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Endogenous Transformations of Kotoite in Calciphyres at Magnesian-Skarn Deposits of Boron

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Abstract—The succession of endogenic transformation of kotoite and accompanying minerals in marbles and calciphyres at hypabyssal magnesian-skarn deposits of boron is proved to be controlled by the anion composition of the hydrothermal solutions and the Mg mole fraction of the carbonate rocks. Early in the postmagmatic stage forming the B ore mineralization, the solutions contain Fe and F, as is reflected in the formation of kotoite and suanite in association with clinohumite, phlogopite, and Al- and Ti-bearing Mg–Fe borates, such as magnesiohulsite and magnesioludwigite. An increase in the F concentration of the hydrothermal solutions stimulates the formation of humites (from clinohumite to chondrodite and norbergite), which are replaced in the presence of kotoite by pertsevite (a hydroxofluorosilicateborate). In the calciphyres of Mount Brooks, Alaska, and at other deposits, the latter mineral is rock-forming in kotoite–clinohumite calciphyres, replaces this association, and is accompanied by fluoborite, nocerite, and fluorite. The further compositional transformations of the solutions with their enrichment in Cl result in the replacement of kotoite marbles and calciphyres and adjacent periclase marbles by sakhaite rocks with newly formed karlite. The neutralization of the hydrothermal solutions and their simultaneous cooling control the replacement of kotoite rocks by borcarite. The endogenic transformations of kotoite end with its szaibelyitization and/or brucitization and the simultaneous development of wightmanite in the marbles and the subsequent carbonatization of the borates. The research was carried out with the use of the author materials from boron deposits in Russia, Korea, Romania, England, France, and the United States.

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INTRODUCTION

Borate mineralization in the form of kotoite marbles and calciphyres was found at many hypabyssal B deposits in magnesian skarns in Russia and other countries in Asia, Europe, and North America [1–11]. In addition to kotoite $Mg_3[BO_3]_2$, a typomorphic mineral of carbonate rocks surrounding B-bearing magnesian skarns developing in dolomites, the rocks may contain minor amounts of kotoite analogues: jimboite $Mn_3[BO_3]_2$, which replaces rhodochrosite in calciphyres [12–14], and takedaite $Ca_3[BO_3]_2$ in calcite marbles [15] surrounding intrusions to which the development of magnesian, manganoan, and calcic skarns is genetically related.

This study was centered on the mineralogy and mineral chemistry of borate ores, including their kotoite and sakhaite varieties, at more than 25 deposits at the Cherskii Range in the eastern Chukot Peninsula, Russia, Banat deposit in Romania, and other deposits in France, Scotland, Alaska, the western United States, and elsewhere. This made it possible to consider not only the geochemistry of processes forming these deposits but also to more comprehensively examine the postmineral alterations of Mg orthoborates and to compare these results with literature data on these minerals.

Kotoite deposits and occurrences are hosted in the outer-contact aureoles of granite, granodiorite, and diorite intrusions emplaced in dolomites, which are replaced by magnesian skarns. The latter genetically correspond to the periclase and monticellite *P-T* facies of the prograde metasomatism stage and are characterized by the occurrence of the following clearly pronounced zoning: intrusive rock // diopside (±spinel) or fassaite skarn—(spinel– or perovskite–monticellite calciphyre)—spinel–forsterite calciphyre—periclase marble—dolomite marble. The rocks of these zones, which compose the outer metasomatic aureoles, are characterized by the inheritance of the Mg/Ca ratio from the pristine dolomites and the presence of low-pressure periclase and, more rarely, monticellite.

Magnesian skarn bodies at contacts with intrusions are often conformable with them [7, 8]. The faulting of the carbonate roofs of the intrusions is favorable for the development of steep skarn bodies (which can be observed at the Hol Kol deposit in North Korea [2] and the Baitsa Bichor deposit in Romania [2, 16]) and stockworks, as at the Gidjarva deposit in Tajikistan [17].

Magnesian skarns produced during the prograde stage of dolomite transformations contain no ore mineralization and endogenic borates. The latter are formed during the postmagmatic stage of the replacement of the rocks composing the outer zones of contact aureoles. All known kotoite deposits and occurrences are localized in marbles and calciphyres.

EARLY BORATE MINERALIZATION

This mineralization consists of suanite and kotoite, Mg borates [16, 18] that successively replace magnesian carbonates in spinel–forsterite calciphyres and periclase marbles or dolomite in steep bodies, which contain none of these rocks [8]. In contrast to suanite, which occurs in borate ores at magnesian skarn deposits of all depth facies, kotoite is a low-pressure mineral [5, 7, 8, 19].

Kotoite is an orthorhombic Mg borate, in whose structure isolated $\{BO_3]^{3-}$ triangles are conjugated with Mg–O octahedra. The mineral belongs to the $Pnmn_3$–D_{2h}^{12} space group, and the parameters of its unit cell, which contains two $Mg_3[BO_3]_2$ molecules, are a_0 = 5.385, b_0 = 8.400 and c_0 = 4.487 Å [3]. The mineral has a density ρ approximately equal to 3 g/cm^3 and Ng = 1.674, Nm = 1.653, Np = 1.652, $Ng - Np$ = 0.022, and 2V = +20°. Kotoite crystals have perfect [110] cleavage, straight extinction, and polysynthetic twins (similar to those of clinohumite). Its crystal structure resembles the structure of forsterite and humites.

In pristine dolomite marble, kotoite inclusions are disseminated in calcite masses and are formed by the reaction

$$\underset{\text{dolomite}}{CaMg[CO_3]_2} + \underset{\text{fluid}}{(0.5K_2B_4O_7)} = \underset{\text{kotoite}}{0.33Mg_3[BO_3]_2} +$$

$$\underset{\text{calcite}}{0.67CaCO_3} + \underset{\text{solution}}{(0.5K_2CO_3)} + \underset{\text{gas}}{0.83CO_2\uparrow}.$$

Aggregates of its similarly oriented crystals resemble dendrites and were reproduced by hydrothermal synthesis of this mineral [5, 19]. This explains the nearly simultaneous extinction of groups of kotoite grains usually observed in thin sections. Kotoite may also rarely compose monomineralic rocks (Fig. 1); as, for example, at the Snezhnoe deposit in Yakutia and at deposits in the Dzhugdzhur Range in the Ayan district, Khabarovsk krai, Russia [16]. It was demonstrated experimentally that kotoite is formed under low CO_2 pressures (no higher than 110 bar) at temperatures of 400–500°C [5, 7, 8, 19]. At higher temperatures, the mineral is partly replaced by suanite $Mg_2B_2O_5$, as was observed in kotoite marbles at the Banat deposit in Romania at Blind Mountains, Nevada; and at Mount Grizzly Gulch, Little Cottonwood Canyon, Utah [7, 8, 16].

Kotoite occurs in marbles and calciphyres in association with early, practically Fe-free minerals, such as spinel, periclase, forsterite, clinohumite, excess calcite, and relict dolomite. It is accompanied by syngenetic magnesioludwigite with a high concentration of the $Mg_2Al[BO_3]O_2$ end member, which is formed because of the unequilibrated character of the association of kotoite with early low-Fe spinel by the reaction

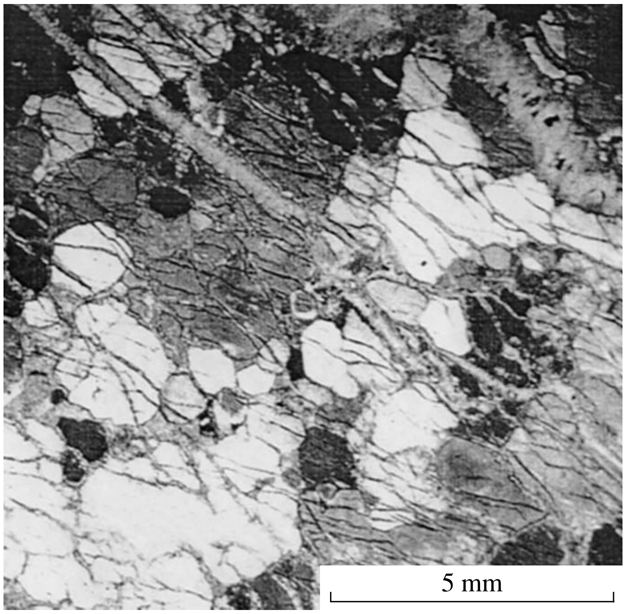

Fig. 1. Monomineralic kotoite rock with szaibelyite veinlets. Snezhnoe deposit, Tas-Khayakhtakh Range, Yakutia. Sample V-0531.

$$\underset{\text{kotoite}}{Mg_3[BO_3]_2} + \underset{\text{spinel}}{(Mg, Fe^{2+})(Al, Fe^{3+})_2O_4} =$$

$$\underset{\text{aluminomagnesioludwigite}}{2(Mg, Fe^{2+})_2(Al, Fe^{3+})[BO_3]O_2}.$$

Data of Watanabe [2] on the chemistry of kotoite-bearing rocks at the Hol Kol deposit in Korea testify that these rocks contain silicates (forsterite), and their SiO_2 contents vary from 2–3 to 7 and even 14 wt % in the absence of F.

The composition of kotoite corresponds to its formula at limited isomorphic admixtures of Fe^{2+} and Mn (Tables 1 and 2). The data of these tables demonstrate that the carbonate rocks surrounding magnesian skarns contain kotoite with less than 1–2.5 wt % FeO, and only occasionally does this mineral in the rocks contain as much as 4.6 wt % FeO (f = 4.3 at %), as in the ludwigite-bearing marbles at Potter Lake, Fresno County, California [20–22], or even >8% FeO (f = 7.7 at %) at the Efkachan deposit in the Selennyakh Range, Yakutia, Russia [23] (Tables 1, 2). The kotoite contains no less than 1% MnO. There is no reliable information on the presence of the takedaite end member in the kotoite, and the low CaO concentrations in kotoite analyses are caused by a calcite admixture [11].

It was determined that kotoite from marbles at many deposits in Yakutia and elsewhere contain practically no Si [16]. Their microprobe analyses indicate that the SiO_2 amounts in the mineral are at a minimum (no more than 0.4 wt %), and the F and Cl concentrations are insignificant (Table 1). Nevertheless, calciphyres some-

