

# Composition, Mineral Assemblages, and Genesis of Serendibite-Bearing Magnesian Skarns

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**Abstract**—Variations in the composition and mineral assemblages of boronaluminosilicates (serendibite, grandidierite, kornerupine, and tourmaline) were studied in the abyssal and hypabyssal skarns of New York and California, United States, the Tazhnyi deposit of southern Yakutia, and deposits of the Pamirs, and compared to their occurrences around the world. The genesis of the boronaluminosilicates depends on the facies of the replaced skarns and the calcareous-skarn alteration of the primary composition of the host rocks. The substitution between Mg and Fe, as well as between Al, Si, and B, was studied in complex boronaluminosilicates and associated minerals. It was shown that *f* of serendibite is determined by that in the replaced skarn minerals (pyroxenes, spinel, sapphirine, and grandidierite) and is inherited in the replacing tourmaline and late silicates. Unlike serendibite, kornerupine is a typomorphic mineral of only bimetasomatic skarns of the abyssal facies. Serendibite, grandidierite, kornerupine, and tourmaline crystallized during the postmagmatic stage of the evolution of boron mineralization at skarn deposits of both the abyssal and the hypabyssal facies, at contact with magnesian carbonate sequences and desilicified aluminosilicate rocks.

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## INTRODUCTION

Many magnesian skarns around the world are characterized by a wide development of borate mineralization, reaching economic concentrations. The mineralization is made up of magnesian borates (suanite, kotoite, and szaibelyite) or ludwigite, which replace marbles, calciphyres, and forsterite skarns in the outer zones of metasomatically altered dolomites. This does not rule out the presence of Mg-bearing boronaluminosilicates in the rear spinel–pyroxene and plagioclase–pyroxene zones of the metasomatic column, on contact with aluminosilicate rocks and granites.

The most abundant of the boronaluminosilicates, tourmaline and serendibite, occur in rock-forming amounts. At some occurrences, these minerals are associated with grandidierite. In addition, corundum-bearing bimetasomatic near-skarn rocks of the abyssal facies locally contain kornerupine, which is, like serendibite, replaced by tourmaline. These minerals form diverse assemblages in the postmagmatically altered magnesian skarns formed after dolomites and magnesites during the prograde metasomatic stage.

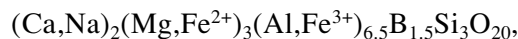
Both a metasomatic and metamorphic origin were proposed to describe the petrochemical conditions under which the boronaluminosilicates discussed here were formed. The metasomatic origin considered in this work suggests that these minerals crystallized during postmagmatic alteration of the rear zones of magnesian skarns, which developed after dolomites during the prograde metasomatic stage. Another viewpoint fol-

lows from the isochemical transformation of aluminous desilicified pelites during prograde metamorphism and rules out the role of the early metasomatic alteration of magnesian skarns at these deposits.

This defines the different viewpoints regarding the source of boron required for the formation of boronaluminosilicates, and, often, borate mineralization at the deposit. We suppose that boron was derived mainly from a magmatic source, with the exception of boron derived by the metamorphism of evaporite sequences.

This work is based on our research of skarn deposits in southern Yakutia (Tazhnyi), New York (Johnsburg), California (Castro pit, New City–Victoria avenue quarry, Riverside), and the collection of the Fersman Mineralogical Museum, Russian Academy of Sciences. In addition, we studied metasomatites from the Stazh Deposit (Nagornyi Badakhshan, Tajikistan), which contain magnesian kornerupine and tourmaline (collection of E.N. Terekhov, Geological Institute, Russian Academy of Sciences, Moscow). Data on the composition and mineral assemblages of the serendibite and other Mg–Fe boronaluminosilicates were compared with literature data on their occurrences in the Baikal area, Sri Lanka, Madagascar, Tanzania, United States, Canada, and Afghanistan [1–23].

Serendibite,



is a typomorphic mineral of magnesian skarns [11]. This mineral is the most abundant in the abyssal skarns (eclogites) of Sri Lanka, New York State, and, espe-

**Table 1.** Compositions (wt %) of serendibite in the abyssal magnesian skarns at the deposits in the United States, Canada, and Sri Lanka

Component	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub>	25.94	20.16	25.56	26.30	24.91	24.05	25.35	25.33	21.88	20.88
TiO <sub>2</sub>	–	–	0.01	–	0.02	0.02	0.04	–	0.03	0.06
Al <sub>2</sub> O <sub>3</sub>	33.01	34.31	32.72	34.05	36.36	35.76	34.04	34.96	36.69	40.20
Fe <sub>2</sub> O <sub>3</sub>	–	–	–	–	1.76	–	–	–	–	–
CaO	16.14	15.50	14.16	13.30	15.49	14.22	14.39	14.56	16.56	17.11
MgO	17.40	15.00	16.46	15.44	14.91	15.34	14.49	14.91	13.71	12.71
FeO	0.00	0.65	1.21	2.76	–	1.94	2.10	4.17	3.28	3.48
MnO	–	–	0.07	–	0.11	0.05	0.09	–	0.12	–
Na <sub>2</sub> O	0.00	–	0.91	–	0.31	0.50	0.63	0.51	0.00	0.02
Σ <sub>1</sub>	92.49	85.62	91.14	91.85	93.86	91.94	92.19	95.83	92.31	94.43
B <sub>2</sub> O <sub>3</sub>	7.51	7.40	7.42*	8.37	6.14*	7.99	9.06	4.17*	10.76*	5.57*
Σ <sub>tot</sub>	100.00	93.02	98.56	100.22	100.00	99.93	101.25	100.00	103.06	100.00
Mineral formula and its <i>f</i> (at %):										
Ca	2.00	2.06	1.78	1.66	1.91	1.77	1.76	1.88	1.99	2.11
Na	–	–	0.20	–	0.07	0.11	0.14	0.15	0.00	0.00
Σ	2.00	2.06	1.98	1.66	1.98	1.88	1.90	2.03	1.99	2.11
Mg	3.00	2.77	2.88	2.68	2.56	2.65	2.64	2.67	2.30	2.18
Fe <sup>2+</sup>	0.00	0.07	0.12	0.26	0.19	0.19	0.20	0.33	0.30	0.34
Al <sup>VI</sup>	0.00	0.16	0.00	0.06	0.25	0.20	0.16	0.00	0.40	0.48
Σ	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Al <sup>VI</sup>	4.50	4.36	4.53	4.61	4.55	4.48	4.32	4.41	4.38	4.00
Fe <sup>3+</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.00
Σ	4.50	4.36	4.53	4.61	4.55	4.48	4.32	4.50	4.38	4.00
Si	3.00	2.50	3.00	3.05	2.87	2.79	2.90	3.05	2.46	2.40
Al <sup>IV</sup>	0.00	0.50	0.00	0.00	0.13	0.21	0.10	0.00	0.54	0.60
Σ	3.00	3.00	3.00	3.05	3.00	3.00	3.00	3.05	3.00	3.00
B	1.50	1.59	1.50	1.59	1.22	1.60	1.78	0.87	2.09	1.11
Al	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.54	0.00	0.39
Σ	1.50	1.59	1.50	1.59	1.27	1.60	1.78	1.41	2.09	1.50
O	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
<i>f</i>	0.0	2.4	4.0	9.0	6.0	6.6	7.0	10.8	12.0	13.0

Note: (1) Fe-free serendibite (calculated composition), (2) Johnsburg, district of Warren, New York, United States [18], (3) same; other components: ZnO = 0.04%, sample USJ-05 (our data), (4) the same [3], (5) Ianipera, Ihosy, Madagascar, (6–7) Russell, New York, United States, other components: BeO = 0.01%, Li<sub>2</sub>O = 0.03%, F = 0.03% [19]; (8) Gangapitiya, Sri Lanka; other components: K<sub>2</sub>O = 0.22%, P<sub>2</sub>O<sub>5</sub> = 0.48%, L.O.I. = 0.69% [1, 2], (9) Melville Peninsula, Canada, other components: F = 0.04, Li<sub>2</sub>O tr. [19], (10) the same [10].

\*Calculated content of B<sub>2</sub>O<sub>3</sub>, %: Σ<sub>1</sub> is the total without B<sub>2</sub>O<sub>3</sub>, Σ is the total of grouped components. All iron was determined as FeO.

cially, at the Tazhnyi Deposit in southern Yakutia. In hypabyssal skarns, serendibite composes almost monomineralic aggregates, for example, in the New City–Victoria Avenue quarry in Riverside, California.

Its composition reflects the diverse isomorphous substitutions of the constituent elements, including the Mg–Fe<sup>2+</sup> substitution. The latter defines the color variations from pale gray–blue, almost colorless, to bright or dark blue and affects other optical properties.

Serendibite and associated minerals were analyzed on a microprobe by M. A. Troneva in the Central Analytical Laboratory at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, to avoid the influence of mineral impurities. It is difficult to get rid of impurities when studying the hand-picked material of large samples by conventional chemical analysis.

