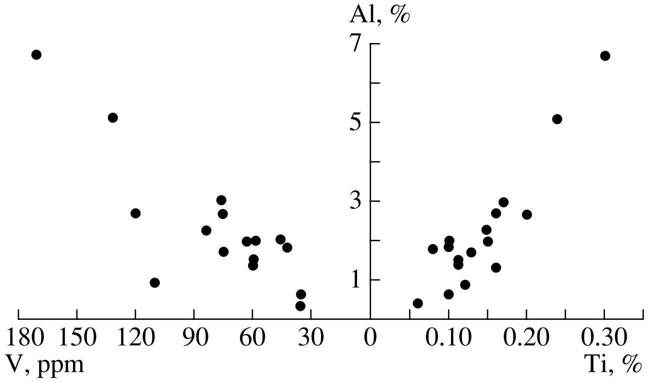

Fig. 7. V and Ti vs. Al in calciphyres of the granulite complex.

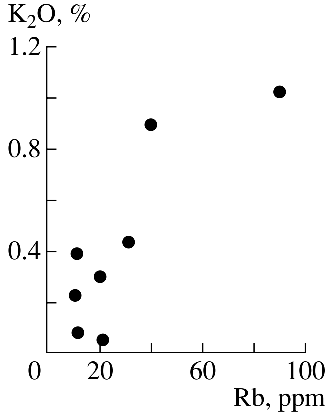

Fig. 8. Rb vs. K_2O in calciphyres of the granulite complex.

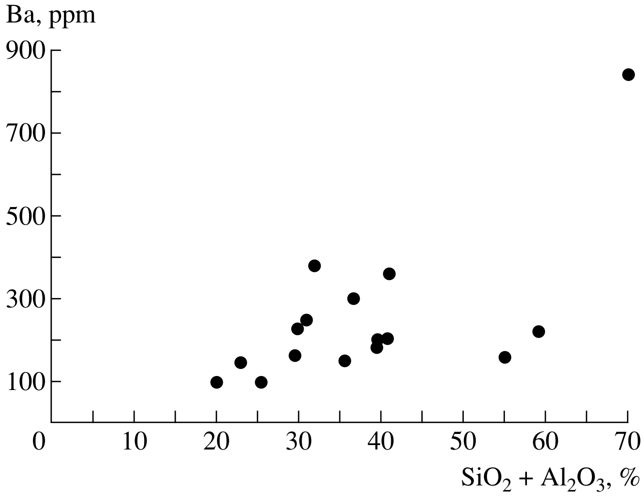

Fig. 9. ($SiO_2 + Al_2O_3$) vs. Ba in calciphyres of the granulite complex.

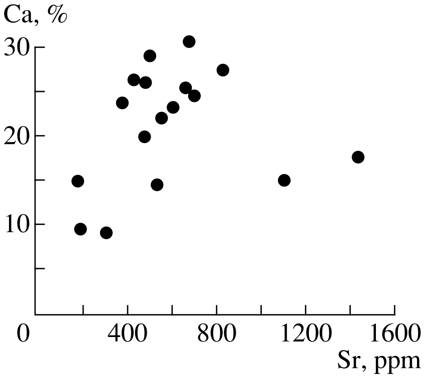

Fig. 10. Sr vs. Ca in calciphyres of the granulite complex.

calciphyres (0.29%, on the average) is higher than that in dolomitic calciphyres (0.18%, average from 7 samples). Phanerozoic dolomites depleted in Mn (relative to limestones) are generally considered sedimentary-diagenetic rocks formed after the primary calcareous sediment (Yudovich, 1981).

According to (Ronov and Ermishkina, 1959), the high Mn content in carbonate rocks indicates humid climate, whereas the low Mn content suggest arid climate. This regularity is observed in the metacarbonate rocks (marbles and calciphyres) of the Khapchan Group (Anabar Shield), which are considered to be formed in an evaporitic paleobasin (Zlobin, 1988). The MnO content in these rocks varies from 0.01 to 0.24% (0.038%, average from 30 analyses).

Thus, the Mn content in the studied calciphyres of the granulite complex indicates that the primary carbonate sediments accumulated in a normal-salinity paleobasin under humid conditions.

Strontium is one of the carbonate-associated trace elements geochemically related to Ca, since it has similar sizes of ionic radii (Ca = 1.04 Å, Sr = 1.20 Å) and can substitute Ca in crystal lattice of carbonate minerals. The studied calciphyres also show Sr–Ca correlation (Fig. 10), suggesting that even the granulite metamorphism (750–900°C, P = 8–10 kbar) could not completely disturb the Sr–Ca bond, which is typical of the sedimentary and low-grade Phanerozoic and Precambrian rocks.

