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Geochemistry and Formation Conditions of Rare-Metal Granites with Various Fluorine-Bearing Minerals (Fluorite, Topaz, and Cryolite)

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Abstract—A comparative geochemical study of rare-metal granitoids with various fluorine-bearing minerals (fluorite, topaz, and cryolite) was carried out. It was shown that these rocks correspond to both plumasitic and agpaitic geochemical types. The fluorite-, topaz-, and cryolite-bearing granites of these geochemical types are distinctly different in geochemical parameters and the character of magmatic evolution. These differences are related to the composition of initial magmas and their sources. Rare-metal granitoids with fluorine-bearing minerals compose small massifs, stocks, and dike swarms. Their formation is independent of the composition and age of the country rocks or geologic structures where they occur.

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INTRODUCTION

Rare-metal lithium–fluorine granites have attracted increasing attention over recent years owing to their unusual (compared to normal granites) geochemical characteristics: primarily, high concentrations of F, Li, Rb, Cs, Be, Sn, W, Ta, Nb, and other elements. These fairly rare natural rocks have been a focus of much interest because of the desire of researchers to evaluate the possible sources of such chemically peculiar magmas and a practical need to unravel their genetic link to ore mineralization. A characteristic mineralogical feature of rare-metal granites is the occurrence of various fluorine-bearing minerals (fluorite, topaz, and cryolite) and F–Li micas. The fluorine content of these rocks varies considerably from 0.3–0.5 to 5–8%.

This paper presents a comparative analysis of petrographic, mineralogical, and geochemical data and the conditions of the formation of Li–F granites from various regions of the world. It was shown that such rocks occur among the granites of plumasitic and agpaitic geochemical types. Thus, the comparative analysis of granites with various fluorine-bearing minerals supported the idea of Tauson [1] that rare-metal granites should be assigned to the Li–F facies of the appropriate geochemical type. The possibility of fluorite, topaz, and cryolite crystallization from natural magmas may suggest that they are formed within a wide range of physicochemical and geochemical parameters and concentrations of fluorine in magmatic melt and coexisting fluid.

These features are considered below by the example of several occurrences of rare-metal granites with fluorine-bearing minerals from various regions.

URUGUDEI–UTULIK INTRUSION–DIKE SUITE OF THE HAMAR-DABAN RANGE, BAIKAL REGION

The Urugudei–Utulik belt of intrusions and dike swarms is located in the Selenga–Vitim structural zone, the major portion of which is occupied by the Late Paleozoic Angara–Vitim granitoid batholith. Small intrusions of rare-metal granites (Kharagul and Urugudei) occur in the region of Urugudei Peak (2758 m) in the western part of the belt. They are made up of early fluorite-bearing biotite granites and late topaz-bearing microcline (amazonite)–albite granites [2]. Dikes of various compositions are more common in the eastern (Utulik) part of the belt. They are composed of both melanocratic (monzogabbro, monzodiorite, and, occasionally, quartz monzonite) and more felsic rocks (granosyenite porphyry, subalkaline granite porphyry, ongonite, and topazite). The Urugudei–Utulik belt of small intrusions of rare-metal Li–F granites and leucogranites and predominantly silicic dikes extends within the Khamar-Daban Range of the Baikal region by over more than 100 km at a width of 5–6 km. The rocks are 318–321 Ma old.

Micas have the most variable compositions among the major minerals of rare-metal granites. The fluorite-bearing granites contain Li-biotite and protolithionite, whereas lithium richer mica varieties, zinnwaldite and ferroan lepidolite were found in the topaz-bearing vari-

Table 1. Average chemical compositions of the rare metal granites and ongonites of the Baikal region

Component	Khamar-Daban Range			
	fluorite-bearing granites (11)	topaz-bearing granites (50)	topaz- and cryolite-bearing	
			granites (3)	ongonites (8)
SiO_2	72.36	74.52	73.05	69.84
TiO_2	0.07	0.06	0.02	0.04
Al_2O_3	14.59	14.54	14.87	18.04
Fe_2O_3	0.94	0.34	0.77	0.62
FeO	0.97	0.35	0.32	0.17
MnO	0.08	0.11	0.05	0.05
MgO	0.05	0.05	0.08	0.13
CaO	0.50	0.17	1.25	0.54
Na_2O	4.82	5.09	3.94	5.54
K_2O	4.97	3.76	3.30	2.17
P_2O_5	0.05	0.09	0.02	0.03
LOI	0.61	0.50	1.14	1.43
F	0.32	0.57	1.84	3.07
Li	295	667	410	714
Rb	450	835	380	510
Cs	11	24	4	7
Ba	52	53	85	119
Sr	24	28	97	108
Sn	25	60	183	152
Pb	84	112	128	30
Zn	133	109	86	25
Nb	50	53	41	52
Ta	9	28	16.5	50
Zr	171	69	66	52
Hf	7.7	7.3	3.6	3.5
K/Rb	92	37	67	35
Nb/Ta	5.5	1.89	2.5	1.04
Zr/Hf	22	9.5	18.3	15
La/Yb	2.75	2	2.7	2.6

Note: The number of analyses is shown in parentheses. Oxides are in wt %, and elements are in ppm. The compositions were determined at the laboratories of the Vinogradov Institute of Geochemistry, Siberian Division, Russian Academy of Sciences using routine chemical analysis for major oxides and ICP MS and flame photometry for trace elements.

eties of granites. Li phengite–muscovite was sometimes observed in association with protolithionite. The fluorite-bearing granites often show a porphyritic texture, and K–Na feldspar is usually more abundant (on average 43.7%) in them than plagioclase (oligoclase, up to 22.8%). The rocks contain up to 1.5% fluorite and 1% magnetite. The microcline and amazonite–albite granites are composed mainly of quartz (40.8–30.3%), albite nos. 3–6 (43.4–25.5%), and microcline (32.4–24.5%). In addition to lithium micas, they contain topaz (up to 1.2%) and often fluorite (less than 1%). Their accessory minerals are cassiterite, monazite, cyrtolite, columbite–tantalite, pyrochlore, and, occasionally, allanite, xenotime, and manganotantalite.