Data on serendibite from abyssal skarn deposits indicate limited variations in *f* (Mg#) at particular

**Table 2.** Composition (wt %) of serendibite in abyssal magnesian skarns from deposits of Yakutia and Sri Lanka

Component	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub>	22.92	24.12	25.69	21.70	24.98	22.54	24.31	23.70	22.00	23.43
TiO <sub>2</sub>	tr.	0.06	tr.	0.07	0.26	0.09	0.24	0.27	0.27	0.12
Al <sub>2</sub> O <sub>3</sub>	34.35	33.60	31.72	34.30	32.46	34.18	33.18	33.86	31.31	34.11
Fe <sub>2</sub> O <sub>3</sub>	3.66	–	4.08	–	2.39	–	–	–	–	–
CaO	13.02	15.06	15.55	15.36	15.08	15.76	15.06	15.17	14.60	15.51
MgO	13.21	15.25	13.37	14.33	12.56	13.63	13.41	13.36	11.17	13.90
FeO	2.04	4.74	3.22	4.80	4.02	5.88	6.09	6.52	13.34	5.69
MnO	0.24	0.05	tr.	0.04	0.16	0.13	0.20	0.16	0.23	0.08
Na <sub>2</sub> O	0.43	0.09	–	0.06	–	0.05	0.10	0.07	0.08	0.23
Σ <sub>1</sub>	93.22	92.98	93.63	90.57	93.27	93.28	92.59	93.11	93.00	93.40
B <sub>2</sub> O <sub>3</sub>	6.32	6.87*	6.38	7.20*	6.63	7.80	7.20*	7.25*	6.77	7.31
Σ <sub>tot</sub>	100.24	99.85	100.43	97.77	99.90	100.08	99.79	100.36	99.79	100.71

Mineral formula and its *f* (at %):

Ca	1.97	1.91	2.00	1.99	1.94	1.995	1.93	1.93	1.92	1.96
Na	0.07	0.02	–	0.01	–	0.005	0.02	0.01	0.02	0.05
Σ	2.04	1.93	2.00	2.00	1.94	2.00	1.95	1.94	1.94	2.01
Mg	2.38	2.68	2.40	2.56	2.24	2.40	2.39	2.37	2.04	2.44
Fe <sup>2+</sup>	0.20	0.32	0.37	0.44	0.40	0.60	0.61	0.63	0.96	0.56
Al <sup>IV</sup>	0.42	0.00	0.23	0.00	0.36	0.00	0.00	0.00	0.00	0.00
Σ	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Al <sup>IV</sup>	4.30	4.43	4.02	4.48	4.05	4.32	4.55	4.56	4.13	4.49
Fe <sup>3+</sup>	0.33	0.13	0.37	0.02	0.48	0.00	0.00	0.02	0.41	0.00
Σ	4.66	4.56	4.39	4.50	4.53	4.32	4.55	4.58	4.54	4.49
Si	2.79	2.85	3.09	2.56	3.00	2.66	2.90	2.82	2.69	2.76
Al <sup>IV</sup>	0.21	0.15	–	0.44	0.00	0.44	0.10	0.18	0.31	0.24
Σ	3.00	3.00	3.09	3.00	3.00	3.00	3.00	3.00	3.00	3.00
B	1.33	1.40	1.32	1.50	1.37	1.59	1.48	1.48	1.43	1.68
Al	0.16	0.10	0.18	0.00	0.13	0.00	0.02	0.02	0.07	0.00
Σ	1.49	1.50	1.50	1.50	1.50	1.59	1.50	1.50	1.50	1.68
O	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
<i>f</i>	8.0	10.65	12.0	15.1	15.3	20.0	20.3	21.6	31.9	18.8

Note: (1) Tazhnyi, Aldan, Yakutia, other components: K<sub>2</sub>O = 0.07%, S = 0.22%, CO<sub>2</sub> = 0.85%, H<sub>2</sub>O<sup>+</sup> = 0.72, H<sub>2</sub>O<sup>–</sup> = 0.04%, sample G-84-5, borehole 261 [7]; (2) same, other components: K<sub>2</sub>O = 0.02%, F = 0.01, ZnO is absent, Sample TC-56-012 (author's data); (3) the same, Sample G-190a/56, other elements: H<sub>2</sub>O<sup>+</sup> = 0.24, H<sub>2</sub>O<sup>–</sup> = 0.18 [7]; (4) same, Sample TKC-0.1, other components: K<sub>2</sub>O = 0.01% (author's data); (5) same, Sample 5406, other components: H<sub>2</sub>O<sup>+</sup> = 1.11%, H<sub>2</sub>O<sup>–</sup> = 0.25% [6]; (6) same, other components: F = 0.02%, Li<sub>2</sub>O = 0.001% [16]; (7, 8) the same, sample 1006 (author's data); (9) same, other components: F = 0.02%, Li<sub>2</sub>O = 0.005% [16]; (10) Sri Lanka, other components: BeO = 0.03%, Li<sub>2</sub>O = 0.005%, SrO = 0.002%, and F = 0.30% [19].

deposits. The lowest *f* is typical of serendibites from Johnsbury and Russell, New York, United States, Sri Lanka, and Tanzania [1–3, 8, 10, 15, 17, 18] (Table 1), which are often associated with grandierite and late tourmaline. Iron-rich serendibite and tourmaline (dravite and uvite) replacing it were found in Canada [10], Madagascar [14], and abundant at the Tazhnyi borate deposit in southern Yakutia [5–8] (Table 2). Compositionally close serendibite was found in accessory amounts in the metasomatites of Ukraine [13].

Serendibite with variable Mg# crystallized in hypabyssal skarns (Table 3), which replace dolomites in the contacts of tonalite intrusion in the Castro quarry (Riverside, California, United States [4]), and gabbro of the Ozerskii Massif in the Baikal area [20]. The serendibite from the United States has *f* (*f* = Fe<sup>2+</sup>/Mg + Fe<sup>2+</sup>, at %) from 20 to 25%, reaching 46% in the superimposed calcareous mineral assemblages in the Baikal area. The serendibite from the Ozerskii occurrence is

**Table 3.** Compositions (wt %) of serendibite in the hypabyssal magnesian skarns of California and the Baikal area

Component	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub>	20.82	20.97	20.74	20.26	22.10	20.31	20.89	21.01	17.07	16.33
TiO <sub>2</sub>	0.10	0.03	0.12	0.08	–	0.12	0.07	0.11	0.30	–
Al <sub>2</sub> O <sub>3</sub>	39.30	39.37	39.71	39.16	36.67	39.18	39.10	39.05	42.99	33.49
CaO	15.97	16.04	15.70	15.80	15.79	15.71	15.22	14.87	14.74	16.92
MgO	11.69	10.82	10.69	11.28	11.48	11.24	10.81	10.84	8.45	9.12
FeO	5.17	5.32	5.45	5.62	6.16	5.72	6.14	6.19	13.00	16.26
MnO	0.24	–	–	0.30	–	0.26	0.29	0.32	0.14	–
Na <sub>2</sub> O	–	0.00	0.03	–	0.04	–	–	–	–	–
Σ <sub>1</sub>	93.29	92.56	92.44	92.50	92.24	92.54	92.52	92.39	96.69	92.12
B <sub>2</sub> O <sub>3</sub> *	7.49	7.28	7.29	7.30	7.27	7.23	7.27	7.27	–	7.88
Σ <sub>tot</sub>	101.78	99.88	99.83	99.80	99.62	100.27	99.82	99.94	96.69	100.00
Mineral formula and its <i>f</i> (at %):										
Ca	2.01	2.04	2.00	2.01	2.02	2.00	1.94	1.90	1.90	2.00
Na	–	0.00	0.01	–	0.01	–	–	–	–	–
Σ	2.01	2.04	2.01	2.01	2.03	2.00	1.94	1.90	1.90	2.00
Mg	2.05	1.92	1.90	2.00	2.05	1.99	1.92	1.93	1.54	1.50
Fe <sup>2+</sup>	0.53	0.53	0.54	0.58	0.61	0.60	0.64	0.65	1.32	1.50
Al <sup>VI</sup>	0.42	0.55	0.56	0.42	0.34	0.41	0.44	0.42	0.18	0.00
Σ	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Al <sup>VI</sup>	4.48	4.46	4.66	4.48	4.47	4.50	4.55	4.59	4.48	4.50
Si	2.45	2.49	2.64	2.41	2.64	2.42	2.49	2.51	2.05	3.00
Al <sup>IV</sup>	0.55	0.51	0.36	0.59	0.36	0.58	0.51	0.49	0.95	0.00
Σ	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
B	1.50	1.50	1.50	1.50	1.50	1.50	1.14	0.85	1.50	1.50
Al	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.00
Σ	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
O	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
<i>f</i>	20.5	21.6	22.3	22.6	23.0	23.1	24.9	25.3	46.0	50.0

Note: Castro pit, New City–Victoria Avenue quarry, Riverside, California, the United States: (1) Sample US-042/2; (2) Sample US-044, other components: K<sub>2</sub>O = 0.01%; (3) Sample US-044: ZnO = 0.05 wt %, F = 0.05%; (4) US-042/2; (5) Sample US-044: ZnO = 0.10%; (6) Sample US-042/2; (7, 8) Sample US-041; (9) Ozerskii, Baikal area [20]; (10) calculated composition of Fe-rich serendibite (*f* = 50%).

spatially separated from the tourmaline-bearing metasomatites.

#### ABYSSAL OCCURRENCES OF BORONALUMINOSILICATES

Abyssal serendibite-bearing metasomatites are the most abundant and known worldwide. They were first found in the Gangapitiya quarry, Kandy, Sri Lanka [1, 2], during the mining of moonstone from quartz-feldspar rocks (granulites). Bodies of carbonate rocks found there were metasomatically altered into spinel-forsterite calciphyres and green spinel-fassaite skarns at contact with aluminosilicate rocks. The latter rocks contain dark-blue serendibite, apatite, plagioclase, sca-

polite, and, possibly, tourmaline in near-contact zone. The metasomatic rocks of Sri Lanka also contain sapphirine [24].

In thin sections, the serendibite exhibits pale yellow, almost colorless, to dark indigo pleochroism and polysynthetic twins like those in plagioclase. Crystal-chemically [2], serendibite is similar to sapphirine, with a refractive index of ~1.7 and  $\rho = 3.42 \text{ g/cm}^3$ . It has *f* ~ 11 at % (Table 1). Serendibite richer in Fe (*f* ~ 19%, Table 2) was found during later investigations [19].