Table 1. Composition (wt %) of kotoite from marbles

No.	Deposit	SiO_2	B_2O_3	MgO	FeO	MnO	CaO	Al_2O_3	F	Cl	Total
1*	Hol Kol, Korea	0.00	36.30	62.70	0.67	0.04	0.00	0.03	–	–	99.74
2*	same	0.00	36.86	61.31	1.75	0.36	0.02	0.01	–	–	100.41
3*	″	0.00	36.17	61.61	1.73	0.41	0.07	0.03	–	–	100.02
4*	″	0.00	36.05	61.36	1.75	0.35	0.02	0.01	–	–	99.54
5*	″	0.00	35.86	60.99	1.89	0.39	0.14	0.05	–	–	99.32
6*	Brooks, Alaska	0.00	36.33	63.02	0.18	0.02	0.03	0.03	–	–	99.61
7*	same	0.00	36.07	62.09	0.98	0.06	0.05	0.00	–	–	99.25
8*	″	0.00	36.31	62.45	1.08	0.14	0.04	0.01	–	–	100.03
9*	″	0.00	36.26	62.28	1.22	0.01	0.10	0.01	–	–	99.88
10*	″	0.00	36.42	63.18	0.18	0.02	0.17	0.03	–	–	100.00
11	Lincoln, Nevada	0.00	36.40	62.82	0.70	0.00	0.01	0.00	–	–	99.43
12	Belky, Yakutia	0.00	36.40	61.81	0.67	0.06	0.02	0.02	–	–	99.98
13*	Efkachan, same territory	0.03	35.03	56.07	8.25	0.25	0.00	0.05	–	–	99.68
14	Belky, ″	0.03	35.91	62.08	0.53	0.06	0.01	0.00	–	–	98.62
15	Costabonn, France	0.03	35.34	62.03	1.44	0.49	0.29	0.06	0.04	–	99.72
16*	Brooks, Alaska	0.04	35.91	62.31	0.18	0.01	0.09	0.00	–	–	98.54
17	Lincoln, Nevada	0.06	36.49	63.18	0.38	0.02	0.01	0.04	–	–	100.18
18	Lyu-Lyu, Yakutia	0.06	35.70	61.08	1.66	0.02	0.17	0.01	0.00	0.03	98.73
19	Belky, same territory	0.07	35.79	61.85	0.61	0.04	0.02	0.01	–	–	98.39
20	same	0.11	36.30	62.72	0.59	0.00	0.02	0.04	–	–	99.78
21*	Pozharskoe, same territory	0.12	36.32	62.53	0.51	0.17	0.08	0.02	–	–	99.75
22*	same	0.12	36.28	62.63	0.63	0.17	0.00	0.01	–	–	99.84
23	Kerel, Yakutia	0.12	36.21	62.30	0.76	0.29	0.20	0.02	0.20	0.00	100.10
24	same	0.12	36.17	62.28	0.58	0.33	0.54	0.06	0.20	0.04	100.32
25	″	0.13	35.91	61.96	0.53	0.20	0.45	0.01	0.17	0.04	99.40
26*	Efkachan, same territory	0.13	35.67	60.33	2.31	0.51	0.14	0.04	–	–	99.09
27	Skye, Scotland	0.13	36.03	61.97	1.11	0.05	0.16	0.03	–	–	99.48
28*	Baia Roshe, Romania	0.15	35.96	61.95	0.79	0.19	0.13	0.00	–	–	99.17
29	Nalednoe, Yakutia	0.16	36.03	61.99	0.90	0.16	0.20	0.01	–	–	99.45
30	Snezhnoe, same territory	0.17	36.38	62.44	1.23	0.12	0.05	0.00	–	–	100.39
31	Kerel, same territory	0.18	35.73	60.85	1.58	0.55	0.32	0.01	0.09	0.02	99.33
32*	Baitsa Bichor, Romania	0.20	36.26	62.46	0.80	0.16	0.13	0.06	–	–	100.07
33	Skye, Scotland	0.20	35.86	61.39	1.36	0.21	0.39	0.01	–	–	99.32
34	same	0.22	36.30	62.55	0.81	0.12	0.08	0.03	–	–	100.11
35	Nalednoe, Yakutia	0.23	36.12	62.05	1.05	0.14	0.31	0.03	–	–	99.93
36	Kebiriin'ya, same territory [24]	0.23	36.08	59.68	3.37	0.45	0.18	0.00	–	–	99.99
37	Nalednoe, Yakutia	0.24	36.03	61.98	0.90	0.16	0.27	0.01	–	–	99.59
38	Kerel, same territory	0.24	35.96	61.62	0.94	0.56	0.20	0.01	0.07	0.03	99.63
39	Snezhnoe, ″	0.24	36.00	60.97	2.46	0.33	0.03	0.02	–	–	100.05
40	″	0.27	35.79	61.60	0.97	0.06	0.19	0.01	–	–	98.89

Note: Microprobe analyses of borates were conducted by M.A. Troneva (TsLAV, Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences). The analytical totals are presented without TiO_2, SnO_2, and Sb_2O_5, whose amounts were insignificant. The B_2O_3 concentrations were calculated from stoichiometric considerations. Dashes mean not analyzed. Additional data on borate deposits in Yakutia are presented in [7, 8, 23, and others]. Marble samples from Costabonn Peak were provided for by courtesy of Prof. B. Guy (Ecole Nationale Superieure des Mines de St. Etienne, France). *Previously published data [16, 24, 25].

Table 2. Composition (wt %) of Si-bearing kotoite from marbles and calciphyres

No.	Deposit	SiO_2	B_2O_3	MgO	FeO	MnO	CaO	Al_2O_3	F	Cl	Total
1	Brooks, Alaska**	0.29	36.10	62.69	0.01	0.00	0.11	0.06	–	–	99.24
2	Lyu-Lyu, Yakutia	0.30	36.21	62.26	0.85	0.28	0.15	0.04	0.13	0.00	100.12
3	Kerel, same territory	0.30	35.56	59.94	2.47	0.78	0.39	0.01	0.21	0.03	99.69
4	Snezhnoe, ″	0.31	36.10	61.13	1.81	0.25	0.03	0.02	–	–	99.65
5	Kebiriin'ya, ″ [24]	0.31	36.83	62.01	0.68	0.08	0.07	0.00	–	–	99.98
6	Fresno County, United States	0.31	34.96	58.09	4.67	0.02	0.06	1.24	–	–	99.35
7	Brooks, Alaska	0.31	36.17	62.27	0.83	0.19	0.12	0.00	–	–	99.89
8	same**	0.32	35.86	61.61	1.43	0.15	0.07	0.01	–	–	99.27
9	Lyu-Lyu, Yakutia	0.32	36.10	61.80	1.33	0.21	0.34	0.01	0.07	0.00	100.18
10	Efkachan, same territory	0.33	35.75	60.53	2.31	0.51	0.14	0.04	–	–	99.61
11	Snezhnoe, ″	0.33	35.86	60.29	3.28	0.32	0.02	0.01	–	–	100.11
12	″	0.35	36.44	61.46	2.70	0.30	0.05	0.00	–	–	100.13
13	″	0.36	35.75	60.61	2.46	0.25	0.07	0.00	–	–	99.50
14	Ozernoe, ″	0.37	35.70	59.97	3.63	–	0.07	0.00	0.03	–	99.97
15	Neichi, Japan	0.39	35.73	60.80	1.91	0.39	0.14	0.06	–	–	99.42
16	same	0.43	35.77	60.91	1.73	0.41	0.07	0.03	–	–	99.35
17	Brooks, Alaska	0.43	35.98	62.05	0.66	0.15	0.13	0.01	0.10	0.01	99.52
18	Toni, Romania	0.43	36.48	60.79	2.06	–	0.03	0.08	–	–	99.87
19	Lyu-Lyu, Yakutia	0.43	35.96	61.44	1.49	0.31	0.34	0.03	0.10	0.03	100.13
20	Gol'tsovoe, same territory	0.43	35.61	60.30	2.29	0.44	0.04	0.03	0.06	0.07	99.27
21	″	0.45	35.59	59.75	3.27	0.39	0.04	0.05	0.00	0.08	99.62
22	Nalednoe, ″	0.45	35.96	61.82	0.84	0.18	0.25	0.04	–	–	99.54
23	Brooks, Alaska	0.45	35.93	61.54	1.23	0.36	0.07	0.01	0.35	0.01	99.95
24	Snezhnoe, Yakutia	0.46	35.91	61.98	0.73	0.02	0.07	0.00	–	–	99.17
25	Brooks, Alaska	0.49	36.05	62.04	0.89	0.14	0.05	0.06	–	–	99.72
26	Lyu-Lyu, Yakutia	0.49	35.82	61.03	1.50	0.60	0.58	0.03	0.00	0.07	100.12
27	same	0.51	35.61	60.26	2.13	0.74	0.42	0.02	0.00	0.04	99.73
28	Alta, Utah [25]	0.52	32.98	62.98	0.55	0.19	0.03	0.02	0.00	–	97.27
29	Snezhnoe, Yakutia	0.53	35.96	61.67	1.29	0.08	0.02	0.04	–	–	99.59
30	Lyu-Lyu, same	0.54	35.82	61.30	1.21	0.42	0.24	0.07	0.10	0.01	99.71
31	Brooks, Alaska	0.55	35.86	61.86	0.62	0.14	0.06	0.00	0.31	0.02	99.42
32	Lyu-Lyu, Yakutia	0.61	35.70	61.10	1.40	0.32	0.39	0.03	0.00	0.02	99.57
33	Gol'tsovoe, same territory	0.61	35.14	59.86	3.48	0.46	0.05	0.03	0.09	0.04	99.76
34	″	0.63	35.68	60.17	2.84	0.39	0.02	0.03	0.19	0.30	100.25
35	Snezhnoe, ″	0.69	35.98	62.03	0.76	0.06	0.08	0.00	–	–	99.60
36	same ″	0.71	35.89	61.43	1.46	0.23	0.06	0.02	–	–	99.80
37	Lyu-Lyu, ″	0.79	35.73	60.71	1.65	0.70	0.44	0.06	0.02	0.04	100.14
38	Hol Kol, Korea	0.79	35.77	61.77	0.66	0.04	0.50	0.03	–	–	99.56
39	same	0.84	35.93	62.05	0.67	0.02	0.29	0.01	–	–	99.81
40	Lyu-Lyu, Yakutia	0.94	35.54	60.57	1.46	0.66	0.25	0.06	0.00	0.03	99.51

Note: See Table 1 for note. ** Kotoite replaced by pertsevite from the Brook aureole, sample AS-0262.

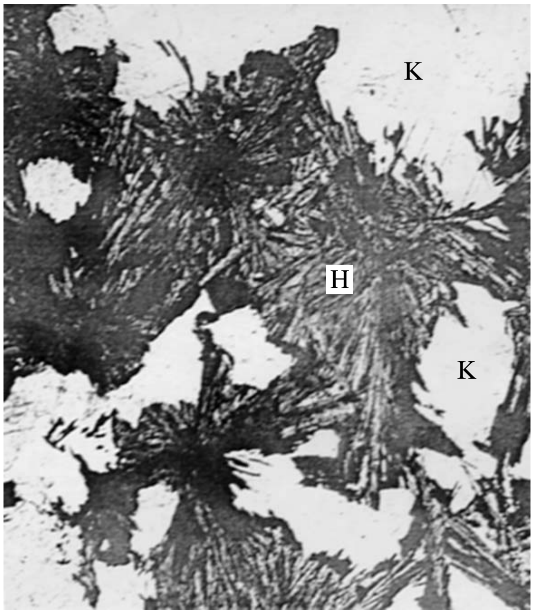

Fig. 2. Polychrome magnesiohulsite (H, gray) with kotoite relics (K, white), Mount Brooks, Alaska, sample AS-0267, transparent thin section. Magnification 25×.

times contain kotoite varieties with higher SiO_2 concentrations (up to 1.5 wt % and more) (Table 2), which should be explained.

The occurrence of forsterite and humites in kotoite calciphyres (in the absence of data on their B and F concentrations during early stages of their studying) led some researchers to hypothesize that this could be explained by the superposition of kotoite and silicate grains and/or their aggregates. Additional analyses of the kotoite for F and Cl (Tables 1, 2) have shown that these elements are contained in the mineral in concentrations only occasionally exceeding 0.5% for F and 0.08% for Cl at some variations in the SiO_2 concentration. As a consequence, this aspect of the mineralogy of kotoite has long been unexplored but deserved attention, as was also confirmed by newly obtained data.

Kotoite is not a stable mineral and is replaced by other borates in endogenic environments. The aim of this research was to reveal the characteristics of this process, which is controlled by the varying anion composition of the hydrothermal solutions. Early in the course of the postmagmatic mineral-forming process, hydrothermal fluids are ubiquitously Fe- and F-bearing, and later their composition is gradually enriched in Cl and eventually becomes aqueous with carbonate ions. This evolutionary tendency is reflected not only in the compositions of the newly formed borates but also in all minerals associated with them, as will be shown below.

MG–FE BORATES IN CALCIPHYRES

The earliest and ubiquitous type of alterations in kotoite-bearing rocks is their replacement by Mg–Fe borates. These minerals belong to the ludwigite–vonsenite series of the orthorhombic system and compositionally correspond to magnesioludwigite, including its Al-, Ti-, and Sn-bearing varieties

$$\underset{\text{kotoite}}{Mg_3[BO_3]_2} + \underset{\text{magnomagnetite}}{(Mg, Fe^{2+})Fe_2^{3+}O_4} =$$

$$\underset{\text{magnesioludwigite}}{2(Mg, Fe)_2Fe^{3+}[BO_3]O_2},$$

or magnesiohulsite, their monoclinic analogue.