In the Utulik flank of the belt, only the apical part of a leucogranite stock is exposed. The rocks are similar in composition to the aforementioned microcline–albite granites, but contain protolithionite (2.0–4.5%), as well as topaz, fluorite, and cryolite (1–3% in total). Their accessory minerals are zircon, apatite, monazite, ilmenite, cassiterite, wolframite, tourmaline, magnetite, and pyrite. The ongonites contain 1.0–1.5% of fluorine-bearing minerals (fluorite, topaz, and cryolite). The most abundant among them is topaz, which forms both rare prismatic phenocrysts and radiated aggregates in the interstices between other mineral grains.

Table 1 gives the chemical compositions of the main varieties of granites and ongonites with fluorine-bearing minerals from the Baikal region. The examination of these data suggests that all the rock types have rather high alkali and low MgO, CaO, MnO, and TiO_2 concentrations. The fluorite-bearing granites show $K_2O/Na_2O > 1$, whereas the topaz- and cryolite-bearing rocks always have $Na_2O > K_2O$. The cryolite-bearing rocks are also most enriched in fluorine, although high fluorine content is characteristic of all the rare-metal rocks considered here. The prevalence of Al_2O_3 over alkalis, especially in the ongonites (up to 18% Al_2O_3), allow us to classify these rocks as plumasitic.

In addition to fluorine, the rocks are rich in Li, Rb, Cs, Be, Sn, Ta, and Nb. Compared with the fluorite-bearing granites, the rare-metal rocks with topaz and cryolite are enriched in F, Li, Sn, and Ta; the maximum enrichment of these elements was observed in the latest subvolcanic ongonites. Compared with them, the early fluorite-bearing granites are somewhat enriched in Be, Zn, and Zr. All the rocks have relatively low Ba and Sr concentrations compared with their average abundances in granitic rocks. The main characteristics of the geochemical evolution of fluorite-, topaz-, and cryolite-bearing rare-metal granites of the Baikal region are also manifested in variations in indicator trace-element ratios, which suggest an important role of magmatic and fluid–magmatic crystallization differentiation during their formation [2, 3].

IVIGTUT GRANITES AND ASSOCIATED CRYOLITE DEPOSIT, SOUTH GREENLAND

The Ivigtut deposit has been studied for 100 years and was long considered as the only cryolite deposit in the world. It was undoubtedly related to the formation of a granite massif, because the extended body of siderite–cryolite composition is confined to the apical part of a domelike stock of leucocratic fine-grained porphyritic

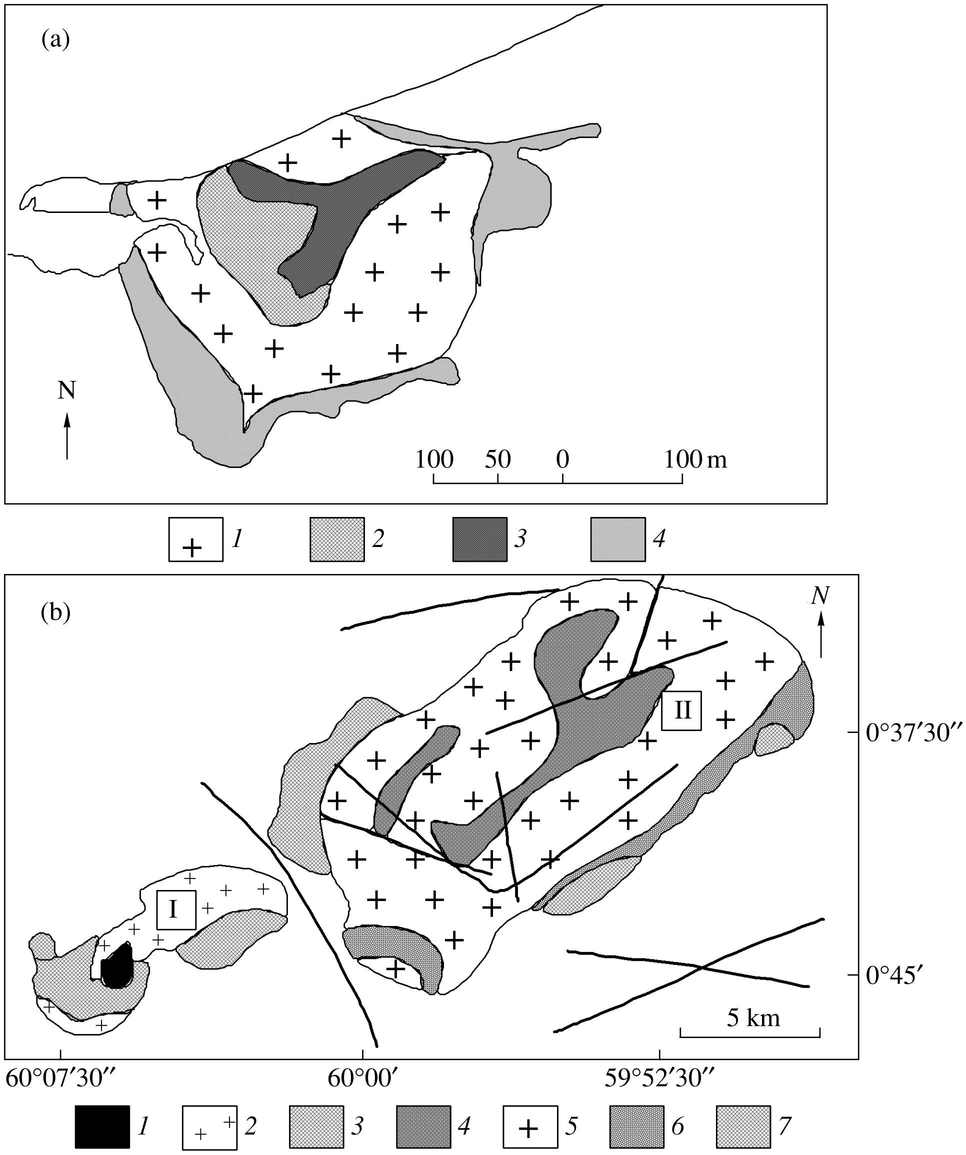

Fig. 1. Sketch maps showing the geologic structures of the (a) Ivigtut deposit in Greenland and (b) Pitinga deposit in Brazil. Ivigtut [4]: (*1*) granite, (*2*) pegmatite, (*3*) cryolite ore, and (*4*) intrusive breccia. Pitinga [9]: (I) Madeira Complex—(*1*) albite granite with cryolite, (*2*) biotite granite, (*3*) rapakivi granite; (II) Aqua Boa Complex—(*4*) topaz granite, (*5*) biotite granite with topaz, (*6*) porphyritic biotite granite, and (*7*) rapakivi granite.