The clarke value for Sr in the Phanerozoic carbonate sediments is 540 ppm (Ovchinnikov, 1990), while the average Sr content in the Phanerozoic carbonate rocks of the Russian and Chinese platforms is 325 ppm (Ronov and Migdisov, 1996). Other authors report different average Sr contents in carbonate sediments: 450 ppm (Yudovich, 1980) and 400 ppm (Condie *et al.*, 1991).

Thus, the Sr content in calciphyres of the granulite complex is insignificantly higher than all values presented above, the dolomitic varieties (Ca 14.46%) being enriched in Sr (603 ppm) relative to the calcareous ones (580.5 ppm, Ca 25.84%). Such Sr distribution is a characteristic feature of the studied rocks. The general elevated Sr content together with its higher content in dolomitic calciphyres suggests a relatively high salinity of the sedimentation paleobasin.

The **Li content** in the studied metacarbonate rocks ranges from 1.6 to 37.0 ppm (average 11.8 ppm for 13 samples). Silicate rocks (felsic granulites) from the same complex have a lower Li content (4.4–19.0 ppm, average 8.6 ppm for 13 samples). However, felsic granulites and garnet gneisses of the Khapchan Group (Anabar Shield) have higher Li contents relative to metacarbonate rocks (Zlobin, 1988). Phanerozoic silicate rocks are also enriched in Li (65–69 ppm in sandy shales and 20–21 ppm in sandstones) as compared to carbonate sediments (6.9–10.0 ppm) (Ovchinnikov, 1990; Ronov and Migdisov, 1996). This is explained by the similar ionic radii of some elements (Li 0.68 Å, Mg^{2+} 0.74 Å, Al^{3+} 0.57 Å, and Fe^{2+} 0.80 Å) and, correspondingly, Li accumulation in the Mg–Fe minerals (amphibole, biotite, and others) and aluminosilicates (muscovite, hydromica, and others).

Thus, higher Li contents in calciphyres relative to felsic granulites reflect a characteristic feature of granulite rocks of the Baltic Shield. This can be related to the higher Li content in materials delivered to the sedimentation paleobasin during the lower sequence formation and the presence of Li-bearing minerals (pyroxenes, amphiboles, phlogopite, and others). The formation of the upper sequence could be accompanied by the lower Li delivery to the paleobasin, while the mineral composition of felsic granulites dominated by the quartz–feldspar assemblage (up to 84–92%, according to (Bibikova *et al.*, 1993)) did not facilitate the accumulation of Li (without taking into account biotite).

The **F content** in calciphyres ranges between 280 and 1800 ppm, with the highest contents (1500–1800 ppm) being observed in the dolomitic varieties.

Table 3. Trace element composition of calciphyres from the Lapland granulite complexe and Phanerozoic rocks

Ordinal no.	Sample no.	Cr	Ni	Co	V	Cu	P	Sc	Mo	Pb	Zr	B	Ba	Sr	Rb	Li	F	Ti	Mn	Fe	Al
Calciphyres of the Kolvitsa zone (Kozlov *et al.*, 1990)																					
1	M-514	140	74	26	130	11	–	–	–	–	–	10	220	180	–	–	–	0.24	0.20	8.80	5.21
2	M-740	35	41	10	46	5	–	–	–	–	–	6	160	180	–	–	–	0.10	0.22	4.82	1.99
3	M-509	170	210	43	170	170	–	–	–	–	–	–	840	310	–	–	–	0.30	0.16	6.22	6.72
Dolomitic calciphyres (original data)																					
4	PB-1	17	–	5	36	–	9	27	–	–	–	20	100	1100	20	1.9	1500	0.06	0.15	2.46	0.43
5	PB-3	41	18	16	35	20	44	10	3	17	30	26	150	480	90	16.0	1800	0.10	0.12	2.85	0.65
6	CE-12	100	85	22	110	90	1047	32	–	51	70	32	90	1430	10	22.0	–	0.12	0.15	2.34	0.90
7	PZ-55	67	50	5	83	50	480	25	–	–	–	8	360	540	30	7.2	–	0.15	0.26	3.54	2.26
Calcareous calciphyres (original data)																					
8	PZ-63	57	25	5	60	–	916	20	–	–	–	7	100	680	–	1.6	–	0.11	0.29	2.77	1.43
9	PB-17	72	45	22	58	40	786	15	4	15	40	12	160	480	10	16.0	470	0.15	0.36	3.63	2.02
10	PZ-59	58	27	5	74	40	786	30	–	–	–	12	230	840	–	4.2	420	0.13	0.32	3.32	1.71
11	143^{z}	32	–	5	42	32	611	16	–	–	–	5	250	425	10	8.4	280	0.08	0.33	3.16	1.81
12	CE-14	60	10	6	60	80	1178	30	1	25	70	20	380	600	40	20.0	–	0.16	0.08	1.48	1.27
13	PZ-43	70	17	5	120	–	829	–	–	–	–	16	300	660	–	37.0	430	0.20	0.29	3.74	2.70
14	PB-16	47	13	5	61	–	786	27	–	–	–	–	150	480	–	–	–	0.11	0.21	2.10	1.54
15	143^{1}	38	63	40	75	–	–	16	2	6	–	–	180	380	–	3.0	600	0.16	0.39	4.31	2.69
16	PE-23	7	52	24	75	55	698	20	2	16	40	19	200	700	20	7.8	720	0.17	0.41	5.03	3.05
17	PZ-73	60	60	5	63	–	480	21	–	–	100	6	190	560	–	8.2	760	0.10	0.24	3.02	1.97
Phanerozoic rocks: sedimentary (Ronov and Migdisov, 1996) and igneous (Ovchinnikov, 1990)																					
Sandstones		36	23	8.6	59	23	480	9	0.7	22	196	86	455	154	76	21.0	363	0.33	0.08	2.24	4.22
Carbonates		13	6	2.1	16	7	349	2.2	–	20	32	61	63	325	15	10.0	581	0.06	0.04	0.78	0.75
Mafic rocks		180	140	48	240	92	1300	30	1.4	6	130	5	290	460	37	15.0	400	1.07	0.17	8.56	8.22
Andesites		54	41	14	140	43	1350	18	1.0	11	170	12	410	410	80	27.5	500	0.61	0.12	5.36	8.95
Granites		5.6	3.5	1	38	10	600	6.5	1.5	19	180	12.5	750	150	180	37.0	820	0.16	0.04	1.56	7.27