These borates in kotoite marbles and calciphyres are highly magnesian, transparent or semitransparent (Fig. 2) depending on their Fe mole fractions, and display pleochroism from bluish green to dark brown. Their orthorhombic analogue is chestermanite $Mg_2\{Fe, Al, (Sb^{5+} + Mg_2^{2+})\}[BO_3]O_2$, which is a rare mineral and was found only at the Potter Lake deposit, Fresno County, California [26].

The kotoite calciphyres of Mount Brooks, Alaska [10, 27], and the Kebiriin'ya deposit, Yakutia [28], contains both orthorhombic magnesioludwigite and monoclinic magnesiohulsite, which are rich in Sn, Al, and Ti and relatively poor in Fe. The minerals are polychromic and moderately transparent.

Magnesioludwigites contained in marbles from Alaska are poor in Fe (Table 3). The magnesiohulsite occurring in association with it is highly magnesian and bears moderate Al_2O_3 concentrations but contains more Sn than its orthorhombic analogue does. The composition of the hulsite varies: $Mg_2\{Fe_{0.47}^{3+}Al_{0.21}(SnMg)_{0.29}(TiMg)_{0.03}\}[BO_3]O_2$ at 10.1 wt % SnO_2 and $Mg_2\{Fe_{0.47}Al_{0.10}(SnMg)_{0.40}(TiMg)_{0.03}\}[BO_3]O_2$ at 12.86 wt % SnO_2 (Mount Brooks, sample AS-0267). The Sn concentration in hulsite from kotoite-bearing calciphyres (sample AS-0261) reaches 21.34% SnO_2 (at 4.94% TiO_2 and 1.09% Al_2O_3), and the composition of the mineral can be written as $Mg_2\{Fe_{0.15}Al_{0.04}(SnMg)_{0.56}(TiMg)_{0.25}\}[BO_3]O_2$. Kotoite rocks containing humites and fluorhydroxylsilicic borates (sample AS-0262) contain hulsite $(Mg_{0.92}Fe_{0.08}^{2+})_2\{Fe_{0.39}^{3+}Al_{0.28}(SnMg)_{0.22}(TiMg)_{0.11}\}[BO_3]O_2$ with 7.96% SnO_2 in association with magnesioludwigite $(Mg_{0.88}Fe_{0.12}^{2+})_2\{Fe_{0.30}^{3+}Al_{0.33}(SnMg)_{0.09}(TiMg)_{0.26}\}[BO_3]O_2$ with 3.09% SnO_2, 5.20% TiO_2, and 8.41% Al_2O_3.

This causes both the independent coexistence of two modifications of Mg–Fe borates in the rocks and the fact that the magnesiohulsite is overgrown by magnesioludwigite (at the Kebiriin'ya deposit in Yakutia [28]). At this deposit, hulsite (space group

$P2/m$, $a_0 = 5.3344$, $b_0 = 3.0300$, $c_0 = 10.506$ Å, $\beta = 94.46°$, $Z = 2$) has the composition

$$(Mg_{1.54}Fe^{2+}_{0.45}Mg^{2+}_{0.01})_2\{Al_{066}(SnMg)_{0.32\text{-}}(TiMg)_{0.04}\}[BO_3]O_2.$$

The younger magnesioludwigite has higher concentrations of Ti^{4+} and Fe^{3+} but lower contents of Sn and Al:

$$(Mg_{1.53}Fe^{2+}_{0.46}Mn^{2+}_{0.01})_2\{Fe^{3+}_{0.50}Al_{0.31}(SnMg)_{0.10}(TiMg)_{0.09}\}_{1.01}[BO_3]O_2.$$

The formulas of orthorhombic and monoclinic Mg–Fe borates were calculated with regard for the isovalent isomorphism between Mg and Fe^{2+} and between Fe^{3+} and Al. Considering the analytically determined high Mg concentrations in these minerals, this does not rule out heterovalent substitutions of 2 Fe^{3+} for an equivalent amount of $(Sn^{4+} + Mg^{2+})^{6+}$ and $(Ti^{4+}$ and $Mg^{2+})^{6+}$ (Table 3).

Note that the Sn concentrations in borates of the ludwigite–vonsenite and hulsite–paigeite series are controlled by the geochemistry of the deposits: these minerals are ubiquitous Sn-bearing borates in boron ores from skarn deposits in Alaska and Yakutia [5, 8, 10, 27–29]. The accommodation of Al in borates is explained by the fact that these minerals replace spinel, whereas the Ti and Sn in them are of postmagmatic origin.

REPLACEMENT OF KOTOITE BY F- AND Si-BEARING BORATES

The subsequent transformations of the mineral composition of kotoite-bearing marbles and calciphyres

Table 3. Composition (wt %) of magnesioludwigite from kotoite marbles at Mount Brooks

Component	1	2	3	4	5	6	7	8	9	10	11
SiO_2	0.09	0.16	0.03	0.06	0.06	0.06	0.12	0.03	0.04	0.02	0.01
TiO_2	1.93	2.38	4.08	5.54	0.25	0.57	0.75	1.49	1.78	2.78	0.02
SnO_2	4.89	4.49	0.45	3.16	1.15	1.82	1.64	1.59	1.74	2.47	6.41
Al_2O_3	5.64	5.84	7.18	4.87	9.26	9.30	6.94	6.40	6.49	6.51	8.01
MgO	37.77	37.65	39.43	40.61	42.06	42.05	40.82	41.34	40.91	42.01	42.07
FeO	30.01	29.23	28.76	25.28	26.61	25.74	29.73	28.55	29.75	26.21	22.49
MnO	0.13	0.12	0.14	0.11	0.06	0.05	0.08	0.08	0.09	0.08	0.08
CaO	0.17	0.09	0.05	0.04	0.06	0.07	0.07	0.07	0.02	0.00	0.04
B_2O_3	17.34	17.27	17.95	17.78	18.22	18.21	17.90	17.99	17.94	18.07	18.28
Total	97.88	97.23	98.07	98.15	97.73	97.87	98.05	97.45	97.76	98.23	97.41
Borate formulae:											
Mg	1.81	1.76	1.79	1.80	1.97	1.96	1.93	1.94	1.92	1.91	2.00
Fe	0.19	0.24	0.21	0.20	0.03	0.04	0.07	0.06	0.08	0.09	0.00
ΣM^{2-}	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Fe	0.55	0.53	0.52	0.46	0.61	0.57	0.66	0.64	0.64	0.55	0.54
Al	0.22	0.23	0.27	0.19	0.35	0.35	0.26	0.25	0.25	0.25	0.30
Ti + Mg	0.10	0.12	0.20	0.27	0.01	0.03	0.04	0.07	0.09	0.14	0.00
Sn + Mg	0.13	0.12	0.01	0.08	0.03	0.05	0.04	0.04	0.02	0.06	0.16
ΣM^{3-}	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
B	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
O	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00

Note: magnesioludwigite in association with pertsevite: (1–4) sample AS-0262, (5–10) sample AS-0268, (11) sample AS-0261. B concentrations are calculated.

containing Mg–Fe borates are genetically related to the action of hydrothermal solutions with increasing F concentrations. The process is accompanied by the replacement of forsterite by humites (from clinohumite to norbergite [27]), depending on the F activity. Kotoite is unstable during this stage, and our data indicate that it is successively replaced by hydroxyl- and fluorine-bearing borates and younger hydroxofluorborates of the fluoborite–nocerite series. As the F concentration increases in the hydrothermal solutions, this mineral can occur not only in association with relict dolomite and calcite but also with fluorite and even sellaite MgF_2 replacing them.

Indeed, we determined that kotoite–forsterite–humite calciphyres in the Mount Brooks contact aureole, Alaska [10, 27]; Potter Lake deposit, Fresno County, California [22]; Baia Roshe deposit, Romania [16]; Efkachan deposit, Selennyakh Range, Yakutia [23]; and elsewhere contain, along with Si-free kotoite (Tables 1, 2), also their variously silicified F- and OH-bearing varieties (Table 4) as rock-forming minerals.

Microprobe analyses conducted at various times but without quantitative F determination indicate that Si-rich mineral phases are characterized by variable concentrations not only of SiO_2 but also of F. Newly obtained data with direct B determinations at an SX-100 microprobe (with danburite $CaB_2Si_2O_8$ as a standard) revealed high B concentrations (Table 4, analyses 14–17).

This allowed us to compare our data with those on the actual composition of the recently discovered mineral pertsevite, whose idealized formula was presented as $Mg_2[BO_3]F$ [24]. In fact, this mineral has a more complicated composition and contains not only B, Mg, and F but also the $[SiO_4]^{4-}$ radical and the $(OH)^-$ group, as was mentioned in [24]. Our data on the wide occurrence of pertsevite at many kotoite deposits significantly expand information on the geochemistry and mineralogy of its endogenic transformations.

Pertsevite (Table 5) was found as a new B-bearing mineral only in one thin section of kotoite calciphyre (from N.N. Pertsev's collection) from the Kebiriin'ya deposit [24]. This deposit is hosted in a contact aureole of the Kyt-Tas granite massif in the Dogdo River valley, in the Tas-Khayakhtakh Range, Yakutia. According to Dorofeev [30], the ore mineralization at this deposit is made up of szaibelyitized suanite and ludwigite ores surrounded by kotoite calciphyres with disseminated warwickite and fluoborite. It was recently determined that the deposit also contains partly brucitized marbles replacing the host dolomites. The ludwigite-bearing pyroxene skarns in the inner-contact zone that underwent calcic-skarn transformations contain clintonite, actinolite, and danburite with secondary datolite.

Pertsevite from this deposit belongs to the orthorhombic system, and its texture and optical properties are close to those of kotoite, forsterite, and humites. The space group of the mineral is *Pna2*, and its unit cell parameters are $a_0 = 20.490(6)$, $b_0 = 4.571(1)$, and $c_0 = 11.890(3)$ Å at $Z = 16$. The mineral is colorless, its density is 3.12 g/cm^3, it is biaxial ($2V = 65°$), and its indices of refraction are $Np = 1.609$, $Nm = 1.620$, and $Ng = 1.642$ [24]. The mineral occurs in association with kotoite, alumomagnesiohulsite, magnesioludwigite, forsterite, clinohumite, and calcite [24, 28].

With regard for these and other available data, we revised microprobe analyses of minerals from kotoite-bearing rocks sampled at more than 25 deposits in Alaska and other areas in the United States and in Yakutia and other areas in Russia and elsewhere. These data provided the basis for this research. Pertsevite is spread most widely in kotoite calciphyres at Mount Brooks, York Range, Seaward Peninsula, Alaska.

Contact Aureole at Mount Brooks

Pertsevite, a mineral whose composition corresponds to F-, OH-, and Si-bearing Mg borate (Table 4), is a rock-forming mineral in kotoite calciphyres in the contact aureole of the Mount Brooks granite massif (Fig. 3). The mineral occurs in association with Mg–Fe borates in the form of lean to rich dissemination of aggregates of Al-, Ti-, and Sn-bearing magnesioludwigite and magnesiohulsite.

In addition to relict kotoite, pertsevite-bearing rocks (Fig. 4) contain forsterite, humites, minerals of the fluoborite–nocerite series, and fluorite. The same rocks contain grains of Zn-bearing spinel $(Mg_{0.95}Fe^{2+}_{0.02}Zn_{0.05})Al_2O_4$ and $(Mg_{0.85}Fe^{2+}_{0.12}Zn_{0.03})Al_2O_4$, which contain 0.16–0.19 wt % SnO_2 and 0.13 wt % TiO_2, calcite, and relict dolomite. Due to the reasons explained above, these data were not published, and thus, the rich borate ore mineralization in metasomatic rocks from Alaska should be characterized.

Magnesian skarns in Alaska replace carbonate rocks (dolomites and their calcite-bearing varieties) of the Port Clarence Paleozoic Formation hosting an Early Cretaceous granite massif in the southwestern and southern slopes of Mount Brooks and a northern satellite of this massif (Fig. 3). The metasomatic zoning of the aureole is composed of contact spinel–diopside skarns or calciphyres, spinel–forsterite calciphyres, and periclase marbles [10, 27].

The development of rhythmically banded brucitized periclase marbles in the peripheral parts of the aureole, with these marbles grading into spinel–forsterite calciphyres, indicates that these rocks replaced pure dolomite with no more than 0.1–0.3 wt % FeO. Calcite contained in the calciphyres bears no more than 1.9–2.8 wt % MgO, which is equivalent to 3–5 mol % $MgCO_3$.

In contact with granites, the calcite–dolomite rocks are transformed into pyroxene calciphyres, whose calcite contains 0.4–0.7 wt % MgO, with all metasomatic rocks of Mount Brooks having a Mg/Ca ratio no higher than one.

Table 4. Composition (wt %) of fluorsilicateborates from calciphyres at Mount Brooks, Alaska, United States

No.	SiO_2	B_2O_3	MgO	FeO	MnO	CaO	Al_2O_3	F	$Total_1$	H_2O	–F=O	Total	*Si*, %	*F*, %
Sample AS-0247														
1	7.85	22.50	62.40	0.31	0.18	0.12	0.01	6.29	99.66	2.84	2.64	99.86	17	51
2	11.40	20.04	61.46	0.38	0.17	0.18	0.04	5.04	98.71	2.79	2.12	99.38	25	46
3	11.58	19.10	61.35	0.31	0.12	0.21	0.03	–	92.70	–	–	–	26	–
Sample AS-0250														
4	10.34	20.65	61.41	1.08	0.24	0.12	0.02	4.71	97.28	2.93	1.98	99.52	23	42.5
Sample AS- 0261														
5	6.36	23.50	61.76	0.47	0.09	0.19	0.01	–	92.38	–	–	–	13.5	–
6	6.87	23.00	60.94	0.45	0.12	0.06	0.04	–	91.48	–	–	–	14.7	–
7	7.29	22.50	61.66	0.01	0.00	0.11	0.02	–	91.59	–	–	–	15.8	–
8	10.30	21.10	62.52	0.31	0.06	0.12	0.00	4.32	98.75	3.42	1.81	100.36	22	37
9	11.14	19.50	60.72	0.00	0.00	0.13	0.07	–	91.56	–	–	–	25	–
10	11.17	19.20	59.68	0.39	0.10	0.04	0.10	–	90.68	–	–	–	25	–
11	11.22	19.00	59.99	0.61	0.21	0.17	0.04	–	91.24	–	–	–	25.5	–
12	11.35	18.90	60.62	0.45	0.16	0.11	0.10	–	91.69	–	–	–	26	–
13	13.17	17.50	59.81	0.48	0.20	0.11	0.01	–	91.28	–	–	–	30	–
Sample AS-0261/2														
14	10.06	21.43	60.36	0.49	–	–	–	4.39	96.75	3.46	1.84	99.37	22	37.5
15	11.42	20.07	60.73	0.49	–	–	–	3.76	96.47	3.40	1.58	98.29	25	34.5
16	11.49	21.41	59.77	0.63	–	–	–	4.06	97.36	3.61	1.71	99.26	26	35
17	12.42	20.83	59.03	0.59	–	–	–	4.76	97.63	3.13	2.00	98.76	28	42
Sample AS-0262														
18	6.48	23.40	62.04	0.53	0.12	0.06	0.05	–	92.68	–	–	–	13.8	–
19	10.38	20.00	60.43	0.60	0.09	0.10	0.04	–	91.64	–	–	–	23	–
20	10.55	19.80	58.92	1.06	0.14	0.13	0.06	–	90.66	–	–	–	23.6	–
21	11.21	19.00	59.16	1.90	0.39	0.15	0.05	–	91.86	–	–	–	25.5	–
22	12.35	18.00	59.22	0.80	0.16	0.20	0. 04	–	90.77	–	–	–	28.5	–
Sample AS-0267														
23	3.57	26.00	62.42	0.62	0.08	0.04	0.38	–	93.11	–	–	–	7.3	–
24	6.12	24.00	61.45	0.49	0.11	0.07	0.38	–	92.62	–	–	–	12.9	–
25	6.74	23.00	60.41	0.36	0.15	0.13	0.01	–	90.80	–	–	–	14.5	–
26	6.94	22.90	61.30	0.32	0.13	0.07	0.02	–	91.68	–	–	–	14.9	–
27	7.16	22.70	60.70	0.32	0.13	0.23	0.00	–	91.24	–	–	–	15.4	–
28	9.01	21.00	61.15	0.23	0.07	0.13	0.03	–	91.62	–	–	–	19.9	–
29	9.82	20.10	59.82	0.31	0.13	0.08	0.03	–	90.29	–	–	–	22	–
30	10.17	20.00	60.62	0.18	0.20	0.10	0.05	–	91.32	–	–	–	22.7	–
31	10.38	19.90	58.73	1.05	0.01	0.15	0.05	–	90.27	–	–	–	23	–
32	11.06	19.10	58.74	1.13	0.21	0.19	0.08	–	90.51	–	–	–	25	–
33	11.95	18.30	59.57	0.74	0.24	0.17	0.03	–	91.00	–	–	–	27	–
Sample AS-0268														
34	6.29	23.50	60.58	0.90	0.16	0.14	0.05	–	91.62	–	–	–	13.5	–
35	11.46	18.80	59.37	1.10	0.20	0.11	0.00	–	91.04	–	–	–	26	–
36	11.99	18.20	61.42	0.63	0.19	0.06	0.09	–	92.58	–	–	–	27.7	–

Note: B_2O_3 and H_2O concentrations were calculated except for sample AS-0261/2, in which B_2O_3 was determined on a microprobe. Cation ratios: $Si = Si/(Si + B)$, %, $F = F/(F + OH)$, %. Analysis 4 is pertsevite $(Mg_{0.99}Fe^{2+}_{0.01})_2[(BO_3)_{0.78}(SiO_4)_{0.22}](F_{0.42}OH_{0.58})_{0.78}$ and analysis 8 is the same mineral $(Mg_{0.99}Fe^{2+}_{0.01})_2[(BO_3)_{0.77}(SiO_4)_{0.23}](F_{0.59}OH_{0.41})_{0.77}$. Kotoite replaced by pertsevite contains 0.26–0.37 wt % SiO_2 and 0.09–0.32 wt % F (sample AS-0247).

Table 5. Composition (wt %) of pertsevite from the Kebiriin'ya deposit, Yakutia

SiO_2	B_2O_3	MgO	FeO	MnO	CaO	Al_2O_3	F	$Total_1$	–O=F	H_2O	Total	*Si*, %	*F*, %
4.37	24.12	49.63	8.48	0.44	0.15	1.55	6.01	94.75	2.53	2.29	94.51	9.5	55
4.85	23.68	56.92	4.01	0.66	0.26	0.14	8.42	98.94	3.55	1.93	97.32	10.6	67
5.32	23.83	59.39	2.13	0.35	0.15	0.06	7.86	99.09	3.31	2.25	98.03	11.4	62
6.23	24.33	58–31	2.14	0.38	0.10	0.06	7.48	99.03	3.15	2.04	97.62	12.9	63
7.03	24.27	59.00	2.09	0.36	0.12	0.03	7.29	100.19	3.07	2.06	99.18	14.4	62
8.25	22.44	57.39	3.71	0.65	0.24	0.10	7.81	100.59	3.29	1.67	98.97	17.5	69
8.75	21.17	58.17	2.48	0.44	0.19	0.07	6.56	97.83	2.76	2.28	97.35	19.0	57
9.86	21.92	58.32	2.47	0.42	0.12	0.04	6.11	99.26	2.57	2.19	98.88	20.7	57
10.28	19.52	57.68	2.55	0.43	0.16	0.06	5.97	96.65	2.51	2.31	96.44	23.3	55
11.66	18.72	57.62	2.57	0.45	0.09	0.07	6.95	98.13	2.93	1.62	96.82	26.5	67

Note: $Total_1$ is the analytical total. Total is the analytical total corrected for –F=O. Molar ratios: *Si* = Si/(Si + B),%; and *F* = F/(F + OH), mol % in Mg silicateborate.

The mineralogy of these rocks was modified by postmagmatic processes with the development of borate mineralization of variable composition. In the marbles of the Kotoite Prospect (Fig. 3, I), kotoite (and suanite) were ubiquitously deposited in association with Mg–Fe borates with low Fe#: magnesioludwigite and magnesiohulsite [10, 27] (Fig. 2, Table 3). The accompanying forsterite is replaced by clinohumite.

F-bearing hydrothermal solutions modified the mineralogy of the kotoite calciphyres and stimulated the formation of humites: clinohumite, chondrodite, humite and norbergite (Table 6), pertsevite, and later, borates of the fluoborite–nocerite series (Table 7) and fluorite. Note that nocerite $Mg_3[BO_3]F_3$ was not previously known at skarn borate deposits.

The rocks of the spinel–diopside calciphyre zone, which occur in the aureole in place of spinel–diopside skarns replacing calcareous dolomite, at the Hulsite Prospect (Fig. 3) contain Sn-rich hulsite of moderate Mg# in association with newly formed phlogopite and minerals of the calc-skarn complex: B-bearing vesuvianite and tremolite in association with scheelite and fluorite [10, 27].

The spinel–pyroxene calciphyres near granite contain not only vesuvianite but also Sn-bearing garnet. At the Paigeite Prospect (Fig. 3), borate in these rocks is monoclinic high-Fe paigeite with moderate Sn concentrations (of the hulsite–paigeite series). The younger borates that replace paigeite are orthorhombic vonsenite with low Sn and Mg concentrations and nordenskioldine $CaSn[BO_3]_2$, as in the Mount Ear contact aureole in Alaska [7–10, 27] and at deposits in northeastern Russia [7, 29]. The latter minerals are associated with newly formed cassiterite. The ore-forming process ended with the precipitation of arsenides and sulfides: loellingite, arsenopyrite, stannite, pyrrhotite, marmatite, and galena [31], which are contained in pyroxene skarns and vonsenite–magnetite ores at the Foggy Day and Rid prospects (Fig. 3).

Pertsevite and, to a lesser extent, fluoborite are rock-forming minerals in the metasomatic rocks of the Kotoite Prospect. It cannot be ruled out that these minerals and other borates can also be contained in the periclase–humite marbles at the Eastern and Northern prospects (Fig. 3, VIII and IX): we still have not examined these rocks. The latter prospect is restricted to contacts between dolomite and an isolated granite stock. The marble hosting this stock is replaced by skarn and calciphyre that grade into brucitized periclase marble with humite. The comparison of the mineral assemblages of pertsevite occurring in the calciphyres of Mount Brooks allowed us to reconstruct the following crystallization sequence of the minerals as a result of coupled reactions:

$$\underset{\text{dolomite}}{CaMg[CO_3]_2} + \underset{\text{fluid}}{4KF} = \underset{\text{fluorite}}{CaF_2} + \underset{\text{sellaite}}{MgF_2} + \underset{\text{fluid}}{2K_2CO_3},$$

$$\underset{\text{periclase}}{MgO} + \underset{\text{fluid}}{[2KF + H_2O]} = \underset{\text{sellaite}}{MgF_2} + \underset{\text{fluid}}{[2K(OH)]},$$

$$\underset{\text{forsterite}}{Mg_2SiO_4} + \underset{\text{sellaite}}{MgF_2} = \underset{\text{norbergite}}{Mg_3\{SiO_4\}F_2},$$

$$\text{and } \underset{\text{kotoite}}{Mg_3[BO_3]_2} + \underset{\text{sellaite}}{MgF_2} = \underset{\text{pertsevite}}{2Mg_2[BO_3]F}.$$

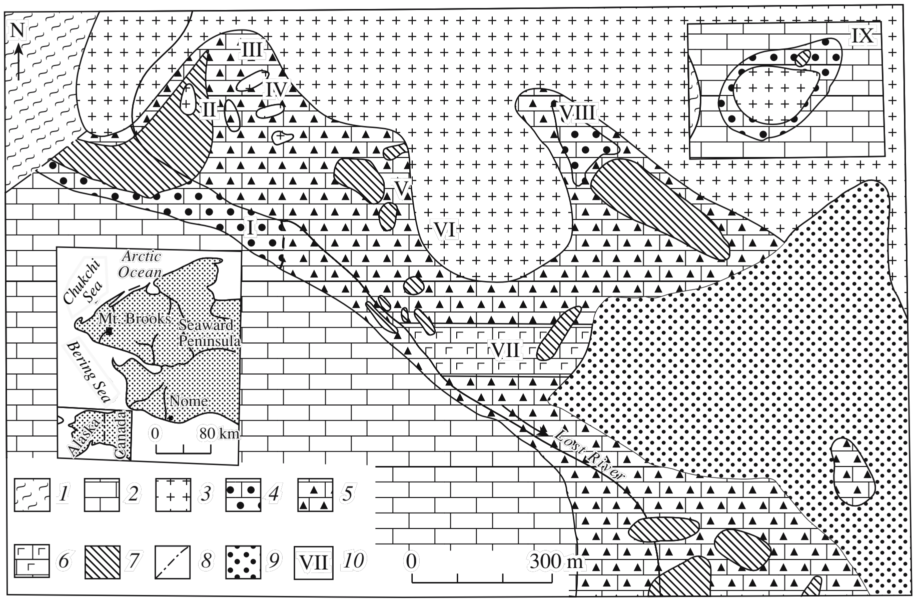

Fig. 3. Geological map of Mount Brooks, Seaward Peninsula, Alaska (prepared based on the materials of T.L. Patton and M.S. Robinson of the University of Alaska, Fairbanks, and the author's materials). Legend: (*1*) shale and (*2*) dolomite of the Port Clarence Formation; (*3*) coarse-grained porphyritic granite; (*4*) brucite and kotoite marbles with humites, magnesioludwigite, and pertsevite; (*5*) spinel–pyroxene calciphyre with vesuvianite and hulsite; (*6*) pyroxene–garnet calciphyre; (*7*) pyroxene–vesuvianite–garnet skarn with paigeite, nordenskioldine, and vonsenite; (*8*) faults; (*9*) Quaternary deposits; (*10*) areas with borate ore mineralization: (I) Kotoite Prospect, where pertsevite was found, (II) Hulsite Prospect, (III) Cameron Prospect, (IV) Foggy day Prospect, (V) Reed Prospect, (VI) Tourmaline Prospect, (VII) Paigeite Prospect, (VIII) Eastern, and (IX) Northern. The inset shows the location of Mount Brooks in the York range and the Northern Prospect.

The latter reaction can also proceed in silicate-free kotoite marbles.

The idealized composition proposed for pertsevite in [24] was deduced from the experimental data of Grigor'ev and Brovkin [32, 33] on the MgO–MgF$_2$–B$_2$O$_3$ system. These data demonstrate that a compound corresponding to α-Mg$_2$[BO$_3$]F exists between the stability fields of sellaite, fluoborite, and kotoite, and F in this compound can be partly substituted for hydroxyl. This mineral phase was detected among the experimental products obtained at a temperature of 350°C and coexisted in these products with kotoite, fluoborite, and szaibelyite and was synthesized as a pure compound at 600° C.

These researchers have established that the unit cell parameters of this F–OH borate are divisible by the unit cell parameters of forsterite and the minerals of the humite group and are comparable with the analogous parameters of kotoite. It has also been demonstrated that the optical properties and X-ray powder diffraction pattern of this phase are barely distinguishable from those of humites. The aforementioned researchers thus arrived at the conclusion that natural fluorohydroxylboratesilicates can exist, which was virtually confirmed by the discovery of pertsevite. As was suggested in [32, 33], the F concentration in the mineral can exceed 60%.

With regard for the actual composition of the minerals examined in our samples and with the assumption that pertsevite is formed in nature with the involvement of kotoite and produced together with minerals of the

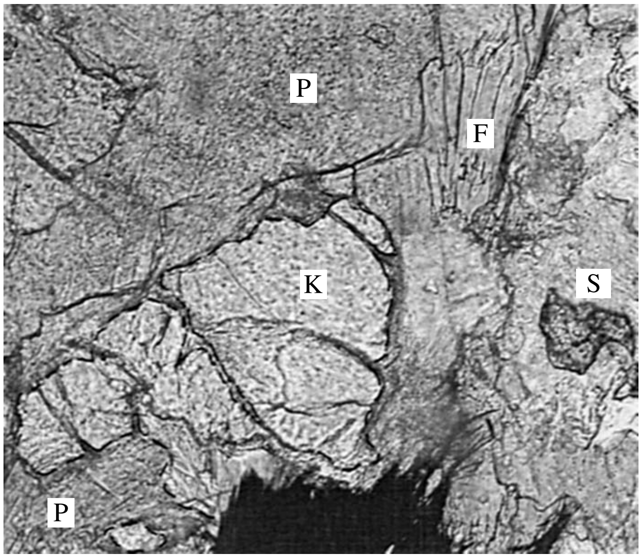

Fig. 4. Kotoite (K) replaced by magnesioludwigite (black), pertsevite (P), and fluoborite (F) with spinel relics (S) preserved in marble. Mount Brooks, Alaska. Sample AS-0251, transparent thin section. Magnification 25×.

Table 6. Composition (wt %) of humites from calciphyres at Mount Brooks, Alaska

No.	SiO_2	TiO_2	MgO	FeO	F	H_2O	$Total_1$	–O=F	Total	*F*, mol %	*OH*, mol %
Sample AS-0265											
1	36.69	0.42	55.81	0.71	–	–	93.63	–	–	–	–
2	37.04	0.38	55.85	0.62	–	–	93.83	–	–	–	–
3	33.36	0.51	59.62	0.59	5.85	1.74	101.67	2.46	99.21	52	48
Sample AS-0268											
4	36.27	0.12	57.83	0.81	5.19	1.46	101.68	2.18	99.50	67	33
5	36.29	0.53	56.98	1.32	5.01	1.32	101.45	2.10	99.35	64	36
Sample AS-0272											
6	28.91	0.12	58.18	0.42	18.93	1.90	108.46	7.95	100.51	90	10
7	29.17	0.10	58.72	0.37	21.11	0.00	109.47	8.87	100.60	100	0
8	29.15	0.11	58.65	0.22	–	–	88.13	–	–	–	–

Note: (1, 2) Clinohumite, Mg/Si = 2.25 and 2.26; (3) chondrodite Mg/Si = 2.5; (4, 5) humite, Mg/Si = 2.375; (6, 8) norbergite, Mg/Si = 3.0, in association with fluoborite and relict dolomite.

Table 7. Composition (wt %) of fluoborite in calciphyres from Alaska and other territories

No.	SiO_2	MgO	FeO	B_2O_3	F	H_2O	$Total_1$	–O=F	Total	*F*, mol %	*OH*, mol %
Mount Brooks, Alaska, United States											
1	0.00	65.00	0.16	18.73	17.28	6.35	107.49	7.26	100.23	56.3	43.7
2	0.07	65.35	0.17	18.42	16.70	6.70	107.34	7.01	100.33	54	46
3	0.04	65.16	0.13	18.21	16.26	6.86	106.62	6.83	99.79	53	47
4	0.05	65.20	0.13	18.80	15.81	7.08	107.28	6.64	100.64	51	49
5	0.04	65.24	0.13	18.20	14.55	7.69	105.81	6.11	99.70	47.3	52.7
6	0.04	65.01	0.10	18.72	13.96	7.90	105.69	5.86	99.83	45.6	54.4
7	0.04	63.84	0.38	18.43	28.40	0.79	111.84	11.93	99.91	94	6
Iten'yurgen deposit, eastern Chukot Peninsula											
8	0.00	64.76	0.10	18.64	14.88	7.41	105.79	6.25	99.54	49	51
9	0.00	64.82	0.15	18.69	17.16	6.36	107.18	7.21	99.97	56	44
10	0.04	63.53	0.39	18.34	24.48	2.78	109.56	10.28	98.98	80	20
11	0.04	63.08	0.10	18.19	27.61	1.03	110.05	11.60	98.45	93	7
12	0.06	63.00	0.56	18.25	28.13	1.32	111.32	11.81	99.51	94	6
Costabonn Peak, Pyrenees, France											
13	0.06	64.69	0.10	18.63	16.90	6.44	106.82	7.10	99.72	55	45
14	0.06	63.18	0.88	18.32	21.79	3.89	108.12	9.15	98.97	72.5	27.5
Gerbets Prospect, Pitkjaranta, Karelia											
15	0.28	64.24	0.57	18.59	20.15	4.87	108.70	8.46	100.24	66	34

Note: Fluoborite from Mount Brooks, Alaska: (1–4) sample AS-0250; (5, 6) sample AS-0261; (7) nocerite, sample AS-0272; fluoborite from the Chukot peninsula: (8, 9) sample VCH-0508; nocerite: (10–12) samples VCH-0358 and VCH-0687; fluoborite: (13, 14) Costabonn peak, Pyrenees, France, sample M-4 (collection of B. Guy, St. Etienne, France); (15) Gerbets, Pitkjaranta, Karelia, sample PK-005.

humite group, the reaction forming pertsevite in nature can be written in the form

$$\underset{\text{forsterite}}{Mg_2SiO_4} + \underset{\text{dolomite}}{CaMg[CO_3]_2} + \underset{\text{fluid}}{(nH_2O + mKF)} =$$

$$\underset{\text{humites}}{xMg_2SiO_4Mg(OH_n, F_m)_2} + \underset{\text{calcite}}{CaCO_3} +$$

$$\underset{\text{fluid}}{0.5K_2CO_3 + 0.5CO_2}$$

$$\text{and } \underset{\text{kotoite}}{Mg_3\{BO_3\}_2} + \underset{\text{norbergite}}{Mg_3[SiO_4](OH, F)_2} =$$

$$\underset{\text{fluorhydroxylsilicateborate}}{Mg_2\{[BO_3]_{1-x}[SiO_4]_x\}(F, OH)_{1-x}}.$$

Pertsevite can also be formed by the aforementioned reaction in silicate-free kotoite marbles, and this will stimulate its replacement by nocerite at high F concentration in the fluid

$$\underset{\text{pertsevite}}{Mg_2[BO_3]F} + \underset{\text{sellaite}}{MgF_2} = \underset{\text{nocerite}}{Mg_3[BO_3]F_3},$$

as is the case with the Mount Brooks marbles (Table 7) and with some other occurrences of this mineral.

Our data demonstrate that pertsevite from Alaska contains Si and F in amounts comparable with those in the reference sample (Tables 4, 5), and the formula of the mineral does not correspond to $Mg_2[BO_3]F$ but can be written in a more general form as $Mg_2\{[BO_3]_{1-x}(F,OH)_{1-x}[SiO_4]_x\}$. This formula reflects the possibility of isomorphism between the boronfluorohydroxyl $\{[BO_3](F,OH)\}^{4-}$ and silicate $[SiO_4]^{4-}$ radicals. The minimum amount of Si contained in pertsevite from Mount Brooks is 3.57 wt %, but the mineral more often contains 6% and occasionally even as much as 12–13% Si and 4 wt % F (Table 4). At the Keberiin'ya deposit [24], pertsevite contains 4.37–11.66 wt % SiO_2 and 6–8.42% F (Table 5).

The younger replacements of kotoite, including the generation of sakhaite, borcarite, and its szaibelyitization, brucitization, and carbonatization were documented at other deposits but are rare (if any) in the Mount Brooks calciphyres.

Other Occurrences of Si-Bearing Mg Borates

In addition to Mount Brooks in Alaska, pertsevite was also found at other deposits. In the western United States, this is the Potter Lake (Twin Lakes) magnesian skarn borate deposit in Fresno County, California [20–22]. This deposit is restricted to metasomatically altered dolomite in contact with a leucogranite dike. In these rocks, pertsevite replaces kotoite marble with magnesioludwigite and its Sb-bearing analogue chestermanite and is accompanied by chondrodite (Mg/Si = 2.7), which contains 5.5 wt % F, fluoborite, and wightmanite. These minerals are relatively poor in Si (Si = Si/B + Si = 13–20%) and rich in F (35–54%, occasionally up to 98%) (Table 8, analysis 4).

Less silicic (*Si* = 7.5%) and less fluorian (46%) pertsevite was found at Banat, Romania (Table 8). It occurs in kotoite–clinohumite calciphyres in steep orebodies at the Baia Roshe deposit [16], where this mineral is accompanied by fluorite and calcite. The adjacent kotoite calciphyres contain newly formed fluoborite (F = 55–58% $Mg_3[BO_3]F_3$) (Fig. 5).

In the Selenyakh Range, Yakutia, pertsevite was found at the Efkachan deposit [23], which is hosted in a remnant block of Silurian dolomite in the roof of the Early Cretaceous Sakhan'ya granite massif. The magnesian skarns and calciphyres hosting bodies of suanite and kotoite ore mineralization are extensively transformed into ludwigite bodies and in the sakhaite rocks.

Pertsevite was determined to develop at the periphery of the zone of kotoite calciphyres and occurs in association with forsterite, chondrodite, magnesioludwigite (Table 9), and younger fluoborite. This pertsevite is characterized by a low Fe# (f = 1.5%) and *Si* = 19% (Table 9). The adjacent kotoite rocks, which also replace kotoite calciphyres, contain younger karlite, borcarite, and szaibelyite (Table 9), whose genesis during the alterations of kotoite ores will be considered below.

At the Ozernoe (Chibalakh Kyuel') deposit in the same area in Yakutia, which is localized in magnesian skarns in the contact aureole of the Syachan granite massif, kotoite marbles extensively replaced by fluoborite contain pertsevite (or, perhaps, its OH-bearing analogue) with the lowest silicity and low F content (Table 8).

A mineral also compositionally corresponding to low-Si and high-OH pertsevite was also found in calcite–dolomite marbles at the Iten'yurgen deposit in the eastern Chukot Peninsula. The mineral has the formula $(Mg_{0.99}Fe_{0.01})_2\{[BO_3]_{0.92}(F_{0.18}OH_{0.82})_{0.92}[SiO_4]_{0.08}\}$ (Table 8). The deposit is spatially restricted to contacts of Mesozoic granite with Paleozoic dolomite and is characterized by widespread rhythmically banded magnesian skarns with early magnetite, which are surrounded by calciphyres [8, 9]. The ore mineralization in the skarns consists of magnesioludwigite and magnesiohulsite, and extensively greisenized rocks contain fluoborite (49–60 mol %) and nocerite (80–94% of the $Mg_3[BO_3]F_3$ end member), respectively (Table 7). The latter mineral occurs in association with sellaite and fluorite and replaces dolomite.

A low-F variety of low-Si pertsevite was also found in szaibelyitized kotoite marble at the Gonochan occurrence of borate mineralization in the Dzhugdzhur Range, Ayan district, Khabarovsk krai (Table 8). The composition of this mineral also testifies to the possible existence of OH-bearing varieties of this mineral.

The data presented above on the occurrence of pertsevite in kotoite marbles and calciphyres suggest that it

Table 8. Composition (wt %) of pertsevite from deposits in the United States, Romania, and Russia

No.	SiO_2	B_2O_3	MgO	FeO	MnO	CaO	Al_2O_3	F	H_2O	$Total_1$	–F=O	Total	*Si*, %	*F*, %
Fresno County, California														
1	5.82	23.15	61.27	0.24	0.06	0.07	0.01	5.30	3.47	99.39	2.23	97.16	13	42
2	8.00	22.01	61.55	0.23	0.09	0.06	0.01	5.26	3.20	100.41	2.21	98.20	17	44
3	8.22	22.06	61.99	0.23	0.09	0.03	0.02	5.47	3.44	100.55	2.21	98.34	20.5	54
4	8.36	21.90	61.90	0.04	0.05	0.02	0.01	11.78	0.76	104.82	4.95	99.87	18	98.5
5	9.32	21.34	61.71	0.31	0.07	0.13	0.02	4.62	3.33	100.85	1.94	98.91	20	39.5
6	10.59	20.02	60.17	0.68	0.08	0.00	0.04	3.85	3.35	98.78	1.62	97.16	23.5	35
7	13.28	18.75	60.96	0.38	0.14	0.05	0.00	4.49	2.72	100.77	1.89	98.88	29	44
Baia Roshe, Romania														
8	3.48	24.60	61.41	0.21	0.20	0.13	0.30	6.16	3.43	99.92	2.59	97.33	7.5	46
Iten'yurgen deposit, eastern Chukot Peninsula														
9	3.46	25.11	62.09	1.02	0.25	0.00	0.71	2.47	5.32	100.43	1.04	99.39	7.5	18
Gonochan deposit, Dzhugdzhur range, Khabarovsk krai														
10	10.30	20.75	60.69	1.68	0.46	0.00	0.20	0.16	5.29	99.53	0.07	99.46	22	1.3
Ozernoe deposit, Selennyakh range, Yakutia														
11	0.52	27.08	62.39	1.84	–	0.17	0.00	2.20	6.04	100.24	0.92	99.32	1	15

Note: (1–7) Potter lake deposit, Fresno County, California, in association with magnesioludwigite $Mg_2\{Fe^{3+}_{0.38}Al_{0.40}(TiMg)_{0.16}(SnMg)_{0.045}(SbMg_2)_{0.015}\}(BO_3)_2$, chondrodite, fluoborite (*F* = 40–44%), calcite, and wightmanite in kotoite calciphyre, sample AS-004; (8) Baia Roshe deposit, Banat, Romania, in association with fluoborite (*F* = 55–58%), magnesioludwigite, calcite, and fluorite, sample R-0.46; (9) Iten'yurgen deposit, eastern Chukot Peninsula, sample VCH-0423; (10) Gonochan occurrence of B mineralization, Dzhugdzhur Range, Ayan district, Khabarovsk krai, in association with szaibelyite, sample Dzh-081; (11) Ozernoe deposit, Selennyakh Range, Yakutia, the mineral in poor Si: $(Mg_{0.985}Fe_{0.015})_2\{[BO_3]_2(F_{0.15}OH_{0.85})\}_{0.99}[SiO_4]_{0.01}$ and in F, in association with kotoite, magnesioludwigite (*f* = 12.5%), and humites, sample V-01674.

can also be found at other deposits in association with magnesian borates, F-silicates, fluoborite, and szaibelyite.

It is also interesting to study other possible products of the endogenic alterations of pertsevite. For example, it is still uncertain what is the genesis of newly formed fluoborite–serpentine aggregates found at the Gerbets deposit near Pitkjaranta, Karelia, where kotoite is known to occur at the nearby Hopunvaara prospect [6, 16]. The F mole fraction of fluoborite at this deposit is 66% (Table 7).

KOTOITE REPLACEMENT BY FLUOBORITE

Minerals of the fluoborite–nocerite series are quite common in kotoite marbles or replace ludwigite. They form a continuous isomorphic series from $Mg_3[BO_3](F_{0.3}OH_{0.7})_3$ to $Mg_3[BO_3]F_3$, are colorless, show no cleavage, are uniaxial and optically negative, and their indices of refraction increase with increasing OH concentration.

The parameters of the hexagonal unit cell of the minerals vary depending on the F concentration from a_o = 9.06 Å at *F* = 30% to 8.805 Å at *F* = 100% and, correspondingly, c_o from 3.06 to 3.097 Å; *Z* = 2. No nomenclature for these borates has been developed.

With regard for the fact that none of their high-OH varieties (with *F* < 25 mol % of the $Mg_3[BO_3]F_3$ end member) were found, we regard fluoborite at its varieties with 25–75 mol % of this end member, whereas more fluorian varieties (with *F* from 75 to 100%) are combined within the group of nocerite (Table 7).

These minerals are ubiquitously accompanied by forsterite replacement by clinohumite, the most magnesian and fluorian member of the humite group (Table 6), in association with early magnesioludwigite or magnesiohulsite. Fluoborite $Mg_3[BO_3](F, OH)_3$ with *F* = 50–60% and more, whose sheaf-shaped aggregates replace kotoite, often occurs in marbles and calciphyres (Fig. 5). The mineral assemblages suggest that B and F came into the dolomites in the form of hydroxofluorborates and hydroxofluorstannates of alkali metals (first of all, K) [27]. This is confirmed by the syngenetic replacement of spinel-bearing calciphyres and magnesian skarns by phlogopite.

The fluoboritization of kotoite marbles is often very extensive, as at the Ozernoe deposit in the Selennyakh

Range, Yakutia [7]. The high *F* of the hydrothermal solutions is favorable for the replacement of nearby dolomites by fluoborite, as at the Iten'yurgen deposit in the eastern Chukot Peninsula. If the conditions are favorable for the formation of Ca and Mg fluorides, nocerite $Mg_3[BO_3]F_3$ is produced (Table 7), which likely rules out the possibility of pertsevite formation as a phase of intermediate composition because of the redistribution of B contained in kotoite:

$$\underset{\text{dolomite}}{CaMg[CO_3]_2} + \underset{\text{fluid}}{4KF} = \underset{\text{fluorite}}{CaF_2} + \underset{\text{sellaite}}{MgF_2} + \underset{\text{solution}}{2K_2CO_3}$$

$$\text{and } \underset{\text{kotoite}}{Mg_3[BO_3]_2} + \underset{\text{sellaite}}{3MgF_2} = \underset{\text{nocerite}}{2Mg_3[BO_3]F_3}.$$

Nocerite with 30.2 mol % *F* was previously found only in the Nocera opencast mine in Sarno, Campania, Italy, in metasomatically altered xenoliths of dolomite marbles contained in the lavas of Vesuvius. In these rocks, the mineral occurs in intricate intergrowths with fluorite [34]. Contact aureole of Mount Brooks, Alaska, includes B-bearing calciphyres with pertsevite, which were the first rocks where nocerite was found (Table 7). In these rocks, the mineral occurs in association with norbergite (Table 6) and fluorite, and its $F = 94$ mol % $Mg_3[BO_3]F_3$. Another occurrence of this mineral is hosted by the rocks surrounding greisenized magnesian skarns at Mount Inten'yurgen in the eastern Chukot Peninsula (Table 7), in which the mineral is contained together with fluorite and sellaite. Nocerite was not previously known at magnesian skarn deposits.

REPLACEMENT OF KOTOITE ROCKS BY SAKHAITE

The compositional evolution of endogenic solutions from F- to Cl-bearing is genetically associated with the transformation of magnesian skarns into calc-skarn associations. This process is manifested in marbles and calciphyres as the development of Si-free carbonatborates of the sakhaite–harkerite series [23].

Sakhaite as a replacement product of brucitized periclase and kotoite marbles and calciphyres (Fig. 6) is widespread at B deposits in the Selennyakh Range, where kotoite marbles with pertsevite occur near sakhaite rocks at the Efkachan deposit, and in the contact aureole of the Verkhne-Tirekhtyakh granite massif in the Tas-Khayakhtakh Range in Yakutia [6, 23]. Sakhaite was also found in calciphyres at Solongo, Buryatia [35].

Harkerite, a carbonatesilicateborate, is spread more widely than sakhaite [23] and is contained mostly in monticellite–forsterite calciphyres. At some deposits in Yakutia, rocks with these minerals occur nearby. Harkerite is characterized by the replacement of its borate radical by the silicon pentamer $\{Al[SiO_4]_4\}^{13-}$ coupled with a decrease in the Cl concentration (compared to that in sakhaite) in the absence of F.

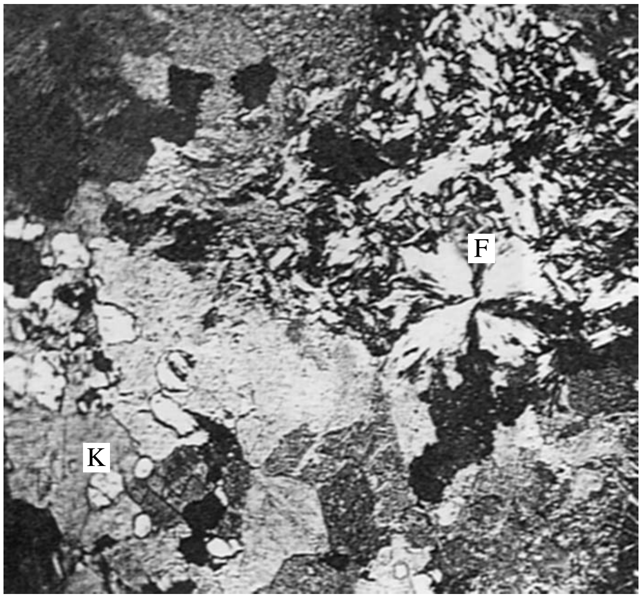

Fig. 5. Replacement of kotoite marble by fluoborite laths (*F*). Baia Roshe deposit, Romania. Sample R-040, transparent thin section. Magnification 25×.

The transformation of kotoite marbles and calciphyres into sakhaite is associated with the partial release of B

$$\underset{\text{kotoite marble}}{0.33Mg_3[BO_3]_2 + CaCO_3} + nH_2O =$$

$$\underset{\text{sakhaite}}{0.33Ca_3Mg[BO_3]_2(CO_3)(Cl, OH) \cdot nH_2O} +$$

$$\underset{\text{excess Mg and B}}{2.67Mg(OH)_2 + 1.34[BO_3]} + \underset{\text{gas}}{0.67CO_2\uparrow}$$

$$\text{and } \underset{\text{calcite}}{xCaCO_3} + \underset{\text{fluid}}{2.67MgCl_2 + 1.34[BO_3]} \longrightarrow$$

$$\underset{\text{sakhaite}}{0.33Ca_3Mg[BO_3]_2(CO_3)(Cl, OH)_x \cdot nH_2O},$$

which results in the replacement of the carbonate constituent of periclase marble by sakhaite, with brucite pseudomorphs after periclase preserved in the marbles in sakhaite masses.

Sakhaite rocks are nearly monomineralic and contain kotoite as relics (Fig. 6). The disseminated magnesioludwigite and silicates are not replaced by sakhaite. The occurrence of clinohumite in sakhaite rocks at many deposits in Yakutia suggests that the F-bearing solutions that transformed the mineralogy of the kotoite marbles and calciphyres came to these rocks earlier than Cl-bearing solutions.

A product of endogenic replacement of sakhaite is karlite $(Mg, Al)_6[BO_3]_3(OH, Cl)_4$ [36] (Tables 9, 10). We are not aware of any documented observations of

Table 9. Composition (wt %) of minerals from kotoite calciphyres at the Efkachan deposit, Selennaykh Range, Yakutia

Component	1	2	3	4	5	6	7	8	9	10
SiO_2	41.50	33.28	0.33	0.08	0.00	7.52	0.14	0.03	0.08	0.04
TiO_2	0.00	0.02	0.02	0.08	0.00	0.02	0.00	0.04	0.00	0.00
SnO_2	0.01	0.05	0.00	0.29	0.99	0.02	0.04	0.00	0.00	0.03
Al_2O_3	0.04	0.06	0.00	0.18	0.29	0.07	0.03	0.01	0.36	0.00
MgO	53.14	56.08	60.72	23.19	34.57	52.03	12.02	6.75	56.12	47.63
FeO	3.76	0.50	2.29	54.87	44.89	1.36	0.53	2.84	7.13	2.81
MnO	0.56	0.07	0.50	1.03	0.50	0.13	0.11	0.00	0.20	0.69
CaO	0.10	0.01	0.10	0.34	0.44	0.03	49.69	39.99	0.01	0.02
B_2O_3	–	–	35.95	15.22	16.85	18.49	17.97	24.83	26.16	41.12
CO_2	–	–	–	–	–	–	13.03	15.70	–	–
Cl	–	0.00	0.05	–	–	0.00	4.27	0.00	1.08	–
H_2O	–	9.97	–	–	–	11.78	1.83	9.62	8.75	10.60
Total	99.11	100.03	99.95	95.31	98.55	91.46	99.64	99.84	99.90	99.35
–O=Cl	–	–	–	–	–	–	0.96	–	0.24	–
$Total_{cor}$	–	–	–	–	–	–	98.68	–	99. 64	–

Note: (1) Forsterite, sample V-01395; (2) chondrodite, Mg/Si = 2.52, sample V-01396; (3) kotoite and (4) ludwigite $(Mg_{0.65}Fe^{2+}_{0.33}Mn_{0.02})_2(Fe^{3+}_{0.98}Al_{0.01}Sn^{4+}_{0.005}Mg_{0.005})[BO_3]O_2$, sample V-0791; (5) magnesioludwigite $(Mg_{0.88}Fe_{0.11}Mn_{0.01})_2(Fe^{3+}_{0.96}Al_{0.01}Sn_{0.015}Mg_{0.015})[BO_3]O_2$, sample V-01406; (6) Si-bearing pertsevite $(Mg_{0.985}Fe^{2+}_{0.015})_2\{[B_2O_3](F,OH)\}_{0.81}[SiO_4]_{0.19}$, sample V-01396; (7) sakhaite $(Ca_{47.89}Mg_{16.11})_{64}(BO_3)_{27.89}SiO_4)_{0.11})_{28}(CO_3)_{16}Cl_{6.5}(OH)_{5.5}$; (8) borcarite, Ca/(Mg + Fe^{2+}) = 4, *f* = 19 mol %, sample V-0791; (9) karlite; (10) szaibelyite $(Mg_{0.96}Fe_{0.03}Mn_{0.01})_2$, $B_2O_3 \cdot H_2O$, sample V-01396. Calciphyres contain fluorborite, which was identified on the basis of optical examination. The contents of B_2O_3, CO_2, and H_2O concentrations were calculated.

kotoite replacement by karlite. At the Efkachan deposit in Yakutia, karlite contains variable Cl concentrations (from 4.76 to 1 wt %). Moreover, sakhaite can be transformed by endogenic processes into polymineralic aggregates of borcarite, sibirskite $Ca_2B_2O_5 \cdot H_2O$, szaibelyite $Mg_2B_2O_5 \cdot H_2O$, and calcite [23, 35]. Younger veinlets in sakhaite rocks are composed of olshanskyite $Ca_3B_4O_9 \cdot 9H_2O$ and other still-unidentified borates [6].

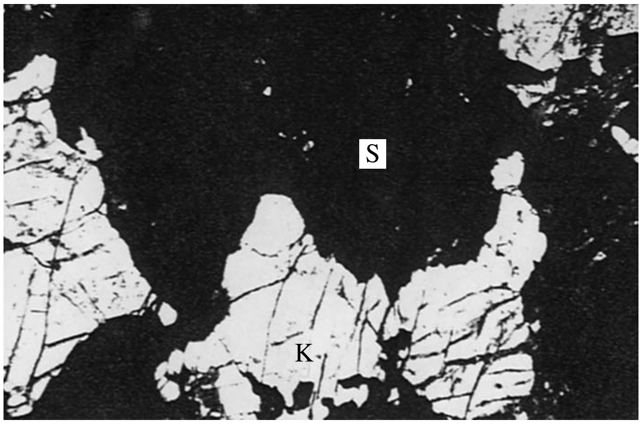

Fig. 6. Kotoite (K, white) relics in sakhaite (S, black). Eifakchan deposit, Selennyakh range, Yakutia. Sample V-0788, transparent thin section. Magnification 20×.

KOTOITE REPLACEMENT BY BORCARITE

A further decrease in the Cl concentration in the hydrothermal solutions is reflected in the relatively rare replacement of kotoite by borcarite $Ca_4Mg[B_4O_6](OH)_6[CO_3]_2$ in marbles and calciphyres partly transformed into sakhaite rocks. This Mg and Ca carbonateborate is a rare mineral. At the Snezhnoe deposit in the aureole of the Verkhne-Tirekhtyakh granite massif in the Tas-Khayakhtakh Range, Yakutia [23], it composes pseudomorphs after kotoite (Fig. 7) or, more often, veinlets in nearby rocks, including szaibelyitized ludwigite ores. As a newly formed phase, it was described in sakhaite from the Efkachan deposit in the Selennyakh Range (Table 9) and in harkerite from the Kerel occurrence in the Tas-Khayakhtakh Range [23]. The mineral was found by Li Don [37] in kotoite marbles at Hol Kol in North Korea and, as a secondary mineral replacing takedaite, in the rocks surrounding B-bearing calc skarns in the Fuko Mine, Okayama, Japan [38].

SZAIBELYITIZATION OF KOTOITE

During the final stage of the endogenic mineral-forming process, this transformation type of Mg and Mg–Fe borates is ubiquitously predominant. The minerals are hydrated (Fig. 1). At the examined deposits, szaibelyite is highly magnesian (Table 10) and composes not only pseudomorphs after earlier borates, including kotoite, but also numerous veinlets in adjacent rocks, thus compensating the volume increase of the newly formed phases relative to the volume of kotoite:

$$\underset{\text{kotoite}}{Mg_3[BO_3]_2} + 2H_2O = \underset{\text{szaibelyite}}{Mg_2B_2O_5 \cdot H_2O} + \underset{\text{brucite}}{Mg(OH)_2}.$$

This does not rule out the pseudomorphic replacement of kotoite (and suanite) only by brucite with the development of szaibelyite in the carbonate constituent of the marbles and calciphyres, as at the Kebiriin'ya occurrence (Table 10) and the Nalednoe (Kerel'ken) deposit in the Tas-Khayakhtakh Range, Yakutia [16]. Rare szaibelyite in the Mount Brooks calciphyres [27] is magnesian variety containing 0.7 wt % FeO and 0.1 wt % MnO (sample AS-0268). Pertsevite in these rocks is replaced by aggregates of szaibelyite and chlorite (clinochlore) or serpentine and chlorite, whose amounts are controlled by the silicity of the precursor borate. Analogous newly formed minerals were described to locally occur at Baia Roshe, Banat, Romania.

In addition to szaibelyite, marbles near kotoite-bearing rocks contain wightmanite $Mg_5[BO_3]O(OH)_5 \cdot 2H_2O$ containing Al, F, and Cl (Table 10). This borate was found by J. Murdoch in marble of the Crestmore quarry in Riverside, California, in association with magnesioludwigite, fluoborite with moderate F concentrations, and szaibelyite [39]. Note that forsterite calciphyre from the same occurrence was determined to contain kotoite in association with magnesioludwigite (sample 124127, collection of the Natural History Museum, Washington, DC, United States). Conceivably, wightmanite was formed before or simultaneously with szaibelyite due to local B redistribution in the course of the dehydration of earlier Mg borates.

Later wightmanite was found by C. Chesterman in dolomitic marble at Potter Lake, Fresno County, California, and we examined the composition of this mineral (Table 10). Its composition is comparable with that of wightmanite from the Crestmore quarry but is more ferrous and fluorian. Crystal chemical data confirm that the mineral has a structure similar to that of Fe–Mg borates and their Mn- and Ti-bearing varieties [40].

The products of endogenic carbonatization, the final process in the alterations of kotoite and other magnesian borates, are hydrotalcite and hydromagnesite, whose formation was associated with B migration.

DISCUSSION

The results of our study demonstrate that kotoite marbles and calciphyres are widespread at hypabyssal magnesian-skarn deposits of the spinel–periclase and spinel–monticellite facies of metasomatism in dolomites throughout the world (Tables 1, 2). All of them were produced in genetic relation with the emplacement of granitoid (including alaskite) intrusions. This type of borate ores is economically promising: their average B_2O_3 concentrations reach 14 wt % and even more (if the ores contain suanite), which can also be expected of rocks with pertsevite and fluoborite.

The data presented above show that the endogenic transformations of kotoite are diverse and evolutionarily successive, thus reflecting the systematic variations in the anion composition of the hydrothermal solutions with time. These solutions are Fe- and F-bearing during the early stages and induce the development of, first, Mg–Fe borates and then hydroxylfluorsilicateborates (pertsevite) after kotoite, simultaneously with an increase in the F contents in the humites that replace early forsterite and reach the compositions of chondrodite and norbergite.

Borates of magnesioludwigite (Table 3) and magnesiohulsite composition in association with forsterite and clinohumite replacing this mineral represent an early replacement type of kotoite-bearing rocks. They are characterized by variations not only of *Fe#* but also by the presence of Al, Sn, Ti, and, perhaps, also Sb.

The presence of F in the endogenic solutions during this stage of the mineral-forming processes is reflected in the development of F-bearing borates and syngenetic humites. The association of kotoite with humites containing high F concentrations is unstable and is transformed into pertsevite (Table 4), which was first found in a single sample of kotoite calciphyre from the Kebiriin'ya occurrence in Yakutia (Table 5).

The results of this research indicate that this mineral is also widespread at other deposits. For example, this mineral in the aureole of Mount Brooks in Alaska (Table 4) is rock forming and widespread (including its low-OH varieties) at the Potter Lake deposit in California and the Efkachan deposit in the Selennyakh Range in Siberia (Tables 8, 9). Conversely, the low-F variety of the mineral ($F = 15\%$ at $Si = 1\%$) was found in kotoite marbles from the Ozernoe deposit in the Selennyakh Range, Gogochan occurrence of B mineralization in the Dzhugdzhur Range, and in the eastern Chukot Peninsula (Table 8).

These data testify that the *Si* and *F* of pertsevite can broadly vary, and its mineral assemblages can include not only calcite and dolomite but also humites (except norbergite) (Table 6), as well as such fluorides as fluorite and sellaite. As was demonstrated above, the latter two minerals can preclude the formation of pertsevite and induce its replacement by Mg hydroxylfluorborates of the fluoborite–nocerite series (Table 7).

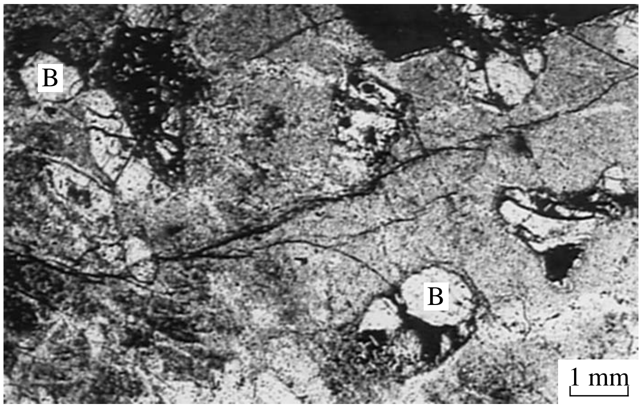

Fig. 7. Borcarite (B) pseudomorphs after oval kotoite grains in marble with magnesioludwigite (black). Snezhnoe deposit, Tas-Kayakhtakh Range, Yakutia. Sample V-0532, transparent thin section.

Similarities between the physical properties of this mineral and the previously synthesized compound $Mg_2[BO_3]F$ are not chemically complete, which is consistent with the data of the researchers who found this mineral and with newly obtained data on it. The actual composition of this mineral is more complicated and can be expressed as $(Mg, Fe)_2\{[BO_3]_{1-x}(F, OH)_{1-x}\}[SiO_4]_x$, which is consistent with the results obtained on pertsevite. The formula reflects not only the variable extent of isomorphism between B and Si but also the variability of F and OH concentrations at limited Mg substitution for F^{2+}.

With regard for these data, it is reasonable to suggest that pertsevite is produced during the endogenic transformation not only of calciphyres with humites but also immediately after kotoite–calcite marbles under the effect of F-bearing solutions. Note that the idea that forsterite is an end member of the pertsevite series is not confirmed genetically and is at variance with the ubiquitous early replacement of this mineral by humites and the absence of B in them. Nevertheless, there are literature data that chondrodite can contain up to 1.2 wt % B_2O_3 [41].

Another type of transformation in kotoite-bearing rocks is their replacement by Mg fluorborates with var-

Table 10. Composition (wt %) of karlite, szaibelyite, and wightmanite

No.	SiO_2	TiO_2	B_2O_3	Al_2O_3	MgO	FeO	MnO	CaO	F	Cl	H_2O	Σ	–F, Cl=O	Total
Karlite														
1	0.02	0.01	22.92	2.96	58.90	2.27	0.17	0.14	0.16	3.26	11.03	101.84	0.80	101.04
2	0.05	0.00	26.12	0.08	58.87	2.69	0.20	0.07	–	4.76	7.79	100.63	1.06	99.57
3	0.01	0.04	26.43	3.07	57.64	1.90	0.16	0.34	0.37	3.69	8.00	101.65	0.96	100.69
4	0.02	0.00	26.43	2.98	57.73	1.96	0.18	0.88	0.19	3.24	8.20	101.81	0.80	101.01
5	0.01	0.02	26.48	3.12	57.61	2.01	0.18	0.26	0.15	3.38	8.20	101.45	0.81	100.64
Szaibelyite														
6	0.04	0.01	40.60	0.36	45.85	1.83	0.29	0.35	0.10	0.03	10.48	99.94	0.05	99.89
7	0.27	0.02	41.08	0.03	47.20	0.29	0.37	0.04	0.00	0.00	10.63	99.92	–	–
8	0.14	0.00	40.68	0.00	46.00	1.79	0.00	0.10	0.00	0.00	10.50	99.14	–	–
9	0.06	0.02	40.38	0.03	47.73	1.45	–	0.03	0.00	0.00	10.63	100.33	–	–
10	0.07	0.02	40.53	0.09	47.68	0.82	–	0.11	–	–	10.75	99.78	–	–
Wightmanite														
11	–	0.16	12.2	2.1	57.8	2.2	–	2.7	1.80	0.94	21.50	101.40	1.01	100.39
12	0.05	0.20	11.77	1.99	60.63	4.47	0.01	0.38	2.43	–	19.42	100.74	1.02	99.72
13	0.28	0.10	10.94	4.16	57.41	5.44	0.05	0.14	3.98	–	19.01	101.51	1.67	99.84
14	0.27	0.18	11.05	4.20	57.01	6.65	0.04	0.25	2.45	–	19.20	101.20	1.03	100.17
15	0.73	0.07	10.91	4.81	56.00	8.85	0.05	0.09	2.01	–	18.95	100.88	0.84	100.04

Note: karlite: (1) Austria [34]; (2) Efkachan, Selennyakh Range, Yakutia (replaces sakhaite), sample V-01396; (3–5) Austria, in association with magnesioludwigite, clinohumite, szaibelyite, and calcite, sample W-7676, collection of the Museum of Natural History, Vienna. Szaibelyite: (6) in association with karlite, clinohumite (F = 0.91 wt %), magnesioludwigite, and calcite, sample W-7676, collection of the Museum of Natural History, Vienna; (7) Gonochan, Dzhugdzhur Range, Ayan district, Khabarovsk krai, Russia (replaces kotoite), sample Dzh-081; (8) Ozernoe deposit, Selennyakh range, Yakutia, sample V-01674; (9, 10) Kebiriin'ya deposit, Tas-Khayakhtakh Range, Yakutia, samples V-0449 and V-0469 (replaces kotoite). Wightmanite: (11) Crestmore, Riverside (in association with fluoborite in marble) [38]; (12–15) Potter lake, Fresno County, California, United States, sample AS-004 (collection of C.W. Chesterman): $(Mg_{0.8}Fe_{0.1}Al_{0.1})_5[BO_3]O(F_{0.2}OH_{0.8})_5 \cdot 2H_2O$, in association with chondrodite, magnesioludwigite, and pertsevite in calcite. B_2O_3 and H_2O concentrations were calculated from crystal-chemical considerations; B in analyses 9 and 10 was determined quantitatively.

ious OH concentrations belonging to the fluoborite–nocerite series. For example, newly formed fluoborite in kotoite marbles at the Korotovskoe deposit in Transbaikalia contains 25 mol % of the nocerite end member [8]. By virtue of the fact that these naturally occurring borates contain no less than 25 mol % $Mg_3[BO_3]F_3$, it seems to be possible to distinguish, within this series, fluoborite (with 25–75 mol % of the fluorine-bearing end member) and nocerite (with F from 75 to 100 mol %).

The data of Table 7 testify that kotoite is predominantly replaced by fluoborite with moderate F (55–70 mol % of the $Mg_3[BO_3]F_3$ end member) in association with carbonates. Conversely, extremely fluorian nocerite (80–94 mol % of the fluorine end member) replace kotoite together with fluorite and sellaite, as is exemplified by deposits in the Chukot Peninsula, at which this association immediately replaces dolomite when magnesian skarns are greisenized. No nocerite was previously found in the latter rocks.

Analyzing the sequence of mineral formation in the kotoite–pertsevite–fluoborite (nocerite)–sellaite (±fluorite) succession at increasing F concentration of the hydrothermal solutions, it seems to be reasonable to suggest that pertsevite replacing kotoite and humites is preserved as a mineral species only in association with fluoborite with moderate F concentrations but becomes unstable during the extensive replacement of dolomites and kotoite marbles by nocerite. Traces of these processes were found not only in eastern Chukotka and Italy but also at many other magnesian skarn deposits and occurrences in Middle Asia (Keregetash in Kirgizia and Karagaily-Aktas in eastern Kazakhstan), the United States (at Hope, Barstow, California), and China (at the Xian Hua Ling deposit) [42].

The systematic compositional evolution of the solutions from F- to Cl-bearing, which is evident from the occurrence of early clinohumite in the rocks, results in the replacement of kotoite marbles and nearby periclase marbles by sakhaite, as is the case with numerous deposits in the Selennyakh and Tas-Khayakhtakh ranges in Yakutia (Table 9) [23]. Cl is partly inherited by newly formed karlite veinlets replacing sakhaite (Table 10). Conversely, the absence of F and Cl in the solutions results in kotoite replacement by pseudomorphs of borcarite, an OH-bearing Ca and Mg carbonateborate, or in the development of veinlets of this mineral in the marbles (Table 9).

It should be stressed that the Efkachan deposit in the Selennyakh Range [33] is the only one where traces of all replacement stages of kotoite calciphyres were identified. These are expressed in the successive formation of forsterite, humites with variable F concentrations, kotoite, magnesioludwigite, ludwigite, pertsevite (Fig. 7), fluoborite, sakhaite, karlite, borcarite, and szaibelyite (Table 9). There are good reasons to believe that this also applies to other borate deposits in magnesian skarns.

During the final stage of endogenic mineral-forming processes, when F and Cl cease to be prevailing in the solutions, early Mg borates are hydrated, as is expressed in the immediate szaibelyitization of kotoite and the coupled formation of brucite and, perhaps, also syngenetic wightmanite (Table 10) in adjacent marbles. The carbonatization of kotoite and other borates marks the final stage of the endogenic transformations of these minerals and is associated with B migration out of the deposits.

All transformation types of kotoite marbles and calciphyres are characterized by the complete inheritance of the high and moderate Mg mole fractions of their ores by all newly formed minerals during the local redistribution of material in the course of their szaibelyitization. Conversely, the processes of their late carbonatization trigger B migration and, consequently, are associated with the depletion of the ores.

The data presented above provide a general idea about the transformation sequence of boron minerals at magnesian skarn deposits and amplify data on the endogenic geochemistry of B, Sn, F, and Cl.

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