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Composition, Mineral Assemblages, and Genesis of Titanite and Malayaite in Skarns

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Abstract—The composition of minerals of the titanite–malayaite series and their mineral assemblages and genesis were examined at the Bol'shoi Kan'on deposit in Magadan oblast and at other deposits. These minerals were demonstrated to be typomorphic Sn-bearing silicates in postmagmatic bimetasomatic hypabyssal calc skarns and skarnoids in tin-bearing provinces. The series of these minerals with similar crystal structures has a miscibility gap, and the minerals are characterized by notably different Sn concentrations. Moreover, titanite may contain Al, Fe, F, and OH, whose concentrations decrease in the Sn-bearing members of the series (malayaite). These silicates were formed at many deposits after the successive transforms of skarn mineral assemblages. The early assemblages include wollastonite in calcic carbonate rocks and diopside and salite in skarnoids. The latter minerals are replaced first by hedenbergite with subordinate amounts of vesuvianite and garnet first of grossular and then andradite composition. This process was syngenetic with the formation of borosilicates (danburite, axinite, and tourmaline). Ti thereby may be accommodated in grossular and Sn in Fe-bearing silicates, mostly, in andradite. Skarns often contain both titanite and malayaite, which were produced in these rocks earlier than cassiterite. The isomorphic series of these minerals has a miscibility gap. The ore-forming processes ended with the crystallization of quartz, fluorite, and rare sulfides, including stannite. The late Sn-bearing minerals at some deposits are stokesite and Mg, Fe, and Ca stannates, which crystallized during malayaite replacement by newly formed calcite–quartz aggregates. The Sn-bearing sulfides are replaced by varlamoffite during supergene processes.

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INTRODUCTION

Titanite (sphene) and malayaite, minerals belonging to a single isomorphic series CaTi(O, OH, F)[SiO_4]–CaSnO[SiO_4] with a miscibility gap, are the most widely spread Ti and Sn silicates in hypabyssal bimetasomatic calc skarns and skarnoids that develop during the postmagmatic transformations of neighboring aluminosilicate and carbonate rocks in the contact aureoles of granite intrusions [1, 2]. This does not rule out the occurrence of these minerals in overprinted calc-skarn associations replacing spinel–pyroxene magnesian skarns at contacts of dolomites with granites.

Titanite and malayaite are monoclinic, optically similar, and are the end members of an isomorphic series [3]. Their crystal structures consist of separated silicon tetrahedra and [CaO_7] and [$(Ti, Sn)O_6$] groups. Their unit cells of four formula units contain twelve oxygen atoms at three distinct sites. In one of them (O_1), oxygen atoms are not linked with [SiO_4] groups and can be substituted for F and OH. Our results demonstrate that titanite has a more complicated composition than that of malayaite: the former mineral pervasively contains not only F and OH in moderately titanian members of the series but also Fe^{3+} and Al. Thereby the oxygen substitution for $(OH, F)^-$ groups facilitates the preservation of the electrical neutrality of titanite with additional cations, including varieties with REE. The possibility of the accommodation of the latter elements in titanite and malayaite at skarn deposits remains unexplored as of yet. Available data suggest that titanite proper (i.e., varieties without Al and Fe) and malayaite have more ordered crystal structures at decreasing concentrations of $(OH,F)^-$ groups in the former mineral. Tin-bearing titanite and malayaite are associated with early borosilicates (danburite and axinite) and later cassiterite. The origin of the latter is predated by the deposition of arsenides (loellingite), including Sn-bearing varieties.

This research was conducted based on our data on the Bol'shoi Kan'on deposit in the Seimchan district, Magadan oblast, northeastern Russia, where Sn-bearing sphene and malayaite are widespread in skarns and cassiterite ores and on the Kitelya deposit in Karelia, Russia, where these minerals were identified in garnet skarns. We have also examined Sn-bearing wollastonite and garnet skarns at Meldon and Red-a-Ven, Dartmoor, Devonshire, England, and other occurrences, including titanite- and malayaite-bearing skarns at the El Hammam deposit in Morocco (the samples were provided for us by courtesy of Ph.M. Sonnet, France) and Sn-bearing titanite from the Stiepelmann mine, Arandis, Namibia (the samples were provided for us by courtesy of P. Ramdohr). To more completely characterize the composition of the Sn-bearing silicates and their genesis, we also used literature data on malayaite occurrences elsewhere and on tin deposits in Malaysia (which were provided for us by courtesy of Sir K.F.G. Hosking of the Camborne School of Mines, Cornwall, United Kingdom).

Our studies were centered on the geochemical environment in which silicates of the titanite–malayaite series were formed and on Ti and Sn isomorphism in these minerals.

BOL'SHOI KAN'ON DEPOSIT

Tin deposits in the Verkhoyansk–Chukotka foldbelt contain various types of ore mineralization. The most widespread deposits and occurrences are of the cassiterite–silicate and cassiterite–sulfide types (Deputatskoe, Ege-Khaya, Kester, and many others) and magnesian skarns, most of which are spatially restricted to the basin of the Dogdo River in the central part of the Tas-Khayakhtakh Range and to the Selennyalh Range. The latter are dominated by Sn-bearing borates (hulsite, paigeite, and ludwigite) and smaller amounts of cassiterite ores, which are localized in overprinted calc-skarn associations, greisenized skarns, and adjacent carbonate rocks. Quartz–cassiterite ores are rare.

The calc skarns with tin ore mineralization are localized in the eastern part of the territory. The largest of these deposits is Bol'shoi Kan'on, which was discovered in 1941 and is situated in the spurs of Mount Aesop, in the watershed area between the Pravyi Seimchan River (a tributary of the Kolyma River) and the Verina River, in the headwaters of Tur Creek. The deposit was developed and mined during the Second World War.

Our samples characterize rocks and ores taken from the underground mine and at surface workings. The deposit has practically no oxidation zone at borosilicate rocks and sulfide-free tin-bearing skarns.

The deposit is restricted to the southeastern contact of the Bol'shoi Kan'on multiphase intrusive massif (Fig. 1), which is made up of diorites, porphyritic biotite and biotite–hornblende granites, and their younger leucocratic (alaskitic) varieties [4–6]. The compositional variations of the intrusive rocks were caused by the decreasing intensity of the assimilation of carbonate rocks by the granitic magma.

This is reflected in the increasing silicity of the rocks, whose SiO_2 concentrations vary from 64.3% in the diorite to 70.4 and 71.5% in the granite and 75.2% in the alaskite [5], and makes it possible to evaluate the temperatures of their dry melts: 1000°C for diorite, 825–795°C for granite, and 700°C for leucocratic varieties [7, 8]. The intrusive rocks contain comparable amounts of Al_2O_3 (close to 14%) and the sum of K_2O and Na_2O (6–8% in the granites and 6% Na_2O at 0.2% K_2O in the albite alaskites). In contact with the latter, no host-rock assimilation was detected.

According to Gracheva and Zolotova [5], the diorites are associated with genetically related iron, base-metal, and cobalt ore mineralization, whereas granite intrusions were accompanied by the development of Sn-bearing skarns.

Metasomatic alterations affected Paleozoic terrigenous and carbonate rocks that compose a large rock block from the roof of the pluton (Fig. 1). The ore-hosting infiltration calc skarns replace calcite marble, and the bimetasomatic skarnoids developed after sandy–clayey and calcareous shales at contacts with both the granite intrusion and the younger alaskites. The metasomatites are hypabyssal, postmagmatic, as follows from the absence of minerals of the prograde metasomatic transformations of limestone and from the occurrence of wollastonite.