Notes: (–) Data are absent. The Ti, Mn, Fe, and Al contents are given in %; other elements, in ppm. Analyses were performed in the Spectral Laboratory of the All-Russia Research Institute of Mineral Resources (K.V. Barsuk, O.A. Plotnikova, and N.V. Pavlova, analysts).

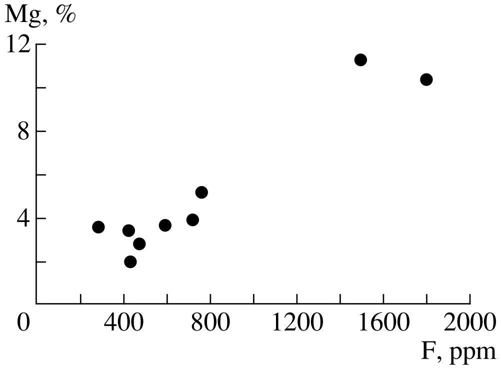

Fig. 11. F vs. Mg in calciphyres of the granulite complex.

Elevated F contents are also observed in other regions: up to 1700–2000 ppm (1300 ppm, on the average) in the Anga Group of the western Baikal region (Makrygina *et al.*, 1994), up to 2200–2600 ppm in the metacarbonate rocks of the Anabar Shield. This is attributed to evaporitization in the paleobasin (Zlobin, 1988 and others). Calcareous calciphyres of the granulite complex are also enriched (although to a lesser extent than the dolomitic varieties) in F (Table 3). The average F content in them (527 ppm, based on seven samples) is significantly higher than the clarke value of 330 ppm for the Phanerozoic carbonates (Ovchinnikov, 1990), but this value is close to that in carbonate rocks of the Russian Plate (581 ppm). The F content in the studied calciphyres well correlates with the Mg content (Fig. 11). Such correlation is typical of carbonate rocks of the arid zone (Ronov *et al.*, 1974 and others).

The **P content** in the studied rocks widely varies (9–1178 ppm), with the highest variations being typical of the dolomitic varieties (Table 3). The average P content in calcareous calciphyres (786 ppm, based on nine samples) is more than two times higher than that in the Phanerozoic carbonate rocks (349 ppm). The high P content in these rocks suggests that the volcanogenic–terrigenous material was dominated by intermediate–mafic rocks with the P content up to 1300–1500 ppm (Ovchinnikov, 1990).

DISCUSSION

Data presented in Table 1 and results of lithochemical calculations (Table 2) show that all of the studied rocks (with rare exception) were primarily represented carbonate sediments (i.e., calcareous and dolomitic sediments) with the subordinate pelitic component. Presumably, material delivered to the sedimentation paleobasin was relatively weakly differentiated. This is indicated by the universal presence of hydromica, chlorite, and plagioclase (occasionally, up to 14–15%) in the normative composition (Table 2). Similar rocks can be formed in the coastal zone of the paleobasin, from which the fine-grained material was removed to the deeper zones. The shallow-water environment is also confirmed by the finding of stromatolitic bioherm, which formed in the photosynthesis zone (Serebryakov and Semikhatov, 1975).