granites, which occur in brecciated gneissic rocks (Fig. 1a). The granite stock is 300 m in diameter and expands with increasing depth. The Ivigtut granite cuts a complex of Archean gneisses with gabbro-anorthosites. The age of the granites was constrained as 1248 ± 25 Ma by the Rb–Sr isochron obtained for main rock varieties [4]. The initial $^{87}Sr/^{86}Sr$ ratio of the granites is 0.7125 ± 0.0048. Recently, a Rb–Sr age of 1141 ± 61 Ma was obtained on the basis of four granite samples (top granite), and the Sm–Nd system yielded an age of 1230 ± 140 Ma and ε_{Nd} values between –3.6 and –2.9 for the granites not affected by secondary alterations [5]. The Ivigtut massif is located in the coast of the Arsuk Fjord of South Greenland and belongs to a series of alkaline central-type intrusions in the Gardar magmatic province. White and gray varieties were distinguished among the Ivigtut granites, which are composed mainly of potassium feldspar (microperthite) and quartz grains, up to 1 cm in size, embedded in a fine-grained groundmass of quartz, microperthite, biotite, and amphibole. The amphibole is represented by Fe-edenite, and riebeckite was found in one sample [5]. The white granite contains albite. The minor minerals of the granites are zircon, fluorite, cryolite, and siderite. Cryolite is usually confined to the interstices between other minerals, and its content may be as high as 15–20%. The siderite–cryolite body is situated in the central part of the granite stock and extends to a depth of almost

150 m. A complex network of quartz–microcline pegmatite veins occurs in the granites of the contact zone. Most of these veins are confined to the southern contact of the siderite–cryolite body. Its apophyses cut the pegmatites, and the granites host cassiterite–quartz and cryolite–quartz veins. The average mineral composition of the siderite–cryolite body has been reported by many investigators as 70–80% cryolite, 15–20% siderite, 1–2% quartz, and 1–2% sulfide. A characteristic feature of the texture of these rocks is the occurrence of small siderite grains between large cryolite crystals. There are also segments enriched in fine scaly paragonite and muscovite, microspherulitic topaz, fluorite, pyrite, chiolite, weberite, stenonite, and jarlite. Dark cryolite often occurs in this mineral association. The latest assemblages are represented by druses of cryolite crystals on the walls of open fractures and the products of its replacement: thomsenolite, pachnolite, and ralstonite.

The gray monofeldspathic granites of the apical part of the Ivigtut massif change with depth by albitized and sericitized varieties, sometimes grading into greisens [6]. Two-feldspar leucogranites were found at a depth of 550 m. The granites are albitized at depths of 700–800 m, and disseminated cryolite was detected in drill-core samples [5]. The cryolite deposit was subdivided into three stages: (1) siderite–cryolite, (2) cryolite, and (3) fluorite–cryolite with thin quartz–siderite veins.

The Ivigtut granites show rather high sums of alkalis, Na_2O predominance over K_2O, and relatively low Al_2O_3 contents (Table 2), which makes them different from the plumasitic granites of the Baikal region. Another notable difference is the enrichment of the Ivigtut rare-metal granites in high field strength elements (Zr, Nb, Ta, and Hf), which is characteristic of agpaitic rocks. The maximum concentrations of these elements, as well as Rb, Sn, Pb, and Zn were detected in the cryolite-bearing granites. Similar to the plumasitic granites of the Baikal region, the Ivigtut agpaitic granites have very low Sr and Ba contents, which is often characteristic of rare-metal silicic rocks (Tables 1, 2).

In the tectonic discrimination diagrams for granitoids, the Ivigtut granites plot within the field of intraplate rocks and A-type granites, which is typical of complexes genetically linked to rift zones [5, 7]. The results of the investigation of the Ivigtut massif [5] suggest that the granites surrounding the cryolite body experienced extensive metasomatism under the influence of F- and CO_2-rich fluids, which resulted in zonal enrichment of the rocks in high field strength and rare earth elements. The isotopic characteristics ($^{87}Sr/^{86}Sr$ and ε_{Nd}) of the fresh granites of the massif indicate their formation from an initial mantle magma with some contribution from crustal contamination.

AQUA BOA AND MADEIRA GRANITIC MASSIFS AND THE ASSOCIATED TIN-RARE-METAL PITINGA DEPOSIT, BRAZIL

The Pitinga rare-metal deposit in Brazil yields 12% of the world's tin production. It is represented by two granite plutons, Aqua Boa and Madeira. The granites are currently explored for possible cryolite mining.

The Aqua Boa massif (Fig. 1b) occupies an area of about 350 km^2 and is composed of three main rock varieties: (1) medium- and coarse-grained rapakivi granites; (2) medium- and coarse-grained biotite granites, which are the most abundant rocks of the pluton; and (3) porphyritic fine-grained topaz-bearing granites forming an extended dikelike body in the apical part of the massif. The topaz-bearing granites contain quartz, K–Na feldspar, and albite phenocrysts in a groundmass of the same minerals and small muscovite and topaz grains. Cassiterite is mined mostly from these granites. Tin mineralization is also confined to cassiterite–topaz–mica greisens and, to a lesser extent, biotite granites. The age of the topaz-bearing granites was determined by the U–Pb method as 1798–1815 Ma [8]. The Madeira intrusive complex (Fig. 1b) is about 60 km^2 in area and is separated by a volcanic complex from the large Aqua Boa pluton. Three main facies were also distinguished in this massif: (1) porphyritic rapakivi granites, (2) fine- and medium-grained biotite granites, and (3) fine-grained porphyritic albite granites with an Ar–Ar age on mica of 1782 ± 5.2 Ma [8]. An oval-shaped body of albite granite occupies an area of about 2.5 km^2 and is situated in the apical part of the pluton among biotite granites. The latter are petrographically similar to the respective granites of the Aqua Boa massif but contain accessory topaz and fluorite. The porphyritic albite granites contain K–Na feldspar, quartz, albite, lepidolite, and scarce arfvedsonite–riebeckite phenocrysts. Their fine- and medium-grained groundmass is composed of the same minerals and zircon and cryolite. Cryolite occurs as small grains (up to 5 mm) coexisting with small albite laths and is confined to the growth zones of quartz. This texture is interpreted as resulting from an almost simultaneous crystallization of quartz, albite, and cryolite [9]. Two cryolite-rich bodies were found 150 m from the outcrop of albite granite. The dispersed mineralization of these granites is represented by zircon, cassiterite, pyrochlore, columbite–tantalite, and xenotime, which make up a considerable part of the Pitinga deposit. Cassiterite forms both individual crystals, up to 5 mm in size, and small inclusions in mica, Na-amphibole, and columbite–tantalite. Among the minor minerals of the albite granites, thorite, magnetite, hematite, pyrite, ilmenite, rutil, and sphalerite were detected.