At the Bol'shoi Kan'on deposit, wollastonite skarns locally developed in the outer contact zone of the granites with calc marbles. They are replaced by pyroxene skarns or younger danburite (Fig. 2). Pyroxene skarns and skarnoids are spread more widely and consist of salite or hedenbergite, which are replaced by vesuvianite and then by garnet of grossular–andradite composition (Table 1). The skarnoids replacing alumina-bearing silicate rocks contain newly formed axinite and, more rarely, tourmaline.

The tin ore mineralization overprinting the skarns and skarnoids consists of titanite and malayaite, whereas cassiterite is a younger mineral and is associated with fluorite. The ores contain sulfides: pyrrhotite, arsenopyrite, chalcopyrite, sphalerite, and stannite, which are the youngest minerals in the ore-forming process.

The deposit comprises more than 20 explored and prospected orebodies, 16 of which contain (according to exploration data) economic tin concentrations (1–5% SnO_2). The orebodies are lenses and irregularly shaped bodies up to 350–400 m in strike length, which were traced for up to 200 m along their dips and have thicknesses of 5–20 m (Fig. 1) [4–6]. The southeastern part of the Bol'shoi Kan'on intrusion hosts known tourmaline–quartz and quartz–chlorite veins with cobaltite and subordinate amounts of arsenopyrite, chalcopyrite, sphalerite, and other sulfides (at the Verkhne Seimchanskoe and Volochek deposits).

In characterizing the rock-forming minerals of the calc skarns, it should be mentioned that, according to Vladimirov [4], the early pyroxene generations are salite, and the younger ones are ubiquitously Mn- and Sn-rich hedenbergite pyroxenes free of TiO_2 (Table 1). The same rocks locally contain vesuvianite (bearing 0.6 wt % B_2O_3) [4]. Diopside is rare in skarns at the deposit [5], a fact suggesting that the calc marbles contained no dolomite.

The garnet contained in skarns at the Bol'shoi Kan'on deposit varies in composition. The early gener-

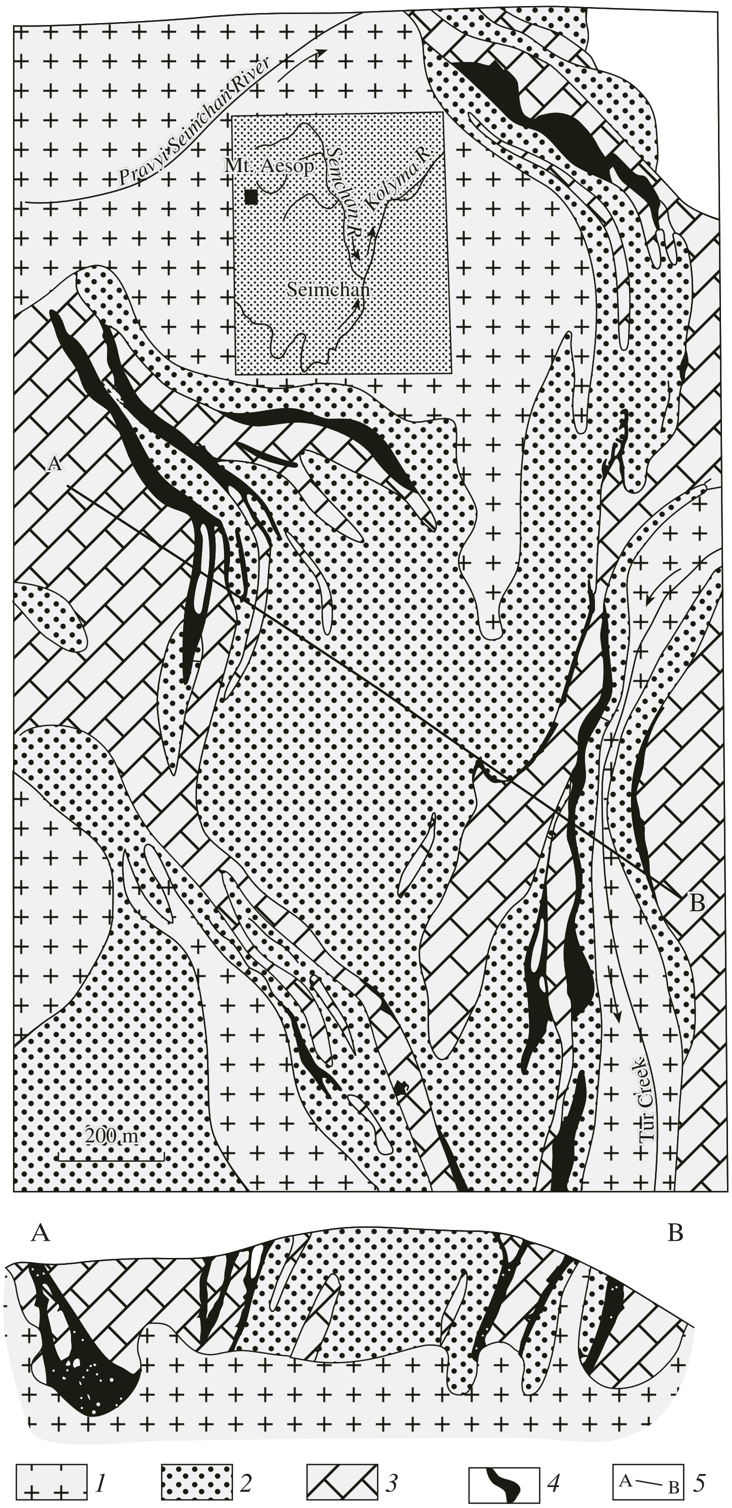

Fig. 1. Geological map of the Bol'shoi Kan'on deposit (modified after [5]).
(*1*) Biotite granite; (*2*) biotite hornfels; (*3*) marble and skarnoid; (*4*) skarn orebodies; (*5*) lines of geological profiles. The inset is a location map of the deposit.

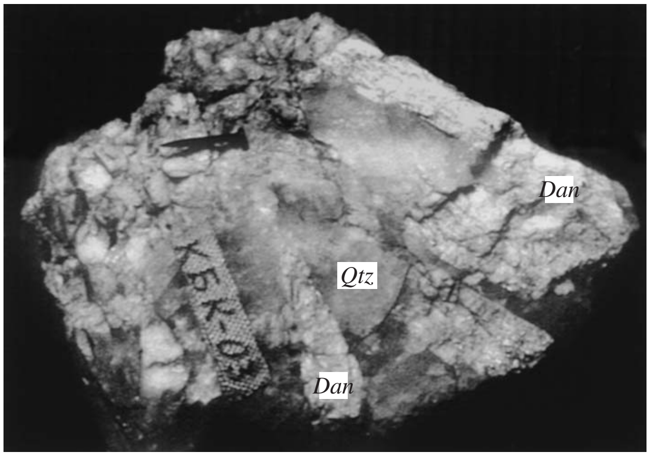

Fig. 2. Danburite (*Dan*) in association with quartz (*Qtz*). Bol'shoi Kan'on deposit. Sample KBK-03. Actual size.

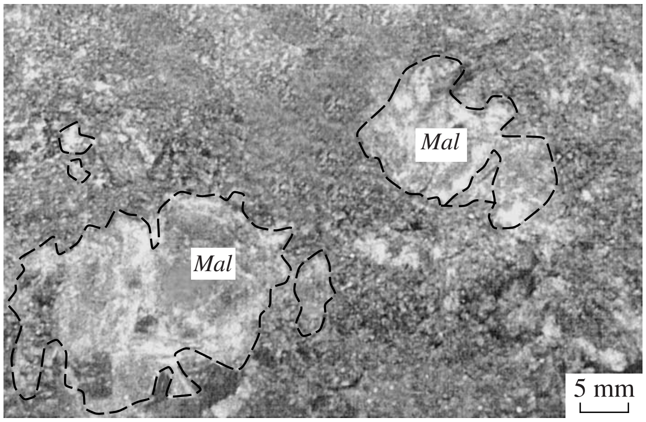

Fig. 3. Malayaite (*Mal*) in pyroxene skarn. Bol'shoi Kan'on deposit. Sample KBK-033.

ations replacing wollastonite are grossular, and younger generations are andradite-rich varieties (Table 1), which replaced hedenbergite and are sometimes predominant in zones with tin ore mineralization. Their tin concentrations are higher than in the hedenbergite.