The high contents of some indicator elements (Fe, Mn, Cr, Co, P, Pb, and others) in calciphyres (Table 3) indicate that the material delivered to the sedimentation paleobasin was derived from a wide spectrum of mafic to felsic rocks. The significant contents of Cr (up to 100–170 ppm), Ni (up to 85–210 ppm), and Co (up to 40–43 ppm) and the occasional presence of serpentine and goethite (Table 2) suggest the contribution of ultramafic material.

The presence of graphite in calciphyres and other metamorphic rocks of the granulite complex (granulites and schists), traces of the vital activity of protozoa (stromatolites), the carbon isotopic signature corresponding to that of marine algae (Ivliev, 1977) indicate a biogenic nature of at least some part of carbonaceous matter (graphite) and well-developed organic life in the paleobasin. In many Precambrian metacarbonate sediments of the world, one can find the carbonaceous matter (graphite), stromatolitic bioherms, oncolites, organic compounds, and bitumoid occurrences (Khristoforova, 1990; Makrygina *et al.*, 1994; Safronov, 1981; Safronov and Ivliev, 1995; Safronov and Stepanova, 1993; Serebryakov and Semikhatov, 1975; Vinogradov, 1975; and Zlobin, 1988).

Positive correlations between Ti, Cr, V, and Al_2O_3 in the studied rocks indicate that these elements were delivered from the terrigenous and volcanogenic–terrigenous materials. The correlation between Rb and K is typical of the normal sedimentary rocks (Makrygina and Petrov, 1971), because this bond is disturbed by metasomatism; i.e., the studied rocks are products of primary sedimentary rather than metasomatic rocks. This is supported by high Sc contents (Table 3) in the granulite rocks relative to the metasomatic rocks that are usually depleted in Sc. For example, metasomatic diopside rocks of the Aldan Shield contain 2–8 ppm Sc (Krylova *et al.*, 1975).

The positive correlation between Ba and (SiO_2 + Al_2O_3) (Fig. 7) suggests its delivery with the silicate component in a sedimentation setting without evaporitization. In the opposite case, Ba should be related with carbonate matter of the rocks. The high MnO contents in the studied calciphyres (Tables 1, 3) indicate humid paleoclimate (Ronov and Ermishkina, 1959). This is supported by the comparison with metacarbonate rocks of the Khapchan Group (Anabar Shield), which formed in evaporitic paleobasin (Zlobin, 1988) with the average MnO content of 0.038% (based on 30 analyses) similar to that in carbonate rocks of the arid zone (0.041%) (Ronov and Ermishkina, 1959).

Thus, sedimentation in the study region occurred under humid–semihumid conditions in the fresh-water lagoon with temporal increase of water salinity. This is indicated by wide variations in the contents of indicator-elements, such as Li, Sr, and F (Table 3), the Sr/Ba ratio, and the B* index (8.5 × B/K_2O) ranging within 82–680. The B* value is as much as 300 in fresh waters, 300–600 in low-salinity waters, and more than 600 in normal salinity waters (Walker and Price, 1963).

CONCLUSIONS

(1) The set of characteristic features (thin intercalation, small thickness, occasional lenslike morphology of calciphyre layers, the predominance of calciphyres with a variable content of sandy material, and so on) indicates a shallow-water sedimentation paleobasin. This is also confirmed by the presence of stromatolitic bioherm, which typically forms in the littoral and sublittoral zones of paleobasins (Serebryakov and Semikhatov, 1975), and high MnO contents (up to 0.50–0.53%) (Ronov and Ermishkina, 1959).

(2) The presence of carbonaceous matter (graphite) in the studied rocks, occasional significant S_{tot} contents (up to 0.20–0.26%), and the universal predominance of FeO over Fe_2O_3 indicate reduced sedimentation setting.

(3) The presence of graphite in rocks of the granulite complex, traces of the vital activity of microorganisms (stromatolites), and the carbon isotopic composition suggest the existence of organic life in the sedimentation paleobasins owing to a significant delivery of important trace elements (Fe, Mn, V, P, and others).

(4) High contents of some major (Fe, Mn, and others) and trace (Cr, Ni, Co, P, Pb, and others) elements suggest that terrigenous and volcanogenic–terrigenous material delivered to the paleobasin was derived from diverse (ultramafic, mafic, intermediate, and felsic) rocks.

(5) Contents of some indicator-elements (Mn, Sr, Li, and F), the Sr/Ba ratio (>3), and correlations between elements suggest that the primary sediments accumulated in a lagoonal paleobasin under semihumid and humid settings.

(6) The enrichment of calciphyres in Sc and the positive correlation of Rb, K_2O, Ti, and V with Al are consistent with the sedimentary origin of metacarbonate rocks of the granulite complex of the Baltic Shield.

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