The rare-metal granites of the Aqua Boa and Madeira massifs with topaz and cryolite are agpaitic rocks with high ($K_2O + Na_2O$) and relatively low Al_2O_3 contents. They are also relatively poor in MgO, CaO, MnO, TiO_2, and P_2O_5 (Table 2). The highest alkali con-

Table 2. Average chemical compositions of rare-metal agpaitic granites from various regions

Component	Pitinga intrusive complex, Brazil				Liruei complex, Nigeria	Ivigtut, Greenland		
	1 (15)	2 (11)	3 (10)	4 (8)	5 (20)	6 (10)	7 (3)	8 (3)
SiO_2	75.96	69.10	75.42	75.52	70.63	72.74	71.59	71.90
TiO_2	0.03	0.02	0.07	0.04	0.14	0.16	0.04	0.04
Al_2O_3	12.1	12.60	12.47	12.63	12.20	12.75	11.58	12.95
Fe_2O_3	0.76	2.20	0.51	0.51	1.13	2.49	2.65	1.51
FeO	1.00	0.58	0.97	0.97	0.95	–	–	–
MnO	0.03	0.04	0.02	0.03	0.06	0.05	0.03	0.03
MgO	0.1	0.03	0.06	0.03	0.05	0.04	0.00	0.00
CaO	0.75	0.09	0.66	0.34	0.06	0.78	0.03	0.03
Na_2O	3.43	6.21	3.40	4.24	7.10	4.44	5.06	6.30
K_2O	5.25	4.04	4.92	4.31	4.10	4.79	3.78	3.99
P_2O_5	0.03	0.05	0.02	0.02	0.02	0.02	0.00	0.00
LOI	0.93	1.49	1.07	0.62	–	0.85	0.97	0.97
F	0.48	6.48	0.52	0.56	3.17	–	–	–
Li	106.5	6801	179	575	630	–	–	–
Rb	803	4595	1063	2600	1400	434	259	1006
Cs	17.8	60	31.7	30	–	–	–	–
Ba	221	31	72	32	20	185	11	21
Sr	27	10	14	13	8	50	32	115
Sn	12.7	1883	34	14.6	–	3.4	15	188
Pb	87	705	23	79	–	28.4	113	143
Zn	57	525	58	30	–	150.8	291	387
Nb	51.1	1404	82	25	95	120.5	311	641
Ta	3.9	179	13	102	300	19.0	56	85
Zr	224	5641	169	267	575	365.4	971	2134
Hf	8.2	294	8.5	10	130	11.6	41.5	72
K/Rb	55	7.31	38.6	13.8	24.4	91.9	122	33
Nb/Ta	13.1	7.8	6.3	0.24	0.31	6.3	5.55	7.54
Zr/Hf	27.3	19.2	20	27	4.4	31.5	23.4	29.6
La/Yb	3	1.76	1.9	1.9	–	7.8	0.24	1.78

Note: (1) Biotite granites of the Madeira complex; (2) albite granites with cryolite of the Madeira complex; (3) biotite granites of the Aqua Boa complex; (4) topaz granites of the Aqua Boa complex [9, 13]; (5) albite–riebeckite granites with cryolite from the Kaffo massif [12, 14, 15]; (6) top granites; (7) granites with fluorite and cryolite; and (8) granites with cryolite [4, 5]. Oxides are in wt %, and elements are in ppm. Dashes indicate no data.

tents were determined in the peralkaline albite granites with cryolite from the Madeira complex. They are also the most enriched in F (up to 7%), Li, Rb, Cs, Sn, Pb, Zn, Nb, Ta, and especially in Zr and Hf, even compared with the topaz-bearing granites from the apical part of the Aqua Boa massif. On the other hand, similar to the rare-metal agpaitic rocks of Ivigtut (Greenland), the Brazilian topaz- and cryolite-bearing granites show low Ba and Sr concentrations.

Thus, there is a general tendency of increasing concentrations of many trace elements (Li, Rb, Cs, Sn, Pb, Zn, Nb, Ta, Zr, and Hf) accompanying the transition from topaz- and fluorite-bearing granites to their later cryolite-bearing varieties in a common evolution series of granites of the agpaitic geochemical type.

The rare-metal granites of the Pitinga deposit form intrusive bodies extending parallel to the orientation of major regional faults (NE–SW). The granites were formed both at the stage of batch crystallization in deep magma chambers and during the ascent of melt and crystals into shallow levels. The final magmatic stage was accompanied by a sharp decrease in pressure and rapid melt crystallization with possible fluid phase release, when albite granites with topaz were formed. It is supposed that the granitic magmas, which were formed at temperatures between 900 to 600°C, were transported from the lower and middle crustal zones into shallow levels, where their gradual or rapid crystallization took place [9].

RARE-METAL GRANITES WITH CRYOLITE MINERALIZATION FROM THE JOS PLATEAU, NORTHERN NIGERIA

The complex of young granites of the Jos Plateau in northern Nigeria comprises about 50 intrusions with ages of 150–160 Ma [10, 11] localized among the ancient Precambrian and Early Paleozoic Pan-African granitoids. The Late Mesozoic granites include the Liruei granite complex, which consists of several intrusions of peralkaline granite. Cryolite mineralization was found in the albite–riebeckite granites of the Kaffo massif. The massif is exposed as a small intrusion, ~0.8–1.0 km^2 in area, cutting the enclosing ancient granites.