The serendibite from Johnsbury, Warren, New York, United States, was studied in more detail [3, 17, 18, 27]. The mineral was found in pyroxene skarns at the con-

**Table 4.** Compositions (wt %) of pyroxenes in magnesian skarns

Component	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub>	53.86	52.09	53.63	48.49	49.55	44.57	51.09	52.90	50.92	37.19
TiO <sub>2</sub>	–	0.06	0.07	0.63	0.53	0.86	–	–	–	1.26
Al <sub>2</sub> O <sub>3</sub>	1.20	4.58	3.35	8.19	7.05	10.95	5.40	6.92	7.15	17.44
CaO	24.43	23.93	23.65	26.89	24.08	24.57	25.86	23.68	24.55	24.14
MgO	16.68	16.84	17.51	14.15	15.57	11.56	15.16	14.93	14.46	7.23
FeO	3.53	1.07	1.09	2.40	1.72	6.85	2.87	2.34	2.33	13.26
MnO	–	0.16	0.12	–	–	0.22	–	–	–	0.15
Na <sub>2</sub> O	0.10	0.40	0.54	0.08	0.12	0.10	0.07	0.04	0.02	0.13
Σ	99.84	99.13	99.96	100.83	100.33	99.68	100.45	100.81	99.43	100.80
Mineral formula and its <i>f</i> (at %):										
Ca	0.96	0.94	0.91	1.040	0.95	0.99	1.01	0.92	0.96	0.96
Mg	0.91	0.92	0.94	0.745	0.83	0.65	0.82	0.80	0.79	0.40
Fe <sup>2+</sup>	0.11	0.03	0.03	0.070	0.05	0.22	0.09	0.07	0.08	0.41
Na	–	0.03	0.04	0.005	0.01	0.01	0.00	0.00	0.00	0.01
Al <sup>VI</sup>	0.03	0.10	0.08	0.140	0.16	0.17	0.09	0.20	0.17	0.22
Al <sup>IV</sup>	0.02	0.10	0.06	0.210	0.16	0.32	0.15	0.09	0.13	0.55
Ti <sup>4+</sup> + Mg	–	–	–	0.035	0.03	–	–	–	–	0.07
Si	1.98	1.90	1.94	1.755	1.81	1.68	1.85	1.91	1.87	1.38
O	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
<i>f</i>	10.6	3.5	3.3	8.6	5.9	24.9	9.6	8.2	8.2	51.0

Note: Diopside: (1) Johnsbury, district of Warren, New York, United States, sample 88306, K<sub>2</sub>O = 0.04% (author's data), (2, 3) Russell, Adirondack, New York, United States [15]. Fassaite: (4) Melville Peninsula, Canada [10], (5) Gangapatiya, Sri Lanka: Fe<sub>2</sub>O<sub>3</sub> = 0.79%, H<sub>2</sub>O = 0.92%, Fe<sup>3+</sup> = 0.02 at % [10], (6) Tazhnyi, Aldan, Yakutia [16], (7, 8) Castro pit, Riverside, California, Sample US-045 (author's data), (9) same, sample US-044, (10) Ozerskii, Baikal area [20].

tact of gneiss granites with Grenville dolomites, in which it occurs in association with partly serpentinized colorless diopside, spinel, sinhalite, yellow phlogopite, plagioclase, and, occasionally, light-green tourmaline [3, 18]. According to our data, the adjacent rocks are made up of light blue (*f* ~ 10%) to colorless diopside (Table 4), low-Fe (*f* ~ 5%), golden-yellow phlogopite, scapolite, and andesine.

According to Larsen and Schaller [3], serendibite from this occurrence has *f* = 9% (Table 1), which is consistent with the high-Mg compositions of the associated spinel (*f* = 9.6%) and other skarn minerals. The Fe-poorer known serendibite (0.65 wt % FeO and 15% MgO, *f* = 2.4%, Table 1) was found there in association with sapphirine (Mg,Al)<sub>8</sub>(Al,Si)<sub>6</sub>O<sub>20</sub> (Table 5), pargasite, (*f* from 2.5 to 3.5%), tourmaline (Table 6), phlogopite (*f* = 5%), and calcite [17, 18]. Our data showed that *f* of the serendibite in association with grandidierite, pargasite, and replacing uvite (Fig. 1) varies from 3 to 4.4% (Table 1). The grandidierite contains a relict spinel, is rimmed by serendibite, and has a more magnesian composition (Mg<sub>0.99</sub>Fe<sub>0.01</sub><sup>2+</sup>)<sub>1.00</sub>Al<sub>2.95</sub>[BO<sub>3</sub>][SiO<sub>4</sub>]<sub>1.05</sub>O<sub>20</sub> (Table 5) than this mineral anywhere else in the world [14]. The uvite

from this skarns also has a magnesian composition (Ca<sub>0.53</sub>Na<sub>0.47</sub>)<sub>1.00</sub>(Mg<sub>2.99</sub>Fe<sub>0.06</sub><sup>2+</sup>)<sub>3.05</sub>Al<sub>6.00</sub>Si<sub>5.95</sub>O<sub>18</sub>(OH<sub>3.73</sub>F<sub>0.27</sub>)<sub>4</sub> (Table 6). However, it shows no deficiency in Al [19].

Our data on the composition and mineral assemblages of Johnsbury serendibite, which were obtained during the study of samples from the collection of the Fersman Mineralogical Museum, Russian Academy of Sciences, and provided for us by the courtesy of N.N. Pertsev, Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, significantly expand literature data on this boronaluminosilicate occurrence.

Serendibite from the borehole core in the Russell skarn, Adirondack, Warren, New York [15, 18], also has *f* = 6.6–7% (Table 1). This serendibite developed after pyroxene skarn and is associated with pargasite, calcite, as well as apatite, scapolite, grandidierite (Table 5), tourmaline, phlogopite, and other minerals. The isotopic composition of boron, which was probably inherited from the sedimentary rocks, suggests its metamorphic–evaporite genesis [18].

Serendibites richer in Fe (*f* = 12–13%) were found at the Melville Peninsula, Franklin district, Canada [10]. They are localized among pyroxene skarns, which

**Table 5.** Composition (wt %) of grandidierite and sapphirine associated with serendibite

Component	1	2	3	4	5	6	7	8	9	10	11
SiO <sub>2</sub>	21.76	21.44	21.14	21.68	21.16	20.81	20.56	13.28	12.65	12.78	14.4
TiO <sub>2</sub>	0.01	0.05	0.01	0.03	0.02	0.03	0.02	–	–	–	–
Al <sub>2</sub> O <sub>3</sub>	51.95	51.97	51.62	51.82	52.56	52.01	51.96	65.10	64.40	65.91	63.8
CaO	0.21	0.12	0.22	0.23	0.05	0.07	–	0.58	0.32	0.13	0.08
MgO	13.66	13.86	14.20	13.55	13.50	13.08	9.81	19.84	19.34	19.72	19.2
FeO	0.22	0.32	0.38	0.43	0.44	1.14	7.17	0.52	0.70	0.64	1.83
MnO	0.05	0.00	0.01	0.00	0.08	0.06	0.15	–	–	–	–
ZnO	0.00	0.07	0.01	0.09	0.05	–	–	–	–	–	–
Na <sub>2</sub> O	0.03	0.00	0.02	0.04	0.01	0.01	–	–	0.05	–	0.09
K <sub>2</sub> O	0.00	0.01	0.00	0.02	0.03	0.03	0.02	–	–	–	–
F	0.04	0.03	0.08	0.01	0.02	–	–	–	0.02	–	–
B <sub>2</sub> O <sub>3</sub> *	11.99	12.02	12.24	11.97	12.01	11.92	11.93	–	1.02	–	0.28
Σ <sub>tot</sub>	99.91	99.89	99.93	99.76	99.93	99.20	101.62	99.32	98.61	99.18	99.68
Mineral formula and its <i>f</i> (at %):											
Mg	0.98	1.00	1.02	0.98	0.97	0.95	0.71	3.43	3.36	3.42	3.34
Fe <sup>2+</sup>	0.01	0.00	0.00	0.02	0.02	0.05	0.29	0.05	0.07	0.06	0.18
Σ	0.99	1.00	1.02	1.00	0.99	1.00	1.00	3.48	3.43	3.48	3.52
Al	2.96	2.95	2.94	2.96	2.99	2.98	2.99	8.91	8.83	9.03	8.80
Fe <sup>3+</sup>	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Σ	2.96	2.95	2.96	2.96	2.99	2.98	2.99	8.91	8.83	9.03	8.80
B	1.00	1.00	1.00	1.00	1.00	1.00	1.00	–	0.21	–	0.03
Si	1.05	1.04	1.00	1.05	1.02	1.01	1.00	1.54	1.47	1.49	1.68
O	9.00	9.00	9.00	9.00	9.00	9.00	9.00	20.00	20.00	20.00	20.00
<i>f</i>	0.7	0.8	0.9	1.2	1.8	4.7	29.1	1.4	2.0	1.8	5.0

Note: Grandidierite: (1–5) Johnsbury, Warren, New York, United States, sample D-02 (author's data); (6) Russell, New York, United States [15]; (7) Ihosy, Madagascar [14]. Sapphirine: (8) Johnsbury, Warren, New York the United States, other components: Li<sub>2</sub>O = 0.013%, BeO = 0.12%, B<sub>2</sub>O<sub>3</sub> = 2.08%, F = 0.04% [18, an. 7]; (9) same, other components: Li<sub>2</sub>O = 0.01, BeO = 0.11% [18, an. 1]; (10) same [18, an. 5]; (11) Kollone, Sri Lanka, other components: insoluble residue = 0.4%, P<sub>2</sub>O<sub>5</sub> = 0.04% [24].

replace dolomites in contact with injections of leucocratic granites and pegmatites. The samples studied in [10] have a zonal structure, where dark-blue tourmaline (uvite, Table 6) with relict diopside is followed by aggregates (up to 5 cm across) of dark-blue serendibite bearing fassaite (Table 4) and accessory minerals, colorless spinel, and calcite, which grades into diopside calciphyre. The serendibites are polysynthetically twinned and have refractive indices  $N_p = 1.700$ ,  $N_m = 1.703$ , and  $N_g = 1.706$ . Vein low-Fe clinozoisite (2.71 wt % FeO), as well as scapolite and scarce prehnite developed at the contact of the two former zones.

As at other deposits, serendibite from the Melville occurrence replaces spinel–fassaite skarn, while tourmaline develops after both skarns and serendibite. Scapolite (meionite) found at the deposit [10] may have developed after the plagioclase–fassaite outer contact nearskarn rocks. The rocks are also known to contain clintonite ( $f < 5\%$ ) [21].

Low-Fe serendibite also occurs in the district of Handeni, northeastern Tanzania. Boden and co-authors [8] identified this mineral by optical properties and X-ray powder diffraction patterns (Debye–Scherrer camera), which were identical to that of serendibites from Johnsbury. Serendibite (and sinhalite) were found in skarns and calciphyres, bearing forsterite, red spinel, yellow–green tourmaline, and Cr-tremolite.

Two other occurrences were found by Nicollet [14] near Ihosy, southern Madagascar. One occurrence was encountered in a quarry at Vohimena's hill, at the contact of forsterite calciphyres with calcite-bearing silicate rocks (gneisses according to [14]). The latter consist of anorthite, scapolite, Al-bearing diopside, amphibole, colorless spinel, and poikilitic blue tourmaline, as well as calcite. In this occurrence, the colorless to pale-green serendibite replaced by tourmaline occurs as dissemination and is compositionally similar to those in the Johnsbury skarns (Table 6). Serendibite of a Prussian-blue color ( $f = 6\%$ ) was found in the Iana-

**Table 6.** Composition (wt %) of tourmaline replacing serendibite

Component	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub>	35.49	36.20	36.35	36.59	35.83	32.93	35.77	36.34	35.40	31.93
TiO <sub>2</sub>	0.08	0.09	0.09	0.09	–	0.27	0.43	0.06	0.05	0.02
Al <sub>2</sub> O <sub>3</sub>	33.03	31.49	32.10	31.32	32.41	30.62	29.52	26.48	29.30	38.59
CaO	3.17	3.37	3.08	3.04	4.67	4.58	5.23	5.69	5.28	2.95
MgO	12.01	12.71	12.14	12.34	12.91	11.97	11.32	14.43	11.53	5.39
FeO	0.45	0.55	0.48	0.41	0.65	1.99	2.79	2.79	4.67	6.89
MnO	0.00	0.00	0.00	0.00	0.02	–	0.00	0.00	0.00	0.04
Na <sub>2</sub> O	1.38	1.35	1.42	1.48	0.51	0.30	0.31	0.03	0.17	1.28
K <sub>2</sub> O	0.04	0.02	0.04	0.02	0.03	–	0.08	0.04	0.01	0.00
F	0.71	0.53	0.42	0.53	–	–	1.29	0.59	0.27	0.01
H <sub>2</sub> O*	2.99	3.05	3.30	3.25	3.52	3.33	2.05	3.33	3.50	3.71
B <sub>2</sub> O <sub>3</sub> *	10.72	10.69	10.73	10.69	10.84	10.22	10.76	9.69	9.90	11.24
Σ <sub>1</sub>	100.07	100.12	100.17	99.76	101.39	96.21	99.55	99.23	99.98	102.07
–F=O	0.30	0.22	0.18	0.22	–	–	0.53	0.25	0.11	0.00
Σ <sub>tot</sub>	99.77	99.90	99.99	99.54	101.39	96.21	99.02	98.98	99.87	102.07
Mineral formula and its <i>f</i> (at %):										
K	0.01	0.01	0.01	0.01	0.01	–	0.02	0.01	–	0.00
Na	0.43	0.42	0.44	0.47	0.15	0.10	0.10	0.01	–	0.40
Ca	0.55	0.57	0.54	0.53	0.80	0.84	0.91	1.01	0.94	0.51
Σ	0.99	1.00	0.99	1.01	0.96	0.94	1.03	1.03	0.94	0.91
Mg	2.90	3.07	2.43	2.99	3.08	3.03	3.22	3.57	2.85	1.30
Fe <sup>2+</sup>	0.06	0.02	0.06	0.06	0.09	0.29	0.36	0.39	0.65	0.93
Σ	2.96	3.09	2.49	3.05	3.17	3.32	3.58	3.96	3.50	2.23
Al <sub>Σ</sub>	6.31	6.00	6.13	6.00	6.13	6.14	5.62	5.18	5.72	7.35
Si	5.75	5.86	5.89	5.95	5.74	5.60	5.78	6.03	5.86	5.16
B	3.00	3.00	3.00	3.00	3.00	3.00	3.00	2.78	2.83	3.13
F	0.38	0.27	0.21	0.27	–	–	0.66	0.31	0.14	0.005
OH	3.62	3.73	3.79	3.73	4.00	4.00	3.34	3.69	3.86	3.995
O	29	29	29	29	29	29	29	29	29	29
<i>f</i>	2.4	2.4	2.0	1.8	2.7	8.6	10.0	9.8	18.5	41.7

Note: (1–4) Johnsbury, Warren, New York, United States, sample M-052, ZnO = 0.00, 0.07, 0.02, and 0.00 (author's data); (5) Ihosy, Madagascar [14]; (6) Melville peninsula, Canada [10]; (7) Tazhnyi, Aldan, Yakutia, sample 1006 (author's data); (8–10) same [16].

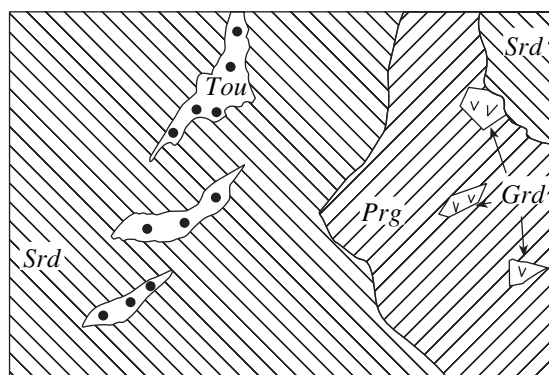
pera occurrence, Madagascar (Table 1). It is associated with magnesian spinel, pyroxene, and amphibole, and is replaced by uvite. Moderately Fe (*f* = 29%) grandidierite (Table 5) and kornrupine were discovered in a Precambrian gneisses of the Ihosy Formation, Madagascar [14].

In Russia, serendibite is abundant in the magnesian skarns of the abyssal boron–iron Tazhnyi deposit, Aldan shield, southern Yakutia. The borate mineralization is made up of magnetite–ludwigite ores replacing forsterite skarns and calciphyres. The latter contain sinhalite and warwickite [5, 7, 9]. In addition, plagioclase–fassaite, spinel–enstatite, and spinel–pyroxene skarns were pervasively tourmalinized. The cores of boreholes

that recovered plagioclase- and spinel-bearing metasomatites contain significant accumulations of serendibite, which developed after these rocks, and is replaced by late tourmaline (uvite).

The properties, chemical composition, and mineral assemblages of serendibite were studied by Shabynin and Pertsev [5, 6, 9, 12], Serdyuchenko and co-authors [7], Grew and co-authors [16, 21], and the authors of this paper.

Unlike aforementioned occurrences, serendibite from the Tazhnyi deposit is mainly a dark blue to a black high-Fe mineral (*f* from 8 to 20%) with variable content of ferric Fe, although pale-colored varieties were also found [7]. Chemical analyses showed that the



**Fig. 1.** Mineral assemblage of serendibite (*Srd*) with grandierite (*Grd*), pargasite (*Prg*), and tourmaline (*Tou*). Johnsburg Deposit, Warren, New York, United States (Sample USJ-05). Magn. 4 $\times$ .

FeO content varies from 3.2 to 4%, while Fe<sub>2</sub>O<sub>3</sub> is from 4 to 2.4%, which is defined by the composition of replaced spinel–fassaite exoskarns or plagioclase-bearing near-skarn rocks. The latter contain the highest-Fe serendibite (Table 2), which is replaced everywhere by tourmaline (Table 6).

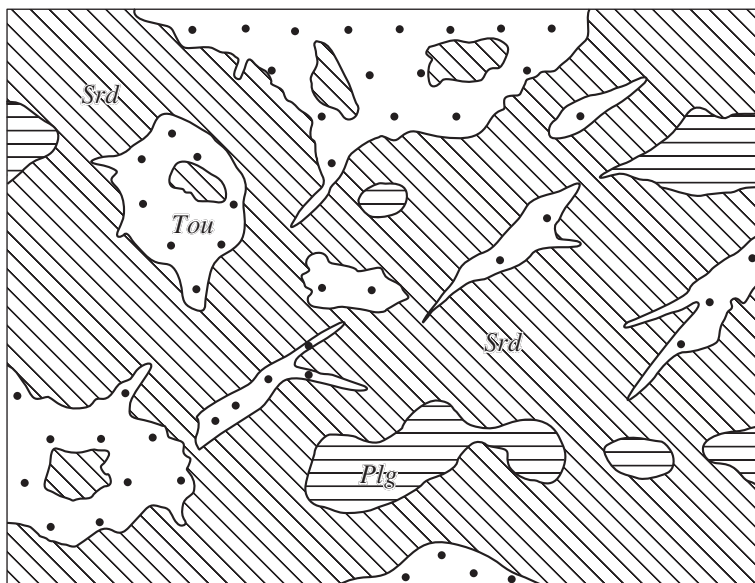
Microprobe analysis showed that serendibite from the core of the borehole that recovered B-bearing skarns of the Tazhnyi deposit (Figs. 2 and 3) contain 4.7 and 6.5 wt % FeO and from 15.2 to 13.4 wt % MgO (Table 2). The serendibite is accompanied by fassaite (*f* up to 20%, Table 4), phlogopite (*f* up to 6%), and spinel (Mg<sub>0.78</sub>Fe<sub>0.22</sub><sup>2+</sup>(Al<sub>1.98</sub>Fe<sub>0.02</sub><sup>2+</sup>)<sub>2</sub>O<sub>4</sub>), and is replaced by tourmaline (Fig. 3). High-Fe serendibite (*f* up to 40%) was also found at this deposit [12, 16], and we

found its rare magnesian variety (*f* up to 12%) in phlogopite–pyroxene skarns adjacent to the zone of spinel–forsterite–clinohumite calciphyre bearing disseminated magnetite and ludwigite (Fig. 4).

Shabynin and Pertsev [5] revealed that the refractive indices of the serendibite from the Tazhnyi deposit depend on the total Fe content. It was shown that their values vary from  $N_g = 1.743$  and  $N_p = 1.738$  (at FeO 5.71%, Fe<sub>2</sub>O<sub>3</sub> 6.38%, and total *f* ~ 12.8% in association with clinopyroxene, phlogopite, and tourmaline, sample 3474a) to  $N_g = 1.730$  and  $N_p = 1.725$  (at 4.72% FeO and 3.30% Fe<sub>2</sub>O<sub>3</sub> in association with clinopyroxene, spinel, and tourmaline, sample 4106). However, a complete chemical analysis [6, sample 3474] showed higher Fe contents in the serendibite (6.06 wt % FeO and 5.05% Fe<sub>2</sub>O<sub>3</sub>). This indicates that the Mg # of serendibite varies even within a single hand specimen. The Tazhnyi deposit is unique among magnesian skarn deposits in having a very high serendibite abundance.

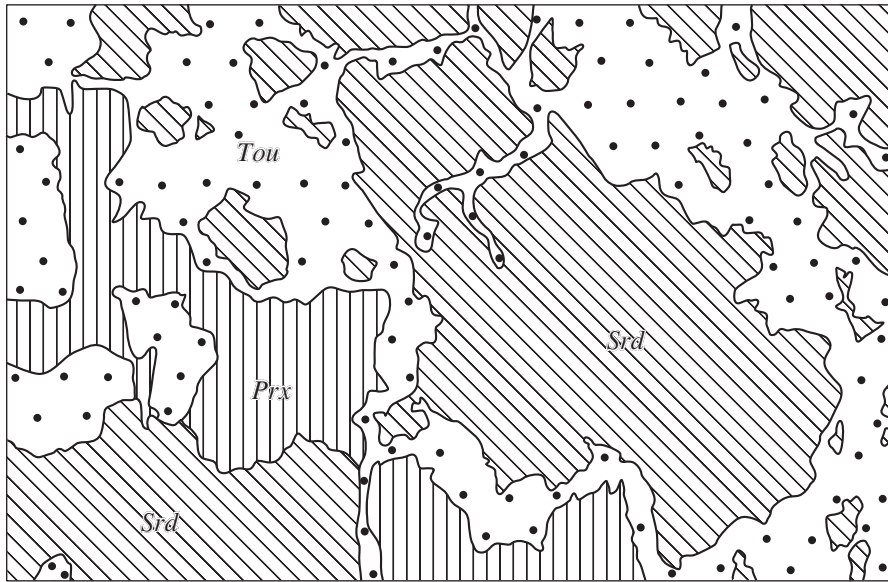
In Europe, serendibite was found in the Razval'e quarry, Pobuzh'e district, in the Ukrainian shield [13], where it was identified in a powder diffraction pattern and by optical properties ( $N_g = 1.739$ –1.740,  $N_p = 1.733$ –1.734), which are similar to those of this mineral from the Tazhnyi deposit. In this occurrence, serendibite was found in spinel- and biotite-bearing feldspar–pyroxene abyssal metasomatites, at the contact of calciphyres with gneisses and crystalline schists.

Thus, serendibite in abyssal skarns is postmagmatic and replaces plagioclase- and spinel-bearing pyroxene metasomatites that developed after dolomites at contacts between aluminosilicate rocks and granites. They have a low- to moderate-Fe composition (Tables 1 and 2).

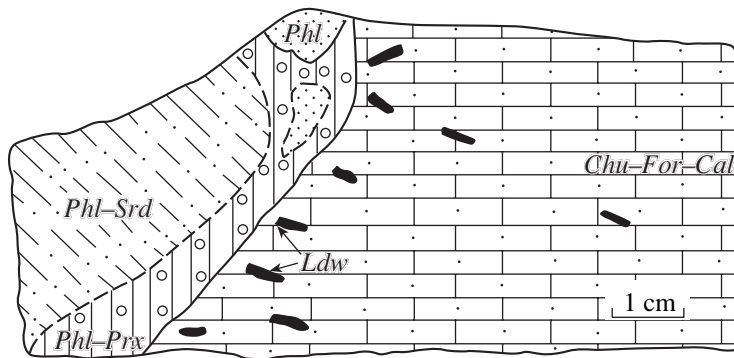


**Fig. 2.** Relict plagioclase (*Plg*) in serendibite replaced by tourmaline. Tazhnyi deposit, Yakutia (Sample TC-01). Scale 1 : 1.





**Fig. 3.** Development of tourmaline after serendibite bearing relict pyroxene (fassaite). Taezhnyi deposit, Yakutia (Sample TC-01). Magn. 40 $\times$ .



**Fig. 4.** Serendibite in the phlogopite-spinel-pyroxene (*Phl-Spl-Prx*) skarn adjacent to ludwigite-bearing clinohumite-forsterite calciphyre (*Ldw-Chu-For-Cal*). Taezhnyi deposit, Yakutia (Sample 5661T). Scale 1 : 1.

Judging from its relations with other boronaluminosilicates, the serendibite formed later than sapphirine and grandierite typomorphic of these facies. Serendibite in these skarns is universally replaced by tourmaline (Fig. 4), unlike the situation in hypabyssal skarns, as is discussed below.

It should be noted that no serendibite occurs in high-Mg skarns that formed after magnesites owing to the extensive desilicification of aluminosilicate rocks (leucocratic granites and gneisses). This does not rule out the development of other boronaluminosilicate (kornrupine and later tourmaline), as is the case with the deposits of Badakhshan and the Hindu-Kush.

Kiselev and Budanov [22] revealed a wide abundance of Precambrian magnesian-skarn deposits in the southwestern Pamirs, Tajikistan. All these deposits are localized in the Goran Group, composed of gneisses and marbles. The latter subsequently vary from calcitic

through dolomitic to magnesite types. Bimetasomatic newly formed corundum-plagioclase rocks and spinel-bearing forsterite and enstatite skarns developed at the contact of magnesian marbles with gneisses.

Kornrupine in the abyssal bimetasomatic skarns of the Stazh deposit located in the Gornyi Badakhshan, southwestern Pamirs, Tajikistan, has a composition similar to the one previously found [23]. Unlike other finds [25], the mineral contains 18.67 wt % MgO, 0.54 wt % FeO, 0.06 wt % CaO, 0.02% MnO, 46.14 wt % Al<sub>2</sub>O<sub>3</sub>, 29.85 wt % SiO<sub>2</sub>, and 0.13 wt % TiO<sub>2</sub>. The calculated formula of the kornrupine is (Mg<sub>0.98</sub>, Fe<sub>0.02</sub><sup>2+</sup>)<sub>3</sub>Al<sub>5.76</sub>(Si<sub>3.17</sub>B<sub>2.07</sub>)<sub>5</sub>O<sub>21</sub>(OH) and suggests the presence of 2.33 wt % B<sub>2</sub>O<sub>3</sub> at an anhydrous analytical total of 97.81 wt % (H<sub>2</sub>O = 1.74), in total accounting for 99.55 wt %.

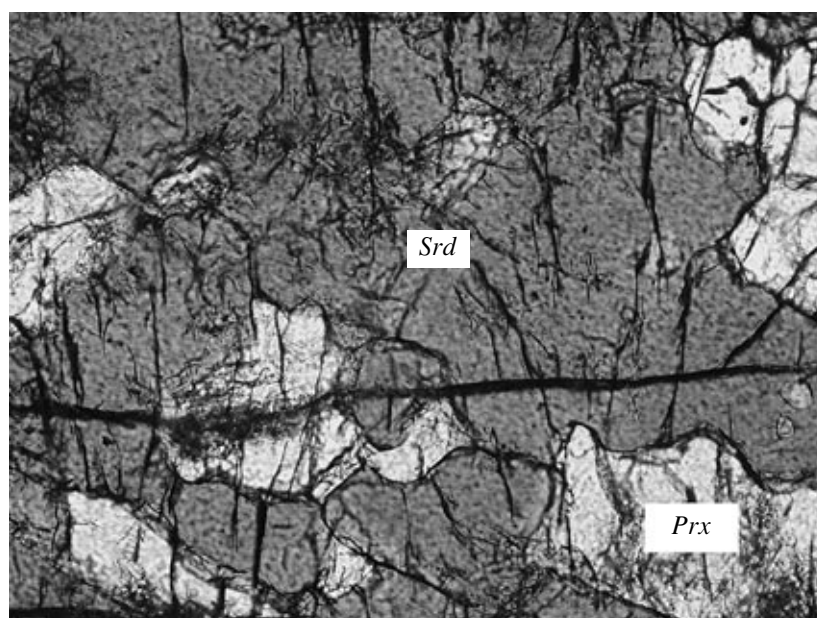


Fig. 5. Serendibite with relict fassaite. Riverside deposit, California, United States (Sample US-044). Magn. 40 $\times$ .

The kornerupine from the Stazh deposit occurs together with corundum and andesine (60 mol % *Ab*, 35 mol % *An*, and 5 mol % *Kfs* end members) in the desilicified aluminosilicate rocks: at the contact with enstatite skarns or immediately with spinel–forsterite skarns (recording  $\text{SiO}_2$  migration required for their formation) grading into primary magnesites [23]. The mineral belongs to the high-Mg species [25]. It is replaced by colorless and pale tourmaline [23]. Its formation could be caused by the fact that the highly magnesian replaced rocks were attacked by postmagmatic hydrothermal solutions with B content was too low to produce serendibite. Skarns at the Pamirs and Hindu-Kush show no postmagmatic calcareous skarn alterations after magnesites and adjacent aluminosilicate

rocks [22, 23, 26, 27], such as in the abyssal metasomatites developing after dolomites elsewhere [28–31].

Kornerupine in this setting is also known in the magnesian skarns of the Sar-e-Sang deposit, Badakhshan province, Afghanistan [27]. It was shown that this mineral occurs in the rhythmically banded metasomatites, associating with magnesite, sapphirine, and phlogopite or with magnesite, forsterite ( $f = 2\%$ ), and phlogopite. Data presented by E. Grew indicate that the kornerupine contains about 0.3 wt % FeO at 1.83 to 3.09 wt %  $\text{B}_2\text{O}_3$ . Another boronaluminosilicate known at this deposit is tourmaline (dravite). It is a later mineral and replaces biotite–feldspar gneisses contained in the marble sequence.

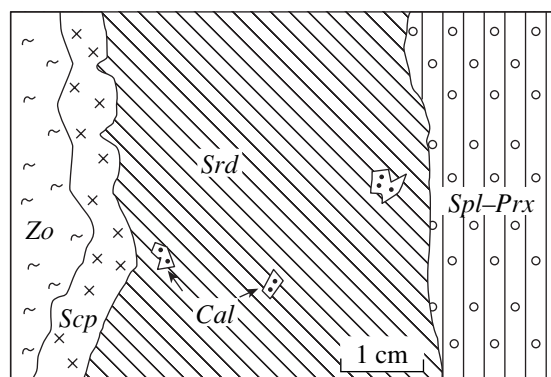


Fig. 6. Development of serendibite after spinel–pyroxene skarn, and scapolite (*Scp*) and zoisite (*Zo*) after plagioclase–pyroxene skarn. Riverside deposit, California, the United States (Sample US-042). Magn. 2 $\times$ .

#### HYPABYSSAL OCCURRENCES OF BORONALUMINOSILCIATES

Serendibite in the hypabyssal magnesian skarns was studied less thoroughly, and is known to occur at the Castro quarry, Riverside, California [4], and in the skarn aureole of the Ozerskii Massif, western Transbaikalia [20]. At both occurrences, the mineral is localized in metasomatites developed after dolomites at contacts with intrusions with relatively low  $\text{SiO}_2$  contents: tonalite and gabbro.

The district of Riverside, California, United States, is characterized by numerous occurrences of magnesian skarns formed at shallow and the shallowest depths after dolomites and their calcareous varieties (dolostones), which are mined for cement production. The most widely known skarns are those of the quarries of Crestmore, New City–Victoria, North Hill, Jensen, and

others, with a unique mineralogical diversity of silicates, oxides, and phosphates [30, 31]. They also contain endogenous boron minerals: kotoite, aluminomagnesiuldwigite, ludwigite, serendibite, axinite, wightmanite, and others.

Serendibite was found in the New City quarry, Riverside county, by Larsen and occurs there in association with pyroxene and andesine–labradorite plagioclase in metasomatically altered dolomites. The mineral was identified based on its optical properties and studied by Richmond [4]. It was shown that the refractive indices of this dark-blue mineral are significantly higher ( $N_p = 1.719$ ,  $N_m = 1.722$ , and  $N_g = 1.724$ ) than those of pale blue to colorless serendibite from the Johnsbury, Warren district, New York, United States ( $N_p = 1.701$ ,  $N_m = 1.703$ , and  $N_g = 1.706$ ) [3], because of its high Fe content.

Our samples of the B-bearing skarns were taken from the Castro pit, New City–Victoria Avenue quarry. They form almost monomineral pockets (5–10 cm across) and dissemination of large (up to 2 cm long) subhedral black serendibite crystals (Fig. 5), with interstices filled with carbonates. The boronaluminosilicate develops after spinel–fassaite (Fig. 6) and, partially, plagioclase–pyroxene exoskarns at contact with pyroxene–biotite–amphibole tonalites (quartz diorites), which contain 62.2% SiO<sub>2</sub>. The latter rocks are made up of andesine (>50 vol %) and quartz (20 vol %). The metasomatic zoning of skarns was supposed to form after dolomites at contacts with a tonalitic melt at a temperature as high as 975°C [28–30].

The following zones can be distinguished in the prograde metasomatic column of skarn aureole in this occurrence: tonalite—plagioclase–pyroxene skarn—spinel–fassaite skarn—spinel–forsterite calciphyre—periclase marble—dolomite. The absence of a monoforsterite skarn zone indicates that exoskarns were not replaced by the melt, which caused Mg redistribution into the outer metasomatic zones. Hence, the skarn aureole belongs to the spinel–periclase hypabyssal metasomatic facies of dolomites [30].

The metasomatic zones significantly changed in composition during the postmagmatic stage. This is expressed in the replacement of spinel and plagioclase–pyroxene skarns by serendibite with the subordinate development of phlogopite. In the adjacent calciphyres, forsterite is transformed into humites and phlogopite (if spinel is present), while periclase in marbles is replaced by brucite pseudomorphs.

The subsequent overprinting of calcareous assemblages on exoskarns and adjacent tonalites, typical of hypabyssal metasomatites [31], is expressed in the appearance of salite  $\text{Ca}_{1.02}(\text{Mg}_{0.53}\text{Fe}_{0.44}\text{Mn}_{0.01})_{0.98}(\text{Si}_{1.99}\text{Al}_{0.01})_2\text{O}_6$ , spinel (gahnite,  $f \sim 27\%$ , ZnO from 7.2 to 8.7%), clintonite ( $f = 6.5\%$ ), vesuvianite ( $f = 36\%$ ), ferroclinozoisite (FeO from 1.9 to 4 wt % depending on the extent of Al

substitution by Fe<sup>3+</sup>: from 3 to 8%), grossular (with 5 mol % andradite), Fe actinolite ( $f = 47\%$ ), amesite ( $f$  from 6.5 to 11.5%), and scapolite with 14–17% marialite (after anorthite).

The serendibite from Riverside, which was not studied previously, contains from 5.17 to 6.19 wt % FeO at MgO decreasing from 11.69 to 10.81%,  $f = 20.5$ –25.3 wt % (Table 3). No tourmaline was found in the serendibite from the Castro quarry.

The Fe-richest serendibite ( $f = 46\%$ ,  $N_g = 1.740$ –1.742,  $N_p = 1.736$ –1.737) was found by Savel'eva and others [20] in altered magnesian skarns after dolomites at the contact of the Ozerskii gabbroid massif in the western Baikal area (Table 3). In this occurrence, spinel–fassaite ( $\pm$ calcite) skarns were locally replaced by clintonite ( $f = 10.5\%$ ).

The magnesian skarns of the prograde metasomatic stage in the gabbroid contacts have a complex composition. In addition to the aforementioned minerals, they bear low-pressure merwinite and associated neomorphic spurrite, kilchoanite, and other high-Ca silicates typical of shallow-depth hypabyssal metasomatites [31, 32].

The serendibite from the Baikal area accounts for up to 5 vol % of the rocks, replacing spinel with 40–52% hercynite, in close association with clintonite and, occasionally, relict fassaite (Table 4) [20]. This indicates that the mineral was formed owing to the calcareous–skarn replacement of magnesian skarns. The subsequent evolution caused the crystallization of vesuvianite ( $f = 45\%$ ) and garnet with 65% grossular in the pyroxene–garnet, spinel–garnet, and garnet rocks. Savel'eva and co-authors [20] documented vesuvianite replacement by serendibite.

Pyroxene and epidote–garnet inner-contact rocks also contain sparse dissemination of serendibite, while the bytownite- and fassaite-bearing rocks contain late uvite and epidote. Serendibite and tourmaline in the skarns of the Baikal area are spatially separated. Like in Riverside county, these rocks contain neither sapphirine nor grandidierite.

Genetically, the skarns of the Ozerskii Massif and Riverside county, California, belong to the spinel–merwinite and spinel–periclase facies of dolomite metasomatism, respectively [30–32].

The aforementioned data indicate that  $f$  in serendibite from hypabyssal occurrences is similar to or significantly higher ( $f$  up to 46%) than those in serendibites from the skarns of the Tazhnyi deposit. Their composition reflects the replacement of high-Fe magnesian skarns and the syngenetic or subsequent evolution of low-pressure minerals. The spinel (pleonast) coexisting with serendibite contains Zn.

## CRYSTAL CHEMISTRY OF SERENDIBITE

The structural study of high-Mg varieties ( $f = 2\%$ ) showed that the serendibite from Johnsbury, United

States [33–35], belong to the triclinic system and have the following unit cell parameters:  $a_0 = 10.02 \text{ \AA}$ ,  $b_0 = 10.39 \text{ \AA}$ , and  $c_0 = 8.63 \text{ \AA}$  at  $\alpha = 106^\circ 21'$ ,  $\beta = 96^\circ 04'$ ,  $\gamma = 124^\circ 21'$ , and  $Z = 2$ , spatial group *P1*. Their values increase with increasing the  $f$  of the mineral. For example, serendibite from the Tazhnyi deposit, Aldan ( $f = 20\%$ ) [19], has the following parameters:  $a_0 = 10.094 \text{ \AA}$ ,  $b_0 = 10.478 \text{ \AA}$ , and  $c_0 = 8.694 \text{ \AA}$  at  $\alpha = 106.36^\circ$ ,  $\beta = 96.00^\circ$ , and  $\gamma = 124.40^\circ$ . There is a linear correlation between the  $a_0$  and  $c_0$  values. In serendibite with  $f \sim 50\%$ , these parameters can reach, respectively, 10.085 and 8.73 Å. It was shown [11, 19, 34] that this mineral is crystal-chemically similar to the aenigmatite group and triclinic (1Ts) sapphirine:  $a_0 = 8.62 \text{ \AA}$ ,  $b_0 = 9.57 \text{ \AA}$ , and  $c_0 = 9.97 \text{ \AA}$  at  $\alpha = 63.85^\circ$ ,  $\beta = 84.80^\circ$ , and  $\gamma = 65.33^\circ$ .

#### CALCULATION OF THE SERENDIBITE FORMULA

The mentioned data revealed the variable composition of serendibites around the world. The structural formula corresponds to  $(\text{Ca,Na})_2(\text{Mg, Fe}^{2+})_3(\text{Al,Fe}^{3+})_{6.5}\text{B}_{1.5}\text{Si}_3\text{O}_{20}$ . Large samples from the Tazhnyi deposit contain  $\text{H}_2\text{O}$  (0.75–1.11 wt % [5]). However, the absence of exothermic and endothermic peaks in the nearly rectilinear thermogravimetric curve until  $1000^\circ\text{C}$  [6] suggests that the mineral is anhydrous.

The chemical formula of the minerals was calculated on the basis of 14 cations. If data on  $\text{B}_2\text{O}_3$  content are absent, the formula was calculated on the basis of 12.5 cations, taking 1.5 atoms B in serendibite, which is possibly not constant assuming its partial replacement by Al.

Our data (Tables 1–3) indicate the possible, but not always necessary, presence of subordinate Na amounts (up to 0.9%  $\text{Na}_2\text{O}$ ) isomorphous with Ca, with a total amounting to less than 2%. Microprobe analysis with all iron determined as FeO were calculated based on the isomorphism of Mg and  $\text{Fe}^{2+}$  accounting in total for no more than 3. If the total was more than 3, the excess FeO was recalculated into  $\text{Fe}_2\text{O}_3$  and was added as  $\text{Fe}^{3+}$  to Al. The presence of iron with different valence in serendibite can be determined by Mössbauer spectroscopy.

Calculations showed that the Al content in the formula of the mineral is always more than 4.5 p.f.u., indicating that this amphoteric element occupies the sites of other ions in the crystal lattice of serendibite: (Ca + Na) (Mg +  $\text{Fe}^{2+}$ ), Si and B. The amount of Si is occasionally less than 3 (Tables 1–3).

Deer and co-authors [11] reported the general formula of serendibite as  $(\text{Ca, Na})_2(\text{Mg, Fe}^{2+}, \text{Fe}^{3+}, \text{Al})_6\text{O}_2[(\text{Si, Al, B})_6\text{O}_{18}]$ . The formula offers the possibility of complex isomorphism in the mineral, including possible partial B substitution for Al, which was taken into account during the calculation of the chemical formulas.

#### MINERAL ASSEMBLAGES OF BORONALUMINOSILICATES

In spite of the general tendency in the serendibite evolution of the replacement of pyroxene-bearing magnesian skarns, which typically consist of fassaite, spinel, and plagioclase, its assemblages depend on the depth facies of metasomatism of the dolomitic sequences. Serendibite from the hypabyssal occurrences is typically associated with syngenetic and later calcareous assemblages, including low-pressure minerals.

As a result, the serendibite assemblages (Table 7) contain relict minerals of precursor replaced magnesian skarns (fassaite, spinel) and near-skarn pyroxene–plagioclase rocks of the prograde metasomatism of dolomites. Abyssal skarns additionally contain sapphirine, grandidierite, sinhalite [36], and newly formed syngenetic phlogopite with a decreasing F mole fraction, as well as calcite, pargasite, zoisite, scapolite, and others.

Clintonite is more typical of hypabyssal skarns of Riverside county, California, and the Baikal area [20], whereas its position [37, 38] in the skarns of Melville, Canada [10], and the Tazhnyi deposit, Aldan [16], remains unclear. The low-pressure nature of clintonite was confirmed in experiments [39]. Its formation owing to the influence of chloride hydrothermal solutions on the spinel–pyroxene skarns is indicative of their calcareous–skarn replacement, which rarely occur in abyssal conditions. Clintonite precedes vesuvianite and garnet, but may be replaced by phlogopite. Hypabyssal deposits contain, in addition to clintonite, salite, tremolite, vesuvianite, and grossular.

Early pyroxenes in serendibite-bearing rocks formed during the prograde stage of magnesian skarns, are ascribed to low-Fe fassaite with a variable Al content, occasionally reaching 17 wt %  $\text{Al}_2\text{O}_3$  (Table 4), or to diopside. The later pyroxenes of the superimposed assemblages correspond to high-Fe salite. The most aluminous pyroxenes are fassaite in hypabyssal serendibite occurrences. They are associated with spinel and are replaced by salite. Abyssal occurrences are dominated by moderately aluminous pyroxenes.

Spinel in abyssal fassaite skarns has either a magnesian composition or is close to pleonast, occasionally containing the  $(\text{Mg, Fe}^{2+})\text{Fe}_2^{3+}\text{O}_4$  end member. The replacement of spinel by serendibite predetermines the presence of more ferric ion in the replacing serendibite than that when fassaite alone is replaced. The rocks can also contain Cr-bearing spinel (in Tanzania). By contrast, the late spinel in hypabyssal occurrences (for example, in Riverside, Californian) is enriched in gahnite (up to 14–17 mol % at  $f \sim 27\%$ ), while spinel from the Ozerskii occurrence contains up to 40–52 mol % hercynite.

Under abyssal conditions, excess Al in the replaced rocks could be simultaneously involved in sinhalite  $\text{MgAlBO}_4$  that developed after spinel simultaneously

**Table 7.** Mineral assemblages of serendibite in abyssal and hypabyssal magnesian skarns

Deposits	1	2	3	4	5	6	7	8	9	10	11
Facies	Abyssal									Hypabyssal	
Diopside, fassaite	x	x	x	x	x	x	x	x	x	x	x
Spinel	x	x	x	x	x	x	x	x	x	x	x
Plagioclase	x					x	x		x	x	x
K-feldspar								x			
Corundum							x				
Phlogopite		x	x					x	x	x	
Calcite		x	x		x		x	x	x	x	x
Zn-bearing spinel										x	
Pargasite		x	x			x	x		x	x	
Scapolite	x	x	x		x	x	x				
Tourmaline		x	x	x	x	x	x		x	x	
Grandidierite		x	x				x				
Vesuvianite										x	x
Clintonite					x				x	x	x
Margarite									x		
Clinozoisite		x			x	x			x	x	x
Sinhalite		x		x					x		
Ludwigite									x		
Grossular						x		x	x	x	x
Sapphirine		x									
Titanite										x	x
Magnetite											x
Anhydrite									x		
Tremolite				x							
Thompsonite					x				x		
Graphite								x			
Scheelite									x		
Pyrrhotite									x		
Pyrite									x		
Chlorite, amesite									x	x	

Note: Deposits and occurrences of serendibite in skarns of the abyssal facies: (1) Gangapatiya, Sri Lanka [1, 2, 19]; (2) Johnsburg, Warren, New York, United States [18 and author's data]; (3) Russell, New York, United States [15]; (4) Handeni, Tanzania [8]; (5) Melville Peninsula, Canada [10]; (6) Ianopeta, Madagascar [14]; (7) Ianapera, Ihozy, Madagascar [14]; (8) Razval'e, Ukrainian shield, Ukraine [13]; (9) Tazhnyi, Aldan shield, Yakutia [6, 7, 9, 12 and author's data]. Deposits and occurrences of serendibite in skarns of hypabyssal facies: (10) Castro pit, Riverside, California, United States [4 and author's data]; (11) Ozerskii, western Transbaikalia.

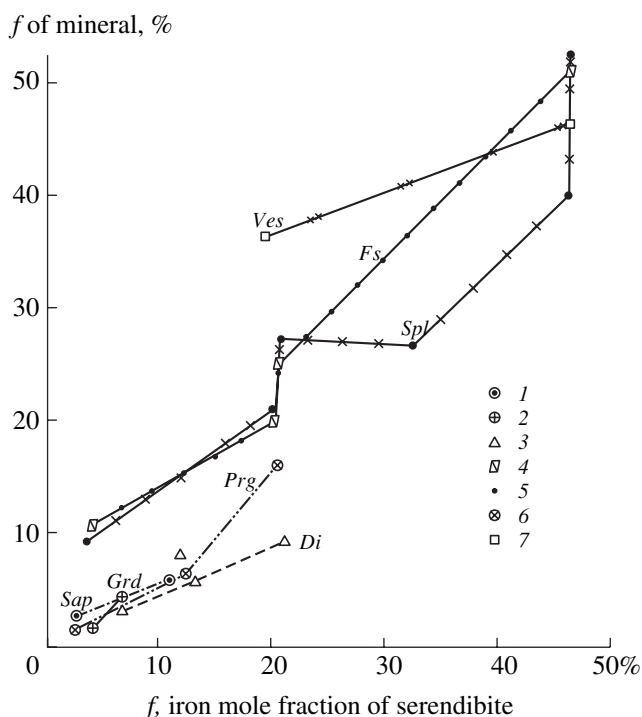
with serendibite [36] or in grandidierite (Table 5) during interaction with B-bearing hydrothermal solutions, as in the skarns of Sri Lanka [1, 2], Johnsburg and Russell in the United States [3, 17, 18], Tazhnyi deposit in Aldan [5–7, 9, 12, 16], and Tanzania [8].

Plagioclase from the near-contact zones of magnesian skarns in Riverside, United States, is anorthite and less abundant bytownite, like those at the Tazhnyi deposit of Aldan. The products of endogenous replace-

ment are serendibite, clinozoisite, scapolite, as well as thompsonite at the Tazhnyi deposit [16].

Magnesian orthosilicates associated with serendibite at the Tazhnyi deposit are low-Fe olivine (11.33–14.55 wt % FeO), which contains 24–30 mol % fayalite [16]. The newly formed clinohumite containing 1–4.3 wt % F has the lowest *f* and FeO of less than 9 wt % [16].

The associated aluminous minerals in the magnesian environment are phlogopite of decreasing Mg#



**Fig. 7.** Correlation of  $f$  in serendibite with those of skarn minerals. (1) Sapphirine (*Sap*); (2) grandidierite (*Grd*), (3) diopside (*Di*), (4) fassaite (*Fs*), (5) spinel (*Spl*), (6) pargasite (*Prg*), and (7) vesuvianite (*Ves*). Initial data are given in tables.

that developed in spinel-bearing rocks (Johnsburg and Russell in the United States, Tazhnyi in Aldan) or scapolite (meionite) containing up to 20 mol % mariolite and thompsonite replacing plagioclase at the Melville deposit in Canada. Serendibite was found, together with pargasite or vesuvianite and clintonite, in the superimposed calcareous-skarn assemblage. These minerals are typical of hypabyssal occurrences in California and the Ozerskii Massif in the Baikal area, and of some abyssal deposits (Melville and Tazhnyi). In addition, clintonite and margarite, which are more typomorphic of superimposed calcareous skarns, were found in association with serendibite at the Tazhnyi deposit [16] of a supposedly abyssal genesis [5–7].

As was mentioned above, data on the stability and phase relations of clintonite do not rule out its formation at shallow depths [37, 38]. Moreover, Khodarevskaya experimentally showed [39] that clintonite is a typomorphic mineral of hypabyssal skarns.

In the rear zones of magnesian-skarn aureoles (near-skarn rock according to Korzhinskii [40]), serendibite also replaces pyroxene-plagioclase assemblages, which is most distinctly expressed at the Tazhnyi deposit (Fig. 2). This process is accompanied by the development of pargasite and clintonite, prior to the replacement of serendibite by tourmaline (Tazhnyi, Fig. 3, and other occurrences). An early mineral at the abyssal serendibite occurrences in Johnsburg (our data)

and in Russell [15, 18] is grandidierite ( $\text{Mg, Fe}^{2+}\text{Al}_3[\text{BO}_3][\text{SiO}_4]\text{O}_2$ ). Sapphirine ( $\text{Mg, Al}_8(\text{Al, Si})_6\text{O}_{20}$  (Table 5) with ~1%  $\text{B}_2\text{O}_3$  was found at the Johnsburg deposit [18]. Serendibite may have replaced grandidierite during the superposition of calcareous skarns.

Later tourmalines in the serendibite-bearing rocks are dravite  $\text{NaMg}_3\text{Al}_6[\text{BO}_3]_2\text{Si}_6\text{O}_{18}(\text{OH})_4$  and uvite  $(\text{Ca, Na})(\text{Mg, Fe}^{2+})_3\text{Al}_5\text{Mg}[\text{BO}_3]_2\text{Si}_6\text{O}_{18} \cdot (\text{OH, F})_6$  (Table 6). They are associated with zoisite replacing plagioclase (Johnsburg, United States, Melville, Canada [10], and Riverside, United States). The phlogopite-bearing skarns of Pamirs [22, 23] contain snow-white or light-brown low-Fe ( $\text{FeO} = 1.44\%$ ,  $\text{MgO} = 28.3\%$ ,  $\text{Na}_2\text{O} = 1.9\text{--}2.5$  wt %) zoned tourmaline (achroite) of the elbaite-dravite series, which possibly replaces kornerupine.

#### CORRELATION BETWEEN THE COMPOSITIONS OF SERENDIBITE AND SKARN MINERALS

It was shown that the composition of minerals composing magnesian skarns strongly affect that of the serendibite replacing them. This can be illustrated by the correlation of their  $f$  (Fig. 7). In particular, high-Mg serendibite is associated with low-Fe diopside and fassaite, whereas pyroxenes richer in Fe are replaced by serendibite of decreasing Mg#, which is most typical of its hypabyssal occurrences. The same tendencies can be observed for spinel. At abyssal deposits, where sapphirine and grandidierite are replaced by early skarn minerals, their  $f$  also defines the composition of serendibite, while tourmaline developed after serendibite inherits its  $f$  at a decreasing  $F$  mole fraction. The related increase in  $f$  of phlogopite replacing spinel-pyroxene skarns is defined by the composition of the replaced skarn minerals. Clintonites and vesuvianite at the hypabyssal serendibite occurrences also record a subsequent increase in the total iron content in the early magnesian skarns.

#### SYNTHESIS AND PHASE RELATIONS OF SERENDIBITE

It was shown in experiments [41] that serendibite is stable within 500–900°C and from 2 to almost  $30 \times 10^8$  Pa. Monomineral serendibite was obtained at 820°C and  $1.2 \times 10^8$  Pa and at 830°C within  $1\text{--}20 \times 10^8$  Pa, which testifies to its formation under both hypabyssal and abyssal conditions. It was noted that serendibite is associated, first, with tourmaline and chlorite, and second, with sinhalite and tourmaline (uvite), which is consistent with natural assemblages (Table 7).

#### CONCLUSIONS

The above data on the genesis, composition, and mineral assemblages of serendibite, grandidierite, kor-

nerupine, and tourmaline in magnesian skarns reflect definite difference in the facies of the replaced metasomatites. The composition ( $f$ ) of the replaced rock-forming minerals is correlated with those of the associated minerals and serendibite. It increases systematically at abyssal deposits, reaching the highest values at hypabyssal deposits.

Grandierite ( $\text{Mg, Fe}^{2+}$ ) $\text{Al}_2[\text{BO}_3](\text{SiO}_4)\text{O}_2$  is characterized only by isomorphous substitution of Mg for  $\text{Fe}^{2+}$ . In particular, low-Fe grandierite ( $f = 2\%$ ) from phlogopitized spinel–diopside skarns at Fort Dauphin, Madagascar ( $N_p = 1.580$ ,  $N_m = 1.619$ ,  $N_g = 1.620$ , and  $2V = 24^\circ$  with unit cell parameters  $a_0 = 10.963 \text{ \AA}$ ,  $b_0 = 10.326 \text{ \AA}$ , and  $c_0 = 5.758 \text{ \AA}$ ) [42, 43], is the most similar in composition to that found in the Johnsbury skarns, New York, whereas grandierite from the Russell deposit has  $f \sim 5\%$  in association with serendibite with  $f = 7\%$  (Tables 1 and 7). If serendibite is absent, the  $f$  of grandierite is as high as 20% [42].

The data presented above show that grandierite occurs in both abyssal and hypabyssal occurrences. The latter can be exemplified by its presence in xenoliths of altered dolomites in the plutonic and volcanic rocks of Cimino and Amiato volcanoes in Italy [44]. The magmatic chamber of the volcanoes of the Rome volcanic province (Lazio district) is rimmed by dolomites, whose alteration products universally contain low-pressure minerals typical of shallow-depth skarns (for example, monticellite, merwinite, perovskite, and harkerrite) [30, 45, 46].

In contrast to the above boronaluminosilicates of magnesian skarns, kornerupine ( $\text{Mg}_{0.98}\text{Fe}_{0.02}^{2+}$ ) $\text{Al}_{5.76}(\text{Si}_{3.17}\text{B}_{2.07})_5\text{O}_{21}(\text{OH})$  is not associated with serendibite and occurs only in abyssal metasomatites. This mineral can be, like grandierite, early post-magmatic and develop after high-Mg minerals at a low B content in the hydrothermal solutions. This is evident from the finds of its B-free analogues [21, 25]. Like serendibite, kornerupine is associated with and replaced by tourmaline [25, 27]. Our data reveal genetic features and characterize the compositions of the studied boronaluminosilicates as typomorphic minerals and the diversity of their assemblages in the postmagmatically altered magnesian skarns, implying a magmatic source of boron.

## CONCLUSIONS

(1) Serendibite is the rock-forming mineral that occurs in rocks of several facies in both abyssal and hypabyssal B-bearing magnesian skarns. Among typomorphic boronaluminosilicates of metasomatic rocks, serendibite is more abundant than grandierite and kornerupine, but is significantly more scarce than tourmaline.

(2) The high Ca contents in serendibite testify to its generation during the superposition of calcareous

skarns on the abyssal magnesian skarns. This is emphasized by the coexistence of serendibite with clintonite and its stability in hypabyssal calcareous assemblages.

(3) Variation in  $f$  of serendibite correlates with that of replaced skarn minerals (pyroxenes, spinel, and pargasite) and early boronaluminosilicates (grandierite). This tendency also follows from the correlation between the compositions of syngenetic minerals (clintonite, vesuvianite, and garnets) and later minerals (tourmaline, phlogopite, and others), as well as those replacing magnesian skarns and/or serendibite.

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