



## Geology

UDC 549.612:550.428: 553.45(572-62)

### TOURMALINE AS AN INDICATOR OF TIN OCCURRENCES OF CASSITERITE-QUARTZ AND CASSITERITE-SILICATE FORMATIONS (A CASE STUDY OF THE VERKHNEURMIYSKY ORE CLUSTER, FAR EAST)

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The research focused on the composition of tourmaline from tin ore deposits and ore occurrences within the Verkhneurmiysky ore cluster in the Amur region. The aim of the study is to determine the indicative signs of tourmaline from cassiterite-quartz and cassiterite-silicate formations. This research is based on the materials of a long-term study of the mineralogy of the Far East deposits, conducted at the Mining University under the scientific supervision of Professor Yu.B.Marin. The relevance of the study involves predicting of tin and associated mineralization. For the first time, SIMS and Mössbauer spectroscopy were used to study tourmaline from this region. We identified the typomorphic characteristics of the tourmaline composition, which are proposed to be used as indicators of tin-ore deposits. Typomorphic characteristics of tourmaline from cassiterite-quartz formation: schorl ( $Mg/(Mg + Fe) = 0.06$ ) with a high content of Al and K;  $Fe^{3+}/(Fe^{3+} + Fe^{2+}) = 0.03$ ;  ${}^2Fe^{3+} = 1\%$ ; impurities: Nb, LREE (La, Ce, Pr), Be, Bi, F, Li, and Mn; LREE content  $> 9$  ppm; positive Gd anomaly. Typomorphic characteristics of tourmaline from cassiterite-silicate formation: schorl-dravite ( $Mg/(Mg + Fe) = 0.22$ ) with a high Ca content;  $Fe^{3+}/(Fe^{3+} + Fe^{2+}) = 0.17$ ;  ${}^2Fe^{3+} = 9\%$ ; impurities: Zr, Y, Cr, V, Sn, In, Pb, W, Mo, Ti, HREE, Eu, Sr, Sb, and Sc; the content of Y is  $> 2$  ppm, of HREE is  $> 3$  ppm, Eu is  $> 0.1$  ppm. The formation conditions of the cassiterite-silicate ore mineralization were more oxidizing than those of the cassiterite-quartz one. Tourmaline, formed under oxidizing conditions, contains such impurities as Sn, In, Nb, Bi, Sc, and LREE. The content of Sn isomorphous impurity in tourmaline reaches 8000 ppm.

**Key words:** tourmaline; typomorphism; indicator; cassiterite-quartz formation; cassiterite-silicate formation; greisens; tourmalinites; Verkhneurmiysky ore cluster; Far East

**How to cite this article:** Alekseev V.I., Marin Yu.B. Tourmaline as an Indicator of Tin Occurrences of Cassiterite-quartz and Cassiterite-silicate Formations (a Case Study of the Verkhneurmiysky Ore Cluster, Far East). Journal of Mining Institute. 2019. Vol. 235, p. 3-9. DOI: 10.31897/PMI.2019.1.3

**Introduction.** The modern basis for the prediction and evaluation of mineral deposits is the identification of ore formations\* [6, 9]. A significant part of metallogenic research is the use of minerals indicator signs to determine the deposits formation type [6, 7, 16]. The article is devoted to the results of the tourmaline study in the framework of long-term research of the mineralogy of the Far East deposits, conducted at the Mining University under the scientific supervision of Professor Yu.B.Marin [1, 2, 8]. The aim of the study is to determine the indicative signs of tourmaline from cassiterite-quartz and cassiterite-silicate formations of Verkhneurmiysky ore cluster, Far East.

**Tourmaline is an indicative mineral of tin ore formations.** The deposits of cassiterite-quartz (CQF) and cassiterite-silicate (CSF) formations are of key industrial importance in the Russian sector of the Pacific ore belt. The geological objects belonging to the CQF are represented by greisen deposits, stockworks, and lenses associated with leucogranite complexes. The geological objects of the CSF are extensive steeply dipping veins and mineralized zones of tourmalinites and chloritites associated with gabbro-diorite-granite complexes [4, 6, 9]. The tin-ore occurrences of various formations are characterized by the presence of tourmaline, which is used as an indicator of the CQF and CSF mineralization [2, 3, 5, 7, 10, 16] (Table 1).

Verkhneurmiysky ore cluster (VUOC) located in the Amur River region is prospective area for tin and associated (W, Cu, Bi, Nb, and In) mineralization. The VUOC is localized within the Verkhneurmiyskiy granite pluton and the adjacent Urmiyskiy ignimbrite volcanogenic area [4, 8, 9]. In this area, there are three deposits (Pravourmiyskoe, Dvoinoeye, and Vysokoye) and tens of tin ore occurrences of CQF and CSF, composed by tourmaline-bearing greisens and tourmalinites. The combination of ore occurrences of different formations and the homogeneous composition of the

\*Ore formations are groups of ore deposits with stable mineral associations of similar composition, formed in a specific sequence in close geological conditions [6].



host strata make the VUOC a convenient area for the study of tourmaline as an indicative mineral of ore mineralization [1, 2, 5, 8].

Table 1

**Tourmaline as an indicator of tin deposits of cassiterite-quartz and cassiterite-silicate formations of Eurasia (according to [2, 3, 7, 14]) and the Verkhneurmisky ore cluster (Far East)**

Typomorphic characteristic	Tourmaline from Eurasia		Tourmaline from Verkhneurmisky ore cluster					
	Cassiterite-quartz formation (610)	Cassiterite-silicate formation (618)	Cassiterite-quartz formation			Cassiterite-silicate formation		
			P	V	Mean value (311)	Dv	D	Mean value (84)
Tourmaline type	Schorl, elbaite	Schorl-dravite	Schorl	Schorl	Schorl	Schorl-dravite	Schorl	Schorl-dravite
Al <sub>2</sub> O <sub>3</sub> , %	31.65	29.7	35.77	35.73	35.34	33.26	31.78	32.64
MgO	1.96	3.9	0.60	0.22	0.68	3.93	1.40	2.87
CaO	1.34	1.39	0.03	0.06	0.13	1.02	0.73	0.90
MnO	0.26	0.08	0.26	0.11	0.26	0.05	0.08	0.06
TiO <sub>2</sub>	0.41	0.72	0.16	0.21	0.26	0.70	0.33	0.55
F	0.77	0.14	0.18	0.13	0.15	0.15	0.06	0.11
Mg/(Mg + Fe)	0.32	0.35	0.06	0.02	0.06	0.30	0.11	0.22
<sup>Z</sup> Fe <sup>3+</sup>	20	30	0	0	1	8	11	9
K <sub>o</sub>	0.04	0.13	0.02	0.05	0.03	0.15	0.21	0.17
Sn, ppm	115	2397	246.1	281.3	445.3	520.6	2446.4	1261.3
W	65	4	0.3	0.4	0.7	1.9	0.9	1.6
Be	17	6	9.9	11.8	11.1	7.9	4.8	6.7
Sc	17	25	32.9	42.1	46.7	56.4	69.0	61.2
V	64	135	25.5	12.2	29.7	130.6	46.3	98.2
Zr	17	63	2.4	1.3	2.6	26.7	27.5	27.0
Pb	20	70	68.4	17.6	40.6	17.9	410.3	168.8
Li	295	6	41.5	21.1	36.7	32.1	22.3	28.4
Y	4	13	1.3	1.1	1.9	9.3	6.2	8.1
Nb	0	3	1.6	3.9	11.4	3.5	11.2	6.5
Sb	0	8	0.9	0.7	1.6	2.8	1.9	2.5
Bi	9	4	3.1	130.1	32.6	2.0	9.2	4.8
LREE	–	91.5	2.9	23.7	15.6	10.3	7.1	9.1
HREE	–	1.65	1.2	2.6	2.9	5.6	3.9	4.9

Note. The mean concentration values of the main components (wt%) and impurities (ppm) in tourmaline composition are given. The number of analyses is indicated in brackets. In the case of the Verkhneurmisky ore cluster, the indicative signs of tourmaline from reference deposits are given (P – Pravourmiyskoe, V – Vysokoe, Dv – Dvoynoye, D – Dozhdlivoe, Mean value are taken by region). <sup>Z</sup>Fe<sup>3+</sup> – the share of Fe<sup>3+</sup> in the Z-site, %; K<sub>o</sub> is the oxidation number of iron Fe<sup>3+</sup>/(Fe<sup>3+</sup>+Fe<sup>2+</sup>). A dash indicates no data.

**Tourmaline samples and analytical methods** The samples were collected by the authors during special geological mapping of the VUOC [1, 8]. Tourmaline was studied at 24 reference areas of Pravourmiyskoe and Vysokoye CQF deposits and Wolfram-Makit, Wolframitovoe, Alenushkino, and Leningradskoye CQF ore occurrences (96 samples); Dvoynoe CSF deposits and Dozhdlivoe and Orokot CSF ore occurrences (26 samples). Formation type of ore occurrences is defined by the criteria of prognostic estimations of territories on solid mineral deposits [6].

The study of the main components content and structure of tourmaline were carried out at the Center for Collective Use of the Saint-Petersburg Mining University under the JEOL JSM-7001F equipped with EDS (747 analyzes, analyzed by I.M.Gembitskaya) and a Shimadzu XRD-7000 X-ray diffractometer (13 analyzes, analyzed by V.G.Povarov), respectively. Operation conditions: an accel-



erating voltage of 20 keV, a sample current of 1 nA, a beam diameter of 3-5  $\mu\text{m}$ , a counting time of 35 s. The reflection radiography was performed under:  $\text{CuK}\alpha$  radiation, accelerating voltage of 40 kV, and current of 30 mA. Tourmaline structural formulae were calculated by normalizing to 6 Si atoms. For the distribution of  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  cations by octahedral positions, we used the technique based on comparing the sizes of Y- and Z-octahedra for different variants of sites occupancy [11].

The content and structural position of  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  in the tourmaline from VUOC were first studied using Mössbauer spectroscopy at the IPGG RAS (12 analyzes, analyzed by N.M.Korolev). Operation conditions: SM-1201 spectrometer,  $^{57}\text{Co}$   $\gamma$ -radiation source in Cr-matrix with an activity of 30 mCi, constant acceleration from  $-7$  to  $+7$  mm/s. Comparison of doublets in the spectra was carried out according to Andreozzi et al. [12]. The accuracy is  $\text{Fe}^{3+}/\Sigma\text{Fe} \pm 0.005-0.01$ .

The SIMS analysis of trace element composition of tourmaline from the VUOC was first performed on the Cameca IMS-4f ion microprobe at the Yaroslavl branch of the Institute of Physics and Technology, RAS (139 analyzes, analyzed by S.G.Simakin). Operation conditions:  $^{16}\text{O}_2^-$  ion beam diameter of  $\approx 20$   $\mu\text{m}$ , accelerating voltage of 15 keV, current of 5-7 nA. The REE-spectra are chondrite-normalized according to McDonough and Sun (1995).

**Tourmaline from Verkhneurmisky ore cluster.** The tourmaline group minerals have the following formula:  $\text{XY}_3\text{Z}_6[\text{T}_6\text{O}_{18}][\text{BO}_3]_3\text{V}_3\text{W}$ , where  $\text{X} = \text{Na}^{1+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^{1+}$ ,  $\square$  (vacancy);  $\text{Y} = \text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Li}^{1+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{V}^{3+}$ ;  $\text{Z} = \text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{V}^{3+}$ ;  $\text{T} = \text{Si}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{B}^{3+}$ ;  $\text{B} = \text{B}^{3+}$ ,  $\square$ ;  $\text{V} = \text{OH}^{1-}$ ,  $\text{O}^{2-}$ ;  $\text{W} = \text{OH}^{1-}$ ,  $\text{F}^{1-}$ ,  $\text{O}^{2-}$  [15]. The multivariate isomorphism and variations of the crystal structure order are typomorphic signs of tourmaline [7, 11, 14, 16]. Our results specify the ideas about the composition and formation conditions of tourmaline from Amur River region [2, 7, 8]. It was revealed that tourmaline from CQF and CSF of the studied area is characterized by a very high iron content:  $\text{Mg}/(\text{Mg} + \text{Fe})$  varies in the limits of 0.0-0.36 and 0.01-0.56, respectively (Table 1). Schorl with a high content of Al and Mn is specific to greisens and veins of CQF, while CSF ores are characterized by schorl-dravite with Ti and Ca impurities (Table 2, Figure 1, a). Both belong to the alkaline group according to Henry et al. [15], but X-sites in schorl and schorl-dravite are enriched in potassium (0.08 apfu) and calcium (0.34 apfu) (Wolframitovoe and Dvoinoe, respectively).

The Mössbauer spectra of the tourmaline from VUOC show quadrupole doublets reflecting the distortion of Y and Z coordination polyhedra and indicating the inequivalent positions of the iron cations in the crystal structure [7, 12]. According to the X-ray data,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  occupy Y- and Z-sites, which confirms that it is precisely schorl in greisens mineral composition (Table 2, Fig.1, b). Schorl has X-site vacancies (0.3 apfu) and is close to foitite [15]. Schorl-dravite from tourmalinites, according to the distribution of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations, have the features of buergerite and «ferric iron tourmaline» [7]; pursuant to modern classification, it is similar to povondraite [13, 15]. The share of  $\text{Fe}^{3+}$  cations in Z-site is 1 and 9 % in tourmaline from CQF and CSF, respectively. An important new result is the determination of the iron oxidation number in tourmaline from VUOC, which is 0.02-0.10 in greisens of CQF, and 0.18-0.27 in tourmalinites from CSF (Table 1).

Table 2

The occupancy of the octahedral Y- and Z-sites in the structure of tourmaline from tin ore occurrences of the Verkhneurmisky ore cluster (Far East)

Object	Y-site	Z-site
<i>Cassiterite-quartz formation</i>		
Pravourmiyskoe (134)	$\text{Fe}^{2+}_{2.22}\text{Al}_{0.26}\text{Mg}_{0.12}\text{Fe}^{3+}_{0.03}\text{Mn}_{0.03}\text{Ti}_{0.02}\square_{0.31}$	$\text{Al}_{5.98}\text{Fe}^{2+}_{0.01}\text{Fe}^{3+}_{0.00}\text{Mg}_{0.01}$
Vysokoye (26)	$\text{Fe}^{2+}_{2.32}\text{Al}_{0.26}\text{Mg}_{0.05}\text{Fe}^{3+}_{0.11}\text{Mn}_{0.01}\text{Ti}_{0.02}\square_{0.23}$	$\text{Al}_{5.94}\text{Fe}^{2+}_{0.02}\text{Fe}^{3+}_{0.01}\text{Mg}_{0.00}$
VUOC (311)	$\text{Fe}^{2+}_{2.25}\text{Al}_{0.23}\text{Mg}_{0.13}\text{Fe}^{3+}_{0.05}\text{Mn}_{0.03}\text{Ti}_{0.03}\square_{0.27}$	$\text{Al}_{5.94}\text{Fe}^{2+}_{0.03}\text{Fe}^{3+}_{0.02}\text{Mg}_{0.01}$
<i>Cassiterite-silicate formation</i>		
Dvoinoe (49)	$\text{Fe}^{2+}_{1.63}\text{Mg}_{0.71}\text{Fe}^{3+}_{0.14}\text{Al}_{0.09}\text{Ti}_{0.08}\text{Mn}_{0.01}\square_{0.35}$	$\text{Al}_{5.71}\text{Fe}^{3+}_{0.15}\text{Mg}_{0.14}\text{Fe}^{2+}_{0.00}$
Dozhdlivoe (35)	$\text{Fe}^{2+}_{2.16}\text{Mg}_{0.26}\text{Fe}^{3+}_{0.22}\text{Al}_{0.07}\text{Ti}_{0.04}\text{Mn}_{0.01}\square_{0.23}$	$\text{Al}_{5.54}\text{Fe}^{3+}_{0.35}\text{Mg}_{0.06}\text{Fe}^{2+}_{0.05}$
VUOC (84)	$\text{Fe}^{2+}_{1.85}\text{Mg}_{0.52}\text{Fe}^{3+}_{0.17}\text{Al}_{0.09}\text{Ti}_{0.06}\text{Mn}_{0.03}\square_{0.30}$	$\text{Al}_{5.64}\text{Fe}^{3+}_{0.23}\text{Mg}_{0.11}\text{Fe}^{2+}_{0.02}$

Note. VUOC - tourmaline from Verkhneurmisky ore cluster The number of analyses is indicated in brackets.

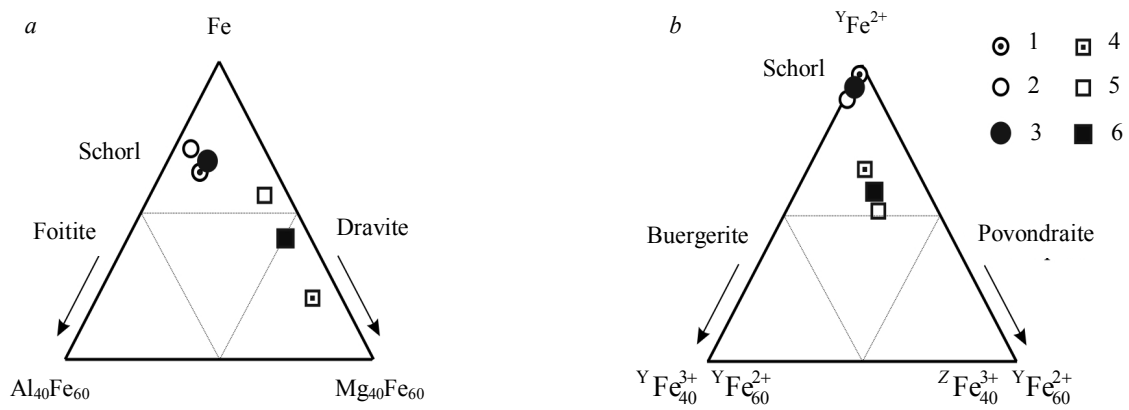


Fig.1. The occupation of the Y-site by the tourmaline main components (a) and the balance of iron cations in the crystal structure of tourmaline (b) from tin ore occurrences of the Verkhneurmisky ore cluster

1-3 – the average composition of tourmaline from cassiterite-quartz formation: 1 – Pravourmiyskoe (134 analyses), 2 – Vysokoe (26 analyses), 3 – Verkhneurmisky ore cluster in whole (310 analyses.); 4-6 – the average composition of tourmaline from cassiterite-silicate formation: 4 – Dvoinoe (49 analyses), 5 – Dozhdliivoe (35 analyses), 6 – Verkhneurmisky ore cluster in whole (84 analyses)

Numerous tourmaline studies show that the host formation can be determined by the content of such trace elements as Sn, Ni, V, Zr, Pb, Zn, Cu, Sc, V, Li, Be, Sr, Cr, Ni, and Ga [2, 3, 7, 11, 14, 16]. Our data confirm that listed impurities are indicative. Tourmaline from greisens and tourmalinites of VUOC differ in the content of Zr, Bi, Ca, and Y (more than 4-fold); Cr, V, K, Sn, In, W, Pr, Dy, Er, Mo, and Mn (more than 2-fold); Ti, Nb, HREE, LREE, Be, Sr, Sb, F, Sc, and Li (more than 1.3-fold). Schorl of CQF contains predominantly lithophile rare elements: Nb, LREE (La, Ce, Pr), Be, F, and Li. Tourmaline of CSF is the main mineral concentrating most of the rare elements in tin ores: Zr, Y, Ca, Cr, V, Sn, In, Pb, W, Mo, Ti, HREE, Eu, Sr, Sb, and Sc (Table 1).

SIMS data were analyzed by the principal component analysis. Due to the strong correlation between trace elements the interpretation of first two factors is reasonable. Analysis of the factor loadings plot allows us to reveal two groups. The first group tourmaline from