Three types of rocks with different associations of mafic minerals were distinguished in the Liruei intrusive complex: amphibole–pyroxene–fayalite, biotite, and albite–riebeckite granites. The biotite granites are often greisenized and contain cassiterite, wolframite, columbite, and minor amounts of monazite, xenotime, thorite, and zircon. The albite–riebeckite granites of the Kaffo massif are fine- and medium-grained porphyritic rocks with rounded quartz phenocrysts and prismatic riebeckite grains in a fine-grained matrix composed mainly of albite and K–Na feldspar. The coarse-grained varieties of granite contain K–Na feldspar and riebeckite–aegirine phenocrysts, up to 1 cm in size. The characteristic minor minerals of the albite–riebeckite granites are cryolite (3–4%), topaz (3.9%), and pyrochlore (~1%). Astrophyllite, thomsenolite, molybdenite, and amblygonite occur in smaller amounts. Drilling to depths of 60 m revealed the presence of cryolite and pyrochlore in the deep zones of these granites.

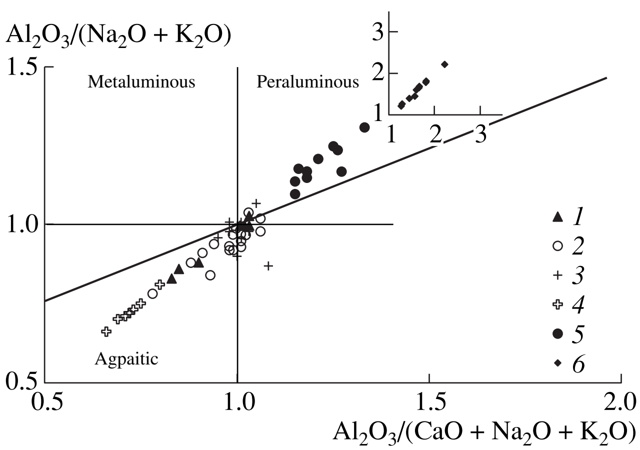

Fig. 2. Shand classification diagram $Al_2O_3/(Na_2O + K_2O)$–$Al_2O_3/(CaO + Na_2O + K_2O)$ for cryolite-bearing granites from various regions: (*1*) Ivigtut granite, Greenland; (*2*) Madeira granite, Brazil; (*3*) Aqua Boa granite, Brazil; (*4*) Kaffo granite, Nigeria; (*5*) Khamar-Daban granite, Baikal region; and (*6*) ongonite, the same complex.

In terms of chemical composition, the albite–riebeckite granites of Nigeria are typical peralkaline granites with an average agpaitic index of 1.35 [12]. They are characterized by a strong predominance of Na_2O over K_2O and rather low concentrations of MgO, CaO, MnO, and P_2O_5, which is similar to the agpaitic granites from other regions (Table 2). Similar to the peralkaline granites of the Ivigtut and Pitinga complexes, the albite–riebeckite granites of northern Nigeria are enriched in fluorine (>3%) and some lithophile (Li and Rb) and high field strength elements (Nb, Ta, Zr, and Hf).

DISCUSSION

Summing up the comparative analysis of the geologic structure, petrography, and geochemistry of granites with fluorine-bearing minerals (fluorite, CaF_2; topaz, $Al_2SiO_4F_2$; and cryolite, Na_3AlF_6), it can be concluded that these rocks belong to different geochemical types: rare-metal plumasitic leucogranites and rare-metal agpaitic granites [1]. Considerable variations of the proportions of Na_2O, K_2O, CaO, and Al_2O_3 in them can be clearly illustrated by the Shand diagram (Fig. 2), where the compositions of the granitoids plot within the fields of both peralkaline and peraluminous rocks. Consequently, Li–F granites, which show a number of characteristic features (presence of typomorphic fluorine-bearing minerals, including topaz, fluorite, and Li–F micas; very high concentrations of F, Li, Rb, Sn, Nb, Ta, and other elements; and an increase in the concentrations of these elements during the magmatic evolution of these rocks [16]), occur among the both geochemical types of granitoids. Therefore, these results support the proposal of Tauson [1] to distinguish the Li–F facies of rare-metal granites showing specific compositions and geochemical parameters.

Characterizing their geologic setting, it is noteworthy that rare-metal granites usually form small intrusions, stocks, or dike swarms, which have been originated in various geologic epochs, from the Precambrian to the Late Mesozoic. They compose allochthonous intrusive or subvolcanic bodies, which were formed independently of the composition and age of the country rocks and geologic environments. Among the rare-metal granites considered here, fluorite-bearing varieties are often the earliest rocks. Subsequently, topaz-bearing granites and their subvolcanic analogs ongonites are formed (Urugudei–Utulik belt of the Baikal region). The latest cryolite-bearing rocks are usually confined to the apical facies of intrusions (Ivigtut in Greenland and Madeira in Brazil). Cryolite also occurs in late pegmatite bodies. For instance, the biotite granites of the St. Peters Dome (Colorado, USA) host a body of coarse-grained pegmatite, where cryolite occurs in a druse cavity with large crystals of riebeckite, microcline, and quartz. In the Ilmen Mountains of the Southern Urals, giant cryolite crystals with cryolithionite encrusted a meter-sized druse cavity in a lenticular body of amazonite pegmatite.

The rocks with cryolite, which often associates with fluorite and topaz, show rather diverse mineralogy. Their matrix is dominated by albite, K–Na feldspar, and quartz and contains lithium micas, alkali amphiboles of the riebeckite–arfvedsonite series, and aegirine. The cryolite assemblage includes a number of minor minerals: siderite, zircon, cassiterite, pyrochlore, columbite–tantalite, thorite, xenotime, magnetite, hematite, ilmenite, rutil, and wolframite. Cryolite is usually accompanied by various aluminofluorides and rare earth fluorides: thomsenolite, ralstonite, weberite, pachnolite, and REE fluorite.

The peculiar mineralogical and geochemical characteristics of the granitic rocks are also reflected in the character of accompanying ore mineralization. In particular, the rare-metal plumasitic leucogranites and ongonites of the Baikal region are genetically associated with quartz–topaz–mica greisens with cassiterite and quartz–cassiterite–wolframite veins, mineralized breccias with wolframite, cassiterite, beryl, and bertrandite, and quartz–topaz–fluorite–cryolite veins. Aluminofluorides became widespread during the final stage of mineral formation [17]. The rare-metal agpaitic granites are associated with combined Nb, Ta, Zr, Sn, and rare earth element mineralization. In addition to these metals, the highest concentrations of which were detected in the Pitinga (Brazil) and Jos Plateau (Nigeria) deposits, the agpaitic granites host high-grade siderite–cryolite mineralization (Ivigtut).

In addition to the above-described mineralogical and petrographic characteristics of granites with various fluorine-bearing minerals, the compositional variations of these rare-metal rocks are clearly seen in the albite–orthoclase–quartz–H_2O diagram (Fig. 3). The normative compositions of plumasitic rocks form a classic evolution trend directed toward the albite apex, from biotite leucogranites with fluorite through amazonite–albite varieties with topaz to albite–lepidolite granites [2, 16]. On the other hand, the normative compositions of agpaitic albite granites with topaz and cryolite fall closer to the quartz–orthoclase join of this diagram and are shifted somewhat toward the orthoclase apex relative to the field of plumasitic rare-metal granites. These differences in the proportions of major normative components may suggest the absence of genetic relationships between the granites of these geochemical types. The similar compositional evolution toward the albite apex of the diagram observed in the granites of both types is explained by high fluorine and water contents in the initial magmas, which are responsible for the displacement of normative compositions in this diagram from the low-P_{H_2O} eutectic compositions of granites.

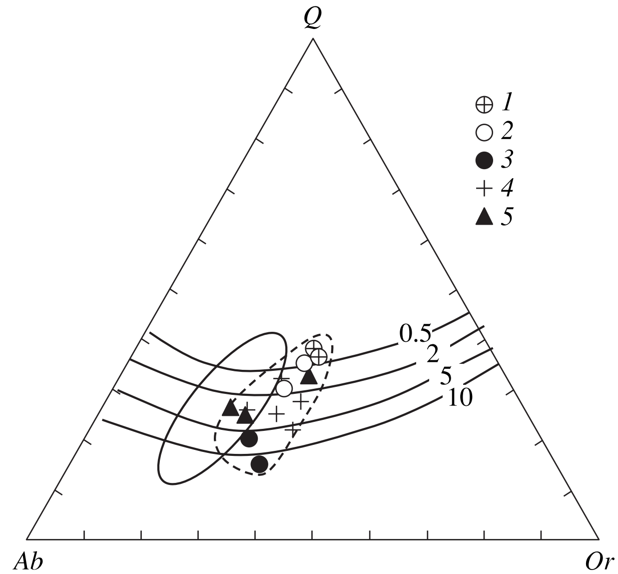

Fig. 3. Normative compositions of rare-metal granites from various regions in the albite–orthoclase–H_2O diagram. (*1*) Biotite granite, Brazil; (*2*) topaz granite, Brazil; (*3*) albite granite with cryolite, Brazil; (*4*) Ivigtut granite, Greenland; (*5*) Kaffo granite, Nigeria. The thick solid line shows the compositional field of the plumasitic rare-metal granites of the Baikal region, and the dashed line shows the field of agpaitic granites. The isobars indicate P_{H_2O} in kilobars.

In order to further scrutinize the conditions of formation of rare-metal granites with various fluorine-bearing minerals, it is very important to determine the physicochemical parameters of their crystallization. To constrain the concentrations of fluorine in these natural silicate melts, Dolejs and Baker [18] carried out an experimental investigation of the stability of fluorite, cryolite, and immiscible fluoride melt in synthetic haplogranite systems. They demonstrated that the stability of fluoride minerals is controlled by both the concentration of fluorine in melt and the activities of oxide components. For instance, early fluorite crystallizes from Ca-rich tonalites and granodiorites (~0.5 wt % F in melt), which prevents fluorine accumulation in natural calc-alkaline series. Topaz crystallizes from Ca-poor aluminous granitic melts with 1.7 wt % F, whereas cryolite precipitates from a peralkaline granitic magma containing 4.2 wt % F (720°C and 100 MPa under H_2O-saturated conditions).

Various types of inclusions were investigated in quartz from the granite porphyries and ongonites of the

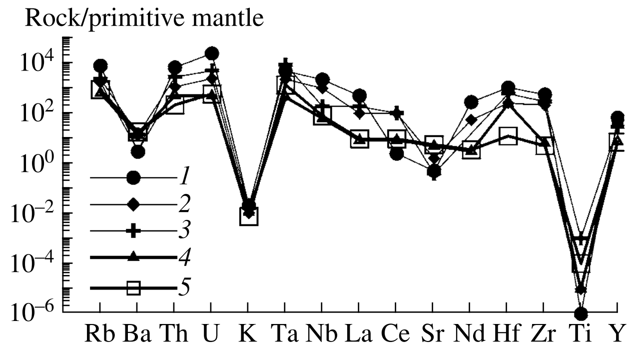

Fig. 4. Spider diagram for cryolite-bearing rocks from various regions of the world. (*1*) Brazil granite, (*2*) Greenland granite, (*3*) Nigeria granite, (*4*) Baikal granite, and (*5*) Baikal ongonite.

Utulik River in the Baikal region. Crystalline inclusions were represented by biotite, zircon, albite, and topaz, which obviously cocrystallized with the quartz phenocrysts. Primary crystallized melt inclusions in quartz were also studied. They are composed of anisotropic crystals and a fluid consisting of liquid and gas phases [19]. Using the method of V.B. Naumov, the authors calculated the concentration of water in the melt (4.7%) and pointed out high fluid pressure in the melt inclusions (no les than 3–4 kbar). Melting began in the inclusions at a temperature of ~600°C, but complete homogenization was never reached because of the decrepitation of the inclusions and volatile loss. Based on the investigation of melt and fluid inclusions from the Ary Bulak massif in Transbaikalia, Naumov et al. [20] demonstrated the reality of magmatic crystallization of topaz and cryolite from ongonite melts. They estimated the temperature (930–580°C), fluid pressure (0.9–3.9 kbar), and water concentration in the melt (0.2–10 wt %) during topaz crystallization. An electron microprobe investigation of partially crystallized melt inclusions in topaz revealed a sodium aluminofluoride mineral (similar to cryolite), which supported cryolite crystallization from a residual ongonite melt. A recent investigation of melt inclusions from this massif [21] showed that the ongonites were formed from a melt similar in composition to the bulk rock at temperatures of 650–720°C. The ongonite magma was rich in water (5.0–8.7 wt %), and the highest fluorine contents of 5–8 wt % were detected in homogenized melt inclusions in topaz from these rocks.

As to the rare-metal agpaitic granites, Watson and Harrison [22] estimated the temperatures of formation of late topaz granites in the apical part of the Aqua Boa massif (Brazil) as 800–750°C. Based on the high contents of fluorine (4.0–9.2 wt %) and petrographic characteristics, they estimated the solidus temperature of the late fine-grained granites with cryolite from the Madeira intrusive complex as <600°C.

The presented petrographic and experimental data suggest that the fluorine-bearing minerals of rare-metal granites could crystallize from magmatic melts. This is supported primarily by the temperature estimates obtained from the analysis of melt inclusions and the relationships of fluorite, topaz, and cryolite with other minerals of granites. The relatively high content of Ca in the early fluorite-bearing granites of the Baikal region promoted fluorite crystallization. Topaz- and cryolite-bearing rocks are usually depleted in calcium and form at lower magmatic temperatures from residual melts. These two minerals very rarely coexist, because topaz crystallizes mainly from the magmas of plumasitic granites and ongonites, whereas cryolite is a product of alkali-rich agpaitic granites and associated pegmatites from the apical parts of intrusions. This is in agreement with early experimental data [6] showing that cryolite is stable in a silicic system enriched in volatile components with a low Ca content and a high $(K_2O + Na_2O)Al_2O_3$ ratio.

The geochemical systematics of rare-metal granites with fluorine-bearing minerals suggests that the high concentrations of fluorine and a number of lithophile elements typical of Li–F granites are reached under the conditions of their magmatic genesis (Tables 1, 2). However, the rocks of different geochemical types show distinctive trace-element distribution patterns, which are clearly seen in the spider diagram (Fig. 4). In particular, the agpaitic granites with cryolite are enriched in Rb, Th, U, Y, and high field strength elements (Nb, Ta, Zr, and Hf). In most cases, they also show elevated Nb/Ta and Zr/Hf ratios. The plumasitic granites and ongonites with cryolite from the Baikal region are characterized by lower normalized concentrations of these elements, which may reflect different sources of initial magmas for these geochemical types of rocks. This conclusion is additionally supported by the maximum enrichment of peralkaline granites in fluorine (up to 7%), as well as Li, Cs, Sn, Pb, and Zn, the highest concentrations of which were detected in the Pitinga cryolite granites (Brazil). The granites of Nigeria (Kaffo) and Greenland (Ivigtut) have somewhat lower concentrations of these elements, but they are higher than the respective values of plumasitic rocks.

The independent origin of plumasitic and agpaitic Li–F granites with fluorite, topaz, and cryolite is supported by the analysis of REE distribution (Fig. 5). Rather large variations were observed in the Li–F granites both in the total content of REE and light to heavy REE ratios. The REE distribution patterns of the plumasitic granites and ongonites of the Baikal region are similar to those of the corresponding rocks from Transbaikalia and Mongolia and characterized by slightly elevated contents of light REE relative to heavy REE, a distinct negative Eu anomaly, and a generally rather low total REE content. Such REE distribution patterns suggest that the plumasitic granites were formed by extensive magmatic differentiation of an initial granitic magma. The feasibility of such a mechanism of granite formation is supported by a regular decrease in the concentration of all REE from fluorite-bearing through

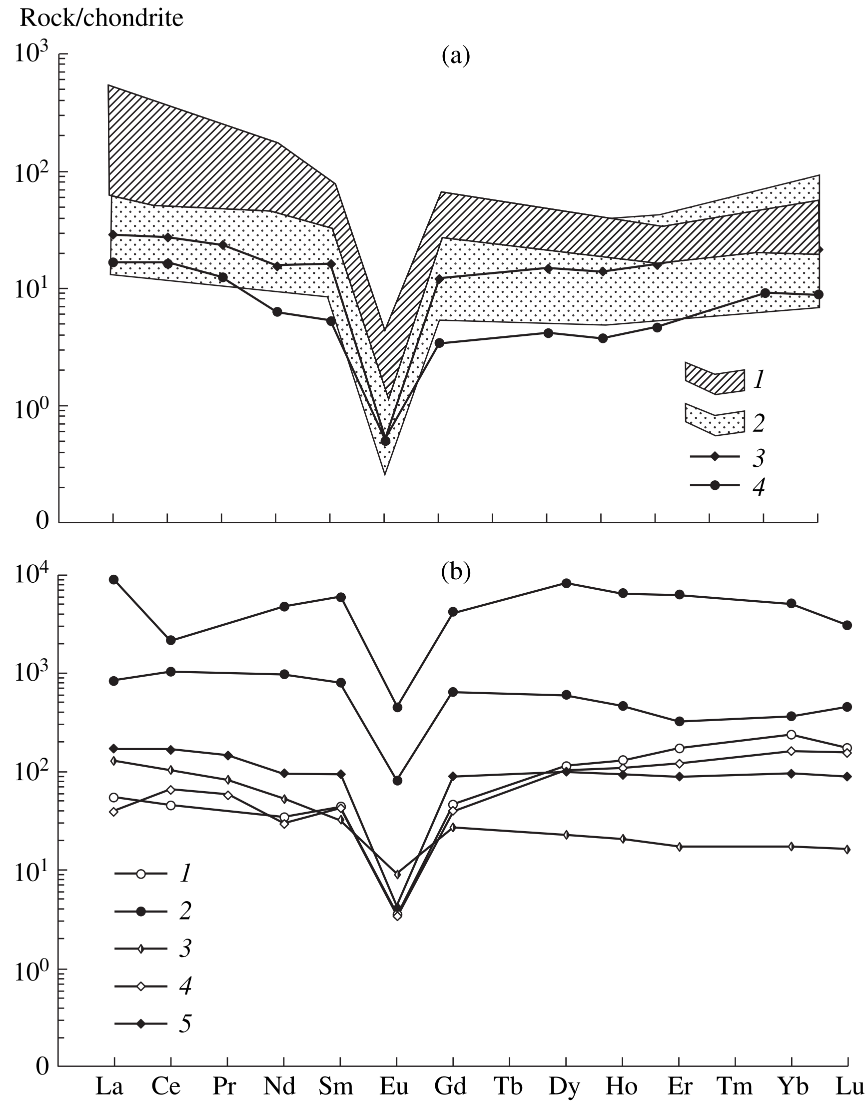

Fig. 5. Distribution of rare earth elements in granites with fluorine-bearing minerals. (a) Baikal region: (*1*) fluorite-bearing granite, (*2*) topaz-bearing granite, (*3*) cryolite-bearing granite, and (*4*) cryolite-bearing ongonite. (b) Brazil and Greenland: (*1*) biotite granite and (*2*) cryolite-bearing granite from Brazil, (*3*) leucogranite, (*4*) granite with fluorite and cryolite, and (*5*) cryolite-bearing granite from Greenland.

topaz-bearing to cryolite-bearing granites with a decrease in La/Yb in the same direction (Fig. 5). Compared with the rare-metal granites of the Baikal region, the cryolite granites of the Ivigtut deposit (Greenland) show almost an order of magnitude of higher total REE content, although these complexes are similar in REE distribution patterns and La/Yb ratios. The topaz- and, especially, cryolite-bearing granites of Brazil have the highest total REE concentrations (55 509 ppm) (Fig. 5) at a low La/Yb ratio of 1.76. It should be pointed out that the late cryolite-bearing granites of the agpaitic type, which are usually confined to the apical parts of massifs are enriched in REE to the highest degree, which is related to another mechanism and source of their formation compared with the rocks of the plumasitic type.

Thus, rare-metal rocks with various fluorine-bearing minerals were found among the granites of both agpaitic and plumasitic geochemical types. Geological and isotope geochemical data suggest that the cryolite-bearing granites of the Ivigtut deposit (Greenland) were formed from a residual silicic magma, which was produced by the fractional crystallization of mantle-derived basaltoid melts. It is believed that crustal processes played a negligible role in the formation of cryolite-bearing rocks [4]. Other researches [5] also accepted the significance of the mechanism of the crystallization differentiation of basaltoid magmas, but they argued that crustal contamination and extensive metasomatic alteration by F- and CO_2-rich fluids were the most important processes for the formation of the cryolite body. The presented geochemical parameters of the rare-metal granites of Greenland, Nigeria, and Brazil, which are strongly enriched in Zr, Hf, Nb, Ta, Y, and REE and have anomalously low Ba and Sr contents, characterize them as typical alkaline rocks. This conclusion is corroborated by the increase of the concentrations of REE and high field strength elements in the late cryolite rocks. The above-cited researchers have provided compelling isotopic and geochemical evidence for the genetic connection of agpaitic rare-metal granites with mantle sources.

The intrusive and subvolcanic rocks of the Urugudei–Utulik belt of the Baikal region host a new type of cryolite mineralization related to rare-metal plumasitic granites. The topaz- and cryolite-bearing leucogranites and ongonites are products of the extensive differentiation of crustal granitic magmas, which resulted in considerable regular variations in the concentration of many elements and, owing to their extensive concentration, gave rise to Sn, Ta, Li, and W mineralization genetically related to these granites. The accumulation of these elements in residual granitic melts is responsible for the crystallization of such minerals as F–Li micas (protolithionite, zinnwaldite, and lepidolite), columbite–tantalite, cassiterite, and occasional wolframite. The extensive development of fluorine-bearing minerals and rare-metal mineralization is typical of both late magmatic and postmagmatic stages. By the example of the Utulik occurrence in the Baikal region, Chernov et al. [17] and Erokhin et al. [19] deciphered the evolution of the mineralization from the Sn–W to cryolite and cryolite–Sn–Ag types. According to these authors, the highest grade cryolite ores are related to quartz–feldspar–topaz veins in the schists enclosing the dike bodies of plumasitic granites.

CONCLUSIONS

The most comprehensive comparative study of the mineralogy and geochemistry of rare-metal (lithium–fluorine) plumasitic and agpaitic granites was conducted by Kovalenko [16] in 1977. Since then, new publications and geochemical data have been presented for the known and new complexes of rare-metal granitic magmatism, which provided an opportunity to consider, in more detail, the geochemical evolution and formation conditions of rare-metal lithium–fluorine granites. Therefore, we considered it necessary to review the available published data and our new results on this problem, with an emphasis on the comparative analysis of the conditions of formation of rare-metal granites with different fluorine-bearing minerals (fluorite, topaz, and cryolite), which have not been done previously.

This approach led us to the following main results:

(1) A regular sequence was established in the formation of fluorite-, topaz-, and cryolite-bearing lithium–fluorine granites in several massifs belonging to both the plumasitic and agpaitic geochemical types. A comparative geological investigation of rare-metal granites showed that they form small intrusions, stocks, and dike swarms or occur as final phases in massifs of normal biotite granites. Rare-metal granites were formed in various geologic epochs, from the Precambrian to the Late Mesozoic. Their generation was independent of the composition and age of the country rocks and the character of the host geologic structures.

For instance, according to isotope geochemical data, the Late Paleozoic rare-metal rocks of the intrusive–dike suite of the Khamar-Daban Range (Baikal region) were formed by the melting of the Precambrian continental crust and subsequent differentiation of granitic magma. The process of anatectic melting of crustal sources could be due to the thermal influence of monzonitoid mantle-derived magma and associating deep-derived fluid enriched in fluorine and other elements [2, 23].

(2) The analysis of petrographic and experimental evidence, including melt inclusion data, suggested that the fluorine-bearing minerals of rare-metal granites could crystallize from a magmatic melt. Among the rocks under investigation, the cryolite-bearing granites are formed during a late magmatic stage in the apical parts of intrusions or in vein bodies (pegmatites, dikes, late veins) from a residual melt under the participation of fluid components, when the maximum contents of fluorine and many other trace elements are achieved.

(3) It was shown that the fluorite-, topaz-, and cryolite-bearing rare-metal granites of different geochemical types are clearly discriminated by trace element characteristics and the direction of magmatic evolution, which is related to the different compositions of initial magmas and their sources. Rare-metal mineralization genetically connected with lithium–fluorine granites is characterized by certain ore element associations: the plumasitic granites are enriched in Sn, W, Li, Rb, Ta, and cryolite, whereas the agpaitic granites are enriched in Nb, Ta, Zr, Sn, REE, and cryolite.

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