The boron minerals are danburite, which replaced wollastonite skarns and quartz–carbonate rocks in the northern flank of the deposit. The orebodies contain axinite and tourmaline, which replaced pyroxene skarns and skarnoids (Table 2). They were formed before the Sn-rich silicates and cassiterite.

The early Sn-bearing minerals at the Bol'shoi Kan'on deposit are titanite and malayaite, which replaced pyroxene skarns (Fig. 3) and pyroxene–garnet skarnoids. These Sn-bearing silicates locally (in the central part of the deposit) account for up to 20% of the ore-hosting rocks. They are concentrated near contacts of the skarns with marbles or are spatially restricted to

Table 1. Composition (wt %) of rock-forming skarn minerals from the Bol'shoi Kan'on deposit

Component	1	2	3	4	5	6	7	8	9	10
SiO_2	46.92	48.20	48.34	47.37	47.90	36.68	38.31	36.98	36.88	37.11
TiO_2	tr	tr	0.04	0.06	0.04	0.94	0.02	0.00	0.17	0.05
SnO_2	–	–	0.08	0.07	0.10	n.d.	0.59	1.40	0.77	1.23
Al_2O_3	tr	–	0.12	0.54	0.53	16.30	10.83	4.24	8.47	3.84
Fe_2O_3	0.87	5.00	–	–	–	3.16	–	–	–	–
MgO	0.28	0.20	1.52	0.45	0.73	2.48	0.02	0.06	0.05	0.07
FeO	0.25	21.20	26.43	26.73	27.01	1.92	14.87	22.65	17.91	23.00
MnO	1.50	3.56	1.94	2.15	1.77	0.04	1.14	0.47	0.56	0.44
ZnO	–	–	0.13	0.06	0.00	0.01	0.05	0.13	0.09	0.00
CaO	43.50	22.06	20.76	22.32	21.83	34.74	32.47	32.93	33.58	33.02
F	–	–	0.00	0.03	0.07	–	–	–	–	–
H_2O^+	0.01	0.12	–	–	–	0.24	–	–	–	–
H_2O^-	0.18	0.02	–	–	–	0.06	–	–	–	–
Total	100.35	100.36	99.37	99.77	100.57	99.52	98.30	98.96	98.64	99.52

Note: (1) Wollastonite, CO_2 = 6.82 wt %, P_2O_5 = 0.02 wt %, SnO_2 n.d.; (2) pyroxene [4], (3–5) same (our data); (6) vesuvianite, contains 0.6 wt % B_2O_3 and 2.25 wt % CO_2 [4]; (7–10) garnet (our data). All analyses were conducted by M.A. Troneva on a CX-100 microprobe at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences. Garnet composition: (7) $(Ca_{0.92}Mn_{0.08})_3(Al_{0.51}Fe^{3+}_{0.49}Sn_{0.01}Fe^{2+}_{0.01})_2Si_3O_{12}$; (8) $(Ca_{0.96}Fe^{2+}_{0.03}Mn_{0.01})_3(Fe^{3+}_{0.72}Al_{0.23}Sn_{0.25}Fe^{2+}_{0.025})_2Si_3O_{12}$; (9) $Ca_3(Fe^{3+}_{0.55}Al_{0.42}Sn_{0.01}Ti_{0.005}Fe^{2+}_{0.015})_2Si_3O_{12}$.

Table 2. Composition (wt %) of boron-bearing minerals from the Bol'shoi Kan'on deposit

Component	1	2	3	4	5	6	7	8	9
SiO_2	48.36	48.45	41.20	41.40	40.98	41.47	42.19	35.11	35.05
TiO_2	tr	–	tr	–	0.01	0.03	0.00	0.61	0.18
SnO_2	–	–	–	–	0.07	0.15	0.07	0.31	0.31
Al_2O_3	0.20	–	18.68	17.06	17.99	18.48	17.43	25.73	28.65
Fe_2O_3	0.32	0.35	2.66	1.37	–	–	–	–	–
MgO	0.08	–	0.25	0.41	0.10	0.13	0.15	4.99	4.44
FeO	–	–	6.85	8.43	8.53	7.94	8.44	15.97	13.68
MnO	–	0.05	3.95	4.11	3.52	3.82	3.89	0.18	0.16
ZnO	–	–	–	–	–	–	–	0.04	0.05
CaO	23.56	23.26	19.28	20.00	18.76	18.49	18.73	1.26	0.92
H_2O_3	26.40	27.35	5.75	5.77	5.97	6.00	6.02	–	–
H_2O^+	0.23	–	0.18	0.84	3.08	3.10	3.11	–	–
H_2O^-	0.06	0.18	0.20	–	–	–	–	–	–
CO_2	0.67	0.18	0.83	0.52	–	–	–	–	–
F	–	–	–	–	–	–	–	0.38	0.19
Total	100.24	100.14	99.86	99.91	99.01	99.61	100.03	84.58	83.64
–F=O								0.16	0.08
$Total_{correct}$								84.42	83.56

Note: (1) Danburite, $Na_2O = 0.36\%$ [4]; (2) same mineral [5]; (3) axinite, $P_2O_5 = 0.03\%$ [4]; (4) same mineral [5]; (5–7) same mineral; (8, 9) tourmaline [(5–9) our data, CX-100 microprobe].

areas rich in quartz–carbonate rocks and contain newly formed younger cassiterite.

With regard for the observed malayaite associations, its formation can be represented by the following set of reactions of Sn-bearing hydrothermal solutions with wollastonite or quartz-bearing limestone, when cassiterite is unstable:

$$\underset{\text{wollastonite}}{CaSi_3O} + \underset{\text{cassiterite}}{SnO_2} = \underset{\text{malayaite}}{CaSnSiO_5} \text{ or}$$

$$\underset{\text{calcite}}{CaCO_3} + \underset{\text{quartz}}{SiO_2} + \underset{\text{cassiterite}}{SnO_2} = \underset{\text{malayaite}}{CaSnSiO_5} + CO_2.$$

Malayaite often replaces pyroxene skarns (Fig. 3)

$$\underset{\text{hedenbergite}}{Ca(Fe, Mn)Si_2O_6} + \underset{\text{cassiterite}}{SnO_2} + \underset{\text{rutile}}{TiO_2}$$

$$= \underset{\text{malayaite}}{CaSnSiO_2} + \underset{\text{quartz}}{SiO_2} + \underset{\text{ilmenite}}{(Fe, Mn)TiO_3},$$

as also follows from the occurrence of quartz and ilmenite $(Fe_{0.75}Mn_{0.25})TiO_3$ in this association.

The Sn-bearing titanite and malayaite, both of which are contained in the ores of the deposit, bear principally different Al and Ti concentrations. The titanite contains from almost 5 to 3% $A1_2O_3$, has an increasing SnO_2 concentration, which reaches almost 9% (i.e., from 2 to 12 mol % of the $CaSnSiO_5$ end member), and contains F (up to >2%) and OH. In contrast to this mineral, the malayaite contains from 77 to 99.6 mol % of the $CaSnSiO_5$ end member and from 20 to 0.3 mol % of the $CaTiSiO_5$ end member (Table 3). The economic importance of the ore minerals at the Bol'shoi Kan'on deposit is determined by the extensive development of younger cassiterite mineralization. Zonally colored cassiterite crystals (from colorless to brown, Fig. 4) contain up to 0.25 wt % TiO_2 and 0.12 wt % FeO. Their color is controlled by the presence of finely dispersed iron oxides alternating with paler zones of crystals. According to Vladimirov [4], the ores contain three cassiterite generations, which differ in crystal morphology and are contained in either hedenbergite (±calcite) skarns or fluorite- and quartz-bearing zones. Vladimirov [5] also described younger sulfides in these ores: pyrrhotite, sphalerite, arsenopyrite; and we determined that the ores also contain Zn-bearing stannite $Cu_2(Fe_{0.94}Zn_{0.06})SnS_4$.

The simultaneous occurrence of zonal dark brown cassiterite (containing up to 0.2 wt % TiO_2 and 0.12 wt % FeO) and malayaite is the most typical of hedenbergite skarns with axinite, but these rocks display no traces of malayaite replacement by early cassiterite. The Sn-bearing silicates at the Bol'shoi Kan'on deposit are locally transformed into calcite–quartz–cassiterite pseudomorphs [9].

The ore-forming process ended with sulfide deposition. At the flanks of the ore field, their Co-bearing varieties were identified. These minerals are oxidized in the supergenesis zone, while titanite, malayaite, and cassiterite are resistant to this process.

Table 3. Composition (wt %) of minerals of the titanite–malayaite series from the Bol'shoi Kan'on deposit, Magadan oblast

Component	1	2	3	4	5	6	7	8	9	10	11
SiO_2	30.22	30.37	29.92	29.19	29.13	25.21	25.01	24.39	24.13	23.86	25.50
TiO_2	32.20	31.50	28.85	30.59	29.03	6.08	5.20	4.69	2.22	1.47	0.08
SnO_2	1.75	3.97	4.71	5.95	8.85	44.81	45.94	46.61	50.66	52.09	53.59
Al_2O_3	4.68	3.97	4.94	3.35	3.01	0.31	0.26	0.31	0.19	0.13	tr
MgO	0.00	0.02	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–
FeO	0.44	0.89	1.00	0.92	0.80	0.48	0.50	0.52	0.29	0.21	0.25*
MnO	0.16	0.06	0.09	0.09	0.01	–	–	0.03	–	–	0.02
ZnO	–	–	–	–	–	0.08	0.07	–	0.07	0.00	–
CaO	28.59	28.25	28.18	28.07	27.87	23.19	22.86	22.45	22.32	21.89	19.57
F	1.61	1.50	2.40	1.63	0.71	–	–	–	–	–	–
Total	99.65	100.53	100.12	99.80	99.42	100.16	99.84	98.99	99.88	99.65	99.69
–F=O	0.68	0.63	1.01	0.68	0.30	–	–	–	–	–	–
$Total_{correct}$	98.97	99.90	99.11	99.12	99.18	–	–	–	–	–	–
Cation and anion proportions											
Ca	0.99	1.00	1.00	1.00	1.01	0.99	0.99	0.99	0.995	1.00	1.02
Sn	0.02	0.05	0.06	0.08	0.12	0.77	0.80	0.81	0.90	0.93	0.996
Ti	0.79	0.78	0.72	0.77	0.74	0.20	0.17	0.16	0.08	0.05	0.003
Fe^{3+}	0.01	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.001
Al	0.18	0.15	0.19	0.13	0.12	0.01	0.01	0.01	0.01	0.01	0.00
Si	0.98	1.00	1.00	1.00	0.99	1.01	1.01	1.01	1.005	1.00	1.19
O	4.92	4.92	4.87	4.92	4.96	5.00	5.00	5.00	5.00	5.00	5.94
F	0.08	0.08	0.13	0.08	0.04	–	–	–	–	–	–

Note: (1–5) Al- and Sn-bearing titanite (sample KBK-033); (6–10) malayaite (samples KBK-033 and KBK-034, analyst M.A. Troneva, CX-100 microprobe); (11) malayaite [9], data of chemical analysis, contains 0.04% Na_2O and 0.65% H_2O.

* Sum of FeO + Fe_2O_3.

OTHER DEPOSITS OF TIN-BEARING SILICATES

Along with the Bol'shoi Kan'on deposit, minerals of the titanite–malayaite isomorphic series are known in Yakutia (in metasomatic rocks of the Burgavli occurrence [9]) and Karelia (Kitelya deposit [1]). At the former locality, I.Ya. Nekrasov found Ti-rich malayaite $Ca_{0.93}(Sn_{0.58}Ti_{0.37}Fe^{3+}_{0.03}Al_{0.02})_{1.15}Si_{0.92}O_5$. The composition of these minerals in pyroxene–garnet metasomatic rocks overprinting magnesian skarns in Karelia broadly varies: from titanite with 5–12 mol % up to >50 mol % of the $CaSnSiO_5$ end member to pure malayaite [1, 2, 10]. As in the ores of the Bol'shoi Kan'on deposit, their crystallization preceded the deposition of cassiterite ore mineralization.

At other deposits in Russia, titanite of still-unknown composition was found, in association with axinite, danburite, fluorite, calcite, and, rarely, quartz, in cassiterite-bearing greisenized calc-skarn, in magnesian skarn boron deposits in the Selennyakh Range (at the Ideal deposit and locality at Sebekchan Creek, a left-hand tributary of the Chybagalakh River) and in the Tas-Khayakhtakh Range (in the basin of the Dogdo River, at the Khalim and Nalednoe deposits and a locality on Tuloyakh Creek) in Yakutia. Titanite was also found in danburite-bearing calc skarns overprinted on magnesian skarns at the Keberiin'ya deposit in the same portion of the Chersky Range (A.V. Dorofeev, personal communication).

Tin-bearing titanite and malayaite were identified at the Meldon Mine, Devonshire, United Kingdom [11, 12]. In contrast to the deposits considered above, here malayaite is hosted in wollastonite skarn replaced by grossular in the contact aureole of the Dartmoor granite massif. According to our data, the composition of rock-forming minerals in the rocks correspond to Mn-wollastonite $(Ca_{0.985}Mn_{0.013}Fe^{2+}_{0.02})SiO_3$, salite $Ca(Mg_{0.8}Fe^{2+}_{0.14}Mn_{0.06})Si_2O_6$, and grossular $(Ca_{2.64}Mg_{0.18}Fe^{2+}_{0.16}Mn_{0.02})_3\{Al_{1.87}(Ti_{4+}Mg)_{0.11}Fe^{3+}_{0.02}\}_2[Si_{2.63}(F_{0.4}OH_{0.6})_{0.37}]_3$. We determined that the garnet contains from 0.02 to 0.2 wt % SnO_2. Malayaite was found in these skarns (Table 4), in which it occurs together with datolite veinlets (replacing wollastonite) and disseminated loellingite [11]. At the nearby Red-a-Ven skarn

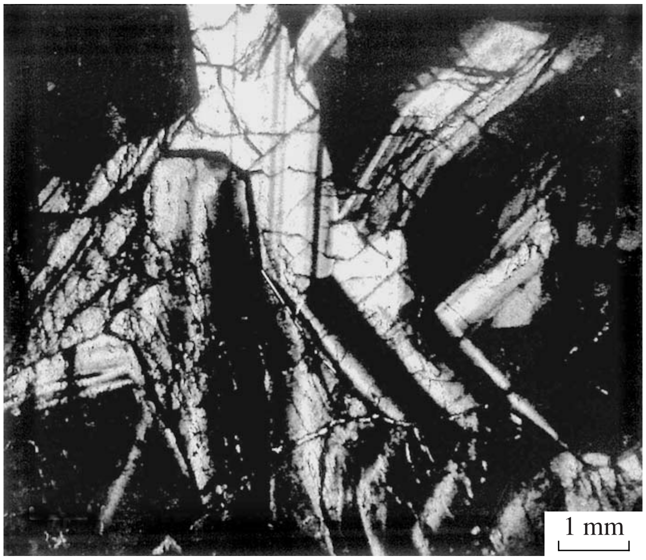

Fig. 4. Zonal cassiterite crystals. Bol'shoi Kan'on deposit. Sample KBK-039.

occurrence, Sn-bearing zonal garnets were found (containing from 0.2 to 1.7% SnO_2) of andradite composition but with grossular cores. No malayaite was found in association with them, but cassiterite was. Boron-bearing minerals (danburite and axinite) were also identified at this occurrence [11].

Another locality with titanite and malayaite (Table 4) in the United Kingdom is the St. Just mining district in Cornwall (Crowns deposit) [13, 14]. Both minerals occur in calc skarns and skarnoids in the contact aureole of the Batallack granite (Land's End). In these rocks, the minerals are accompanied by Sn-bearing epidote (from 0.47 to 2.84% SnO_2) and Fe-rich pargasite (up to 0.7 wt % SnO_2), which replaces the garnet-bearing rocks, and cassiterite. The cassiterite contains 0.54% TiO_2 and 1.02% Fe_2O_3. The accommodation of Sn in amphibole and epidote occurs as $Sn^{4+} + Fe^{2+} \longrightarrow 2\,(Al, Fe^{3+})$, whereas the substitution in the titanite is predominantly via the isovalent substitution of Ti for Sn. As at the Bol'shoi Kan'on deposit, titanite from this one contains, along with Fe and Al, also F and $(OH)^-$, which are atypical of malayaite. The latter mineral contains no Ti, and its FeO concentration is 0.48% (Table 4).

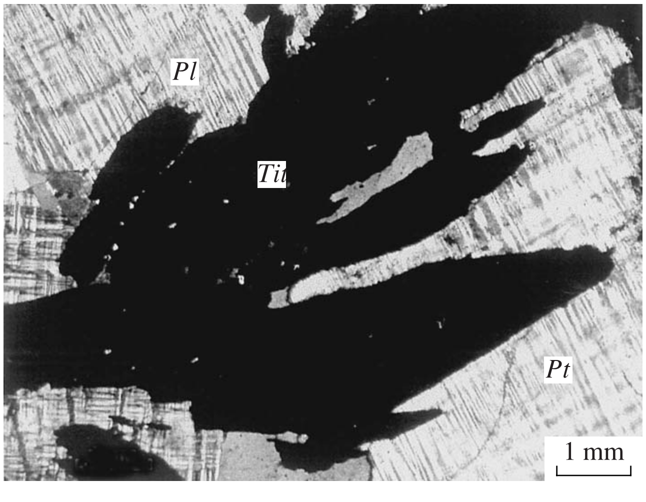

Fig. 5. Tin-bearing titanite (*Tit*) in association with plagioclase (*Pl*). Stiepelman Mine, Namibia (sample from the collection of Prof. P. Ramdohr).

In Africa, minerals of the series are known at Arandis in Namibia [15] and El Hammam in Morocco [16, 17]. At the Stipelmann mine in Arandis, Namibia, Ramdohr found Sn-free titanite and its varieties with close to 10% SnO_2 (Fig. 5) in wollastonite skarns, in which these minerals occur together with cassiterite and plagioclase.

Our data on samples from Arandis (which were made available for us by courtesy of P. Ramdohr) indicate that the titanite contains 15–20 wt % SnO_2 and 20–15 wt % TiO_2, 2% Al_2O_3, and up to 2–4% Fe oxides (Fig. 4). This corresponds to 22–35% of the $CaSnSiO_5$ end member at decreasing concentration of $CaTiSiO_5$ (51–44%).

At the El Hammam deposit in central Morocco [17], metasomatic rocks in the aureole of a granite massif consist of wollastonite, plagioclase–pyroxene, and grossular (87–53% $Ca_3Al_2Si_3O_{12}$) skarns and skarnoids with up to 0.8% TiO_2, replacing pelites, as well as their salite (88–57 mol % $CaMgSi_2O_6$), hedenbergite (89 mol % $CaFe^{2+}Si_2O_6$), and andradite (79–89% $Ca_3Fe_2^{3+}Si_3O_{12}$) varieties. The garnet contains up to 0.2 wt % SnO_2 in grossular and from 1.6 to 5.6 wt % SnO_2 in andradite. The latter contains vesuvianite inclusions. Axinite in the skarnoids is rich in Fe or, more rarely, Mn. It contains up to 1.7% SnO_2, replaces aluminous minerals, and occurs in association with scheelite and malayaite.

Tin-bearing wollastonite–garnet skarns were traced at this deposit for 150 m and had the thickness of 5 m. The bulk SnO_2 concentration in these rocks amounted to 14 wt %. The rocks consist of green grossular-andradite (with wollastonite relics), and their andradite contains up to 1.6 wt % SnO_2 and more. The wollastonite-free garnet skarns contain malayaite, which bears less than 0.3% TiO_2. In the plagioclase–pyroxene skarnoids, titanite is replaced by malayaite (containing up to 4.5 wt % TiO_2, which is equivalent to 14% $CaTiSiO_5$). The pyroxene skarns, in which plagioclase becomes an accessory mineral, malayaite, contains no TiO_2.

The younger newly formed minerals at the El Hammam deposit are actinolite, datolite, fluorite, and quartz-bearing associations with sulfides: pyrrhotite, chalcopyrite, stannite, and others, including their Au-bearing varieties. The endogenic process ended with the carbonatization of earlier minerals. Malayaite was thereby replaced by calcite–quartz–cassiterite and

Table 4. Composition (wt %) of minerals of the titanite–malayaite series from various deposits worldwide

Component	1	2	3	4	5	6	7	8	9	10	11
SiO_2	23.2	29.07	22.87	28.49	28.13	27.08	23.83	23.76	22.22	22.62	18.29
TiO_2	0.2	31.51	0.00	18.81	18.15	15.08	0.00	0.00	0.60	0.08	0.07
SnO_2	53.3	6.71	55.39	14.90	19.83	22.82	52.73	52.62	56.72	55.59	47.10
Al_2O_3	–	3.34	0.00	1.96	1.64	1.15	0.24	0.25	–	0.39	–
MgO	–	0.00	0.00	0.05	0.04	0.05	0.00	0.00	–	0.02	0.13
FeO	0.7	1.02	0.48	5.57	4.83	5.01	0.25	0.26	0.05*	0.22*	2.70**
MnO	–	0.00	0.00	0.09	0.13	0.15	0.05	0.06	–	0.00	–
CaO	22.32	8.09	21.91	25.40	24.94	24.20	20.56	20.21	20.61	20.64	19.97
Total	100.6	100.96	100.65	95.29	97.68	95.54	97.68	97.16	100.20	100.01**	89.73**
Cation and anion proportions											
Ca	1.00	1.02	1.03	0.99	0.97	0.98	1.00	1.00	0.98	0.97	1.00
Sn	0.97	0.09	0.97	0.22	0.29	0.35	0.98	0.98	1.00	0.97	0.88
Ti	0.01	0.80	0.00	0.51	0.49	0.44	0.00	0.00	0.02	0.00	0.00
Fe_{Σ}	0.02	0.03	0.02	0.18	0.15	0.16	0.01	0.01	0.00	0.01	0.11
Al	–	0.13	0.00	0.09	0.07	0.05	0.01	0.01	–	0.02	–
Σ M	1.00	1.04	0.99	0.97	1.00	0.99	1.00	1.00	1.02	1.00	0.99
Si	1.00	0.98	1.00	1.04	1.02	1.03	1.00	1.00	0.99	0.99	0.85
O	5.00	4.97	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
F	–	0.03	–	–	–	–	–	–	–	–	–

Note: (1) Meldon, Devonshire, United Kingdom, in association with diopside, vesuvianite, datolite, and minor amounts of loellingite, insoluble residue 0.9% [17]; (2) titanite, F = 1.22%; (3) malayaite, Cornwall, United Kingdom [13]; (4–6) titanite, Arandis, Namibia (sample from the collection of P. Ramdohr); (7, 8) El Hammam (sample from the collection of Ph.M. Sonnet); (9) Sampo, Japan [17]; (10) Toroku Mine, Japan [17]; (11) Pinyok Mine, Thailand [17], other components: $H_2O^+ = 1.36$, $H_2O^- = 0.12$ wt %.

* Determined as Fe_2O_3,

** other components: $Na_2O = 0.28$, $K_2O = 0.04$, $H_2O^+ = 0.08$, $H_2O^- = 0.03$, $P_2O_5 = 0.02$ wt % [17].

axinite–chlorite–quartz–calcite, and datolite is replaced by calcite–quartz aggregates. The malayaite-bearing garnet skarns contain rare Sn-bearing minerals: stokesite, wickmanite, burtite, and varlamoffite (which replace Sn sulfides) [16].

In the samples provided for our study by Ph.M Sonnet, practically Ti-free malayaite (Table 4) occurs together with salite, hedenbergite, vesuvianite (up to 2% F), and Sn-bearing (1–3.5% SnO_2) garnet of grossular–andradite composition.

Other malayaite occurrences are skarn deposits in Japan, China, Malaysia, Thailand, Australia, and, Canada. This mineral was found in Japan at the Sampo deposit in Okayama Prefecture [12], Tsumo in Shimane Prefecture [18], and in the southwest of the country, in the Mitate pyroxene skarns and in the Hoei and Kuga garnet skarns [19, 20].

Pyroxene–garnet calc skarns at the Sampo deposit replace carbonate rocks in the contact aureole of an intrusion of leucocratic biotite granites and host bodies of sulfide-bearing magnetite ores with fine-grained disseminated cassiterite. Malayaite was found in wollastonite–pyroxene skarns with green garnet in association with fluorite and subordinate amounts of actinolite. The composition of the malayaite corresponds to $Ca_{0.98}(Sn_{1.00}Fe^{3+}_{0.00}Ti_{0.02})_{1.02}Si_{0.99}O_5$ (Table 4). Tin-bearing titanite [21] is also known in the Toroku wollastonite–diopside–garnet skarns in Miyazaki Prefecture (Table 4).

Titanite containing 0.1–3% SnO_2 was found in skarn deposits in southern China [22]. In the Xilu skarns, this mineral occurs in a number of generations. The early titanite occurs in association with diopside, vesuvianite, and andradite and contains no more than 0.17–0.26% SnO_2, whereas the late generations of this mineral are accompanied by actinolite, chlorite, and fluorite and contain as much as 1.72–2.72% SnO_2. Varieties of malayaite composition were found in the contact aureole of the Yangshan intrusions of leucocratic granites (Jenjialong deposit), in which malayaite was found in calcite veins cutting across diopside–garnet skarns [22].

In the skarns of the Pinyok Mine in Thailand [23], practically Ti-free malayaite (Table 4) was found in cassiterite-bearing diopside–andradite skarn in association with calcite and quartz.

Table 5. Composition (wt %) of minerals of the titanite–malayaite series from various skarn deposits worldwide

Component	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	22.83	21.26	24.15	30.27	30.47	30.27	30.76	30.77	30.34	30.59	29.91	23.11
TiO_2	0.00	–	1.65	39.02	28.52	26.98	31.57	33.40	32.44	32.04	27.40	3.57
SnO_2	56.18	58.48	55.65	0.00	0.28	0.63	0.94	1.69	2.07	2.21	9.26	53.08
Al_2O_3	–	–	0.08	1.28	6.48	7.49	4.46	3.45	2.84	2.86	1.21	0.19
MgO	–	–	0.00	0.01	0.02	0.04	0.04	0.02	0.04	0.08	0.00	–
FeO	–	–	0.33	0.38	1.01	1.40	0.59	0.58	1.44	1.54	2.17	0.56
MnO	–	–	0.00	0.00	0.01	0.06	0.03	0.00	0.06	0.04	0.02	–
ZnO	–	–	–	–	0.06	0.00	0.00	0.05	0.00	0.06	0.05	–
CaO	20.55	19.40	19.53	28.96	28.27	28.50	28.11	28.80	27.54	27.56	26.07	22.68
F	–	–	–	–	3.05	2.91	2.82	0.67	1.44	1.93	0.14	–
Total	99.56	99.38*	101.46	100.04	98.40	98.46	99.47	99.50	98.29	98.93	95.65	102.19
–F=O	–	–	–	–	1.28	1.22	1.18	0.28	0.60	0.81	0.06	–
$Total_{correct}$	–	–	–	–	97.12	97.24	98.29	99.22	97.69	98.12	95.59	–
Cation and anion proportions												
Ca	0.98	0.89	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Sn	1.00	1.00	0.93	0.00	0.005	0.01	0.01	0.02	0.03	0.03	0.135	0.86
Ti	0.00	–	0.055	0.94	0.715	0.67	0.80	0.83	0.82	0.815	0.755	0.11
Fe^{3+}	–	–	0.01	0.01	0.025	0.04	0.01	0.015	0.035	0.04	0.06	0.02
Al	–	–	0.005	0.05	0.255	0.29	0.18	0.135	0.115	0.115	0.05	0.01
ΣM	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Si	1.02	0.91	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	4.00	4.00	4.00	4.00	4.00	5.00
F	–	–	–	–	0.32	0.30	0.30	0.29	0.15	0.21	0.015	–
OH	–	–	–	–	1.68	1.70	1.70	1.79	1.85	1.79	1.985	–

Note: (1) Malayaite, Perak, Malaysia [26], in association with varlamoffite; (2) same [26]; (3) malayaite (other components: Na_2O = 0.02%, NiO = 0.05%); (4) titanite (other components: Na_2O = 0.01%, Cr_2O_3 = 0.02%, NiO = 0.09%) from skarns in New South Wales, Australia [27]; (5, 11) titanite from the Mount Lindsay skarns, Tasmania [28] [other components in (5): WO_3 = 0.13%, K_2O = 0.01%, (OH) = 1.60%], [other components in (6): WO_3= 0.13%, Na_2O = 0.03%, (OH) = 1.54%], [other components in (7): WO_3 = 0.09%, Na_2O = 0.03%, (OH) = 0.53%], [other components in (8): CuO = 0.02%, WO_3 = 0.06%, K_2O = 0.03%, (OH) = 0.5%], [other components in (9): WO_3 = 0.10%, Na_2O = 0.07%, K_2O = 0.01%, (OH) = 1.71%], [other components in (10): Na_2O = 0.02%, K_2O = 0.5%, (OH) = 1.07%], [other components in (11): CuO = 0.04%, Na_2O = 0.07%; K_2O = 0.01%, (OH) = 3.35%]; (12) malayaite, Clea, Yukon Territory, Canada.

As a new mineral, malayaite was first found at the Kinta Valley tin skarn deposit in Perak Province, Malaysia [24], where this mineral occurs in association with cassiterite and varlamoffite [25]. Analyses (Table 5) confirm its affiliation with this mineral species [26].

Skarns at some tin deposits in Australia contain titanite and, in New South Wales, malayaite (Table 5). Characterizing its associations in the pyroxene–garnet skarns and plagioclase-bearing banded skarnoids at the Doradilla via Burke deposit, Plimer [27] noted that the rocks contain wollastonite, salite, rare vesuvianite, and garnet of grossular–andalusite composition. In the latter, greenish yellow grossular is older and composes the cores of green andradite crystals. The pyroxene–garnet skarns and compositionally similar skarnoids are cut by veinlets of calcite–malayaite composition. The same veinlets contain disseminated titanite, cassiterite, arsenopyrite, and sulfides, including stannite, and fluorite.

It was demonstrated [27] that Sn concentrations in garnet are relatively low in grossular-rich varieties (approximately 0.1% SnO_2) but notably increases in andradite (to 3% SnO_2), whereas Ti preferably enriches aluminous garnet (up to 2.15 wt % TiO_2) compared to andradite (0.07%). Conversely, the SnO_2 concentration in pyroxene of the composition $Ca(Mg_{0.25}Fe^{2+}_{0.75})Si_2O_6$ is as low as 0.1%. In skarns at this deposit, malayaite is rich in Sn: contains from 94.8 to 99.9 mol % of the Sn-bearing end member, whereas the titanite is close to the end member of the series and contains 99.9 mol % of the $CaTiSiO_5$ end member (Table 5).

Tin-bearing titanite containing 0.28–9.26% SnO_2(Table 5) is also known in vesuvianite–garnet skarns at deposits in Tasmania [28] and contains 1–25 mol % of the malayaite end member. Kwak [28] determined that Sn is also contained in the tremolite (up to 0.79% SnO_2) and ilvaite (up to 1.08%).

In North America, at deposits in the Yukon Territory, Canada, Dick [29] found and examined Al-bearing titanite $Ca(Ti_{0.69}Al_{0.27}Fe_{0.03}Sn_{0.015})_{1.05}Si_{0.985}O_5$ (at the Bom locality) and malayaite $Ca(Sn_{0.91}Ti_{0.05}Fe_{0.025}Al_{0.017})_{1.04}Si_{0.97}O_5$ (Clea locality). They were found in the skarn aureole of the Seagull granite batholith and are accompanied in these rocks with Sn-bearing garnet, axinite, epidote, cassiterite (which replaces malayaite), and Fe sulfides, including stannite. The granites are tourmalinized.

According to Dick [29], green andradite with the highest Sn concentrations contain from 0.89 to 4.44% SnO_2 in the Can skarns and from 1.52 to 2.28% SnO_2 at the Clea locality. At the latter locality, epidote contains 2.40–6.23% SnO_2.

We examined minerals of this series from the United States using materials collected at the New City–Victoria Avenue Mine in Riverside County, California, where magnesian skarns replaced dolomites. Titanite $Ca(Ti_{0.76}Al_{0.20}Fe^{2+}_{0.02}Sn_{0.02})SiO_5$ contains 1 wt % F and occurs as small crystals in originally plagioclase–fassaite outer-contact skarns transformed into andradite–grossular associations. The grossular contains the morimotoite end member $(Ca_{2.73}Fe^{2+}_{0.22}Mn_{0.05})_3(Al_{1.52}Fe^{3+}_{0.36}Ti^{4+}_{0.06}Mg_{0.06})_2Si_3O_{12}$ and occurs in association with relict anorthite $(Ca_{0.98}Na_{0.02})Al_2Si_2O_8$. Titanite with higher Sn concentrations $Ca(Sn_{0.3}Ti_{0.2}Al_{0.3}Fe^{3+}_{0.2})SiO_5$, which contains from 27 to 30% SnO_2 and 8–9% TiO_2, was found at this deposit in vesuvianite–cuspidine metasomatic rocks with gahnite, harkerite, and fluorite [30]. Tin was previously identified at this mine only in the ludwigite (0.53% SnO_2) [31]. Note that literature on skarn deposits in Riverside County, where several borates and borosilicates were found, provides no information on the Sn concentrations in the titanite and other minerals.

DISCUSSION

The data presented above indicate that the rock-forming minerals (including titanite and malayaite) of calc-skarn associations of various genesis in tin ore provinces are tin concentrators. The crystallization of these minerals preceded the development of the cassiterite ore mineralization and later deposition of sulfides (including stannite).

When considering the successive transformations of Sn-bearing minerals during the development of calc skarns replacing carbonate rocks and pelites and the subsequent ore-forming processes in them, it is necessary to emphasize their evolutionary relations.

Practically all of the skarn deposits considered above are localized in the contact aureoles of granite intrusions, which often consist of many intrusive phases, as follows from literature and our data. The Sn-bearing metasomatic rocks are obviously spatially related to intrusions of leucocratic biotite granites.

Hypabyssal calc skarns are postmagmatic and developed during the retrograde metasomatism stage. The early wollastonite exoskarns are pervasively replaced by overprinted pyroxene and garnet varieties without clearly pronounced metasomatic zoning. The adjacent aluminosilicate rocks (pyroxene–garnet skarnoids) are replaced by amphiboles and epidote.

In contrast to them, magnesian skarns developing after dolomites are produced at contacts with magmatic melts during the prograde metasomatic stage. Their bodies typically have clearly pronounced but variable zoning without endoskarns [1, 2, 7, 8]. During the postmagmatic stage, their rear, predominantly pyroxene-bearing zones are variably replaced by calc-skarn associations, whose typomorphic minerals are successively formed salite, vesuvianite, garnet (mostly of grossular composition), and finally, wollastonite in the immediate contact with the intrusive rock [32, 33].

The Sn concentrations in the rock-forming minerals of calc-skarn associations of both types display certain tendencies: the early wollastonite of calc skarns is replaced by salite and/or grossular. As was demonstrated above, these minerals either are free of Sn and Ti or contain Ti in the form of the morimotoite end member $Ca_3(Fe^{2+}Ti^{4+})[SiO_4]_3$ in grossular. For example, in California and Tasmania [28], grossular is enriched in Ti (up to 6–8 wt % TiO_2), which is accommodated in the crystal structure according to the scheme $2Al^{3+} \longrightarrow Ti^{4+} + Fe^{2+}$. This seemingly testifies that Ti is brought to the metasomatic rocks earlier than Sn.

The later development of Fe-rich pyroxene (hedenbergite, which contains not only Fe^{2+} but also Fe^{3+}) in the skarns created favorable conditions for the limited heterovalent incorporation of Ti and Sn into the structure of the mineral according to the scheme $2Fe^{3+} \longrightarrow [(Ti, Sn^{4+}) + Fe^{2+}]$ [10, 31–33].

The Sn and Ti concentrations in the garnet increase in their andradite varieties. This can be illustrated by the example of zonal garnet crystals whose cores consisting of grossular and peripheral parts are made up of newly formed andradite. The latter can contain up to 6 wt % SnO_2, as in skarns of Morocco and Canada.

As follows from literature and our data, these minerals at the skarn deposits of Sn-bearing silicates are syngenetic with or are accompanied by B-bearing minerals (danburite, axinite, tourmaline, and others, including late datolite). Their genesis was controlled by the introduction of endogenic boron and the original mineral composition of the replaced associations. The wol-

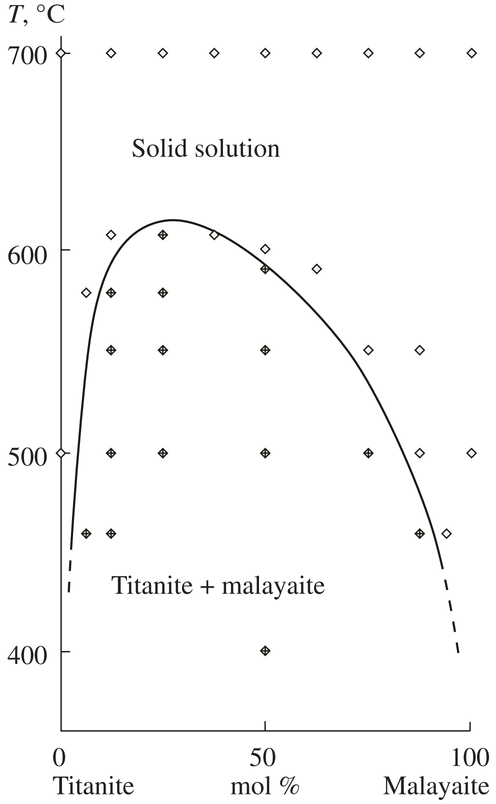

Fig. 6. Stability field of minerals of the titanite–malayaite series [19].

lastonite and quartz–calcite rocks are replaced by danburite, whereas Al-bearing pyroxene and garnet skarns are replaced by axinite. The skarnoids, including their feldspar-bearing varieties, often contain tourmaline. The postores datolite mineralization developed in the form of veinlets.

As was demonstrated above, titanite was formed before and after malayaite, a fact that predetermines their practically constant coexistence in tin-bearing skarns. During the inflow of tin-bearing hydrothermal solutions, these minerals replaced both wollastonite skarns or calcite–quartz assemblages and, possibly, also tin-bearing andradite.

The data presented above on the composition of titanite and malayaite provide evidence that this series contains practically no mineral members containing from 35 to 75 mol % of the $CaSnO[SiO_4]$ end member (Tables 3–5). At the same time, skarn deposits only rarely contain Sn-free titanite but instead usually bear its varieties with increasing Sn concentrations, whose maximum is reached in titanite from Arandis, Namibia.

Varieties of this mineral with moderate Sn concentration are characterized by the accommodation of Al, whose highest concentrations were identified in titanite with 35 mol % of the $CaSnO[SiO_4]$ end member. This likely reflects the increasing role of isomorphic Ti substitution for Al and, to a lesser degree, Fe. Their occurrence indicates that Sn-bearing titanite can incorporate certain components of replaced minerals at the limited supply of Ti and Sn with the hydrothermal solutions and at decreasing temperature.

Conversely, malayaite containing more than 75 mol % of the $CaSnO[SiO_4]$ end member is relatively poor in Al and Fe, and the mineral successively approaches its stannian end member (Tables 3–5). This is consistent with the results obtained by Takenouchi [19] on the hydrothermal modeling of the formation of mineral belonging to the titanite–malayaite series.

These experimental data [19] confirm that the titanite–malayaite series is characterized by practically unlimited continuous isomorphism at high temperatures. Crystal chemically, this is expressed in the systematic variations in the reflections $d(200) = 3.239 + 0.0034x$ and $d(002) = 2.996 + 0.0051x$ with increasing mole fraction x of the $CaSnSiO_5$ end member. The fluorescence of the solid solutions under the effect of short-length ultraviolet radiation was noted to vary from yellowish green for pure malayaite to bluish for Sn-bearing titanite, whereas Sn-free titanite does not fluoresce at all.

The hydrothermal synthesis of titanite, malayaite, and the intermediate compositions of the solid solution was conducted by Takenouchi [19] at temperatures from 400 to >600°C. The stability field of titanite turned out to be narrower than that of malayaite (Fig. 6). It is worth mentioning that the proportion of the stannian and titanian end members in the products of experiments at temperatures slightly higher than 615°C is 3 : 1 (Fig. 6, field *I*), whereas the series showed a miscibility gap in the experiments at 500°C and lower temperatures, and this led to the formation of either titanite with limited Sn concentrations or Ti-bearing varieties of malayaite (Fig. 6, field *II*). Ti and Sn isomorphism in these silicates became unlimited only at temperatures higher than 600°C, and the malayaite field expanded. Thereby no data were obtained on the role of Al and Fe in the synthesis of titanite.

The comparison of these data with materials on naturally occurring minerals led us to hypothesize that the absence of minerals containing from 35 to 75 mol % of the $CaSnO[SiO_4]$ end member at the examined deposits is not a coincidence (Fig. 7). These varieties could be formed only at high temperatures, whereas natural titanite and malayaite likely crystallize at temperatures below 400–500°C. This is consistent with the coexistence of both minerals in the skarns of the examined deposits (Tables 3–5) and the fact that these minerals were formed at these deposits at temperatures close to those of cassiterite crystallization, a mineral that was hydrothermally synthesized at 300°C [34].

In skarns with titanite and malayaite, cassiterite as an ore-forming mineral often occurs in several generations, which differ in the crystal habit of the often zonal crystals of this mineral, including its newly formed colloform aggregates (as at the Kitelya deposit in the

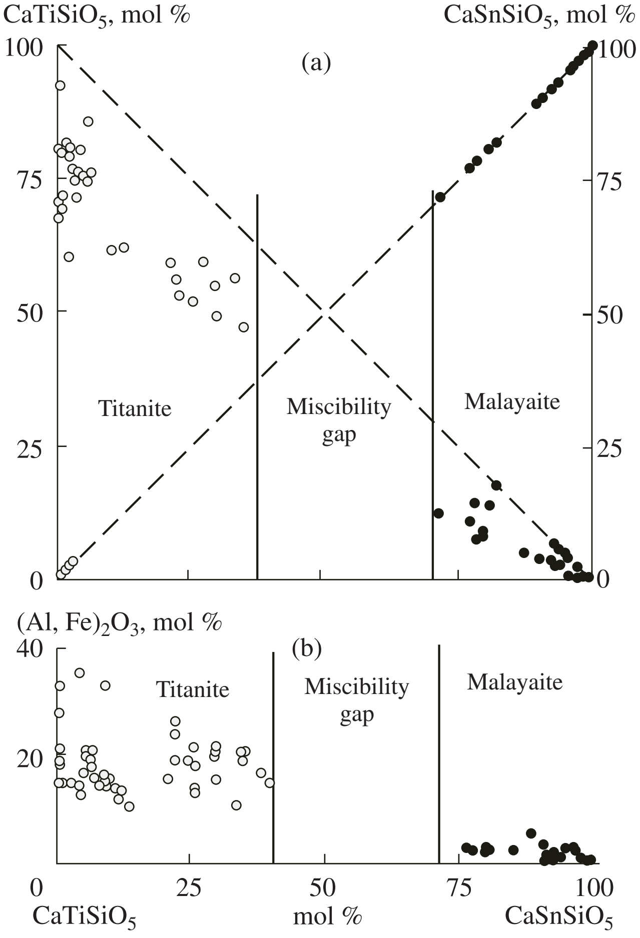

Fig. 7. Composition of minerals of the titanite–malayaite series: our and literature data.

(a) Composition of Sn-bearing titanite and high-Sn malayaite.

(b) Total molar Al and Fe concentrations in titanite and malayaite.

Ladoga area [35]) and quartz–calcite pseudomorphs with cassiterite after malayaite [9]. The development of cassiterite in greisenized skarns is related to the appearance of fluorite or, as a younger Sn-bearing mineral in Morocco, stokesite [17].

Iron, copper, and zinc sulfides are the youngest ore minerals at the deposits. At the Bol'shoi Kan'on deposit, in Morocco, and in Canada, these minerals are accompanied by stannite. Its supergene alterations can produce stannates (schoenfliesite, burtite, and others) and varlamoffite, a hydrated cassiterite variety.

The materials presented above characterize both the genesis and mineralogy of skarns and the evolution of the occurrence modes of Ti and Sn in these rocks in the course of the endogenic and supergene processes. This provided us with deeper insight into the genesis of tin deposits and to demonstrate the possibility of passing from isomorphic modes of Sn occurrence in rock-forming and ore minerals in skarns to the development of cassiterite and sulfide ore mineralization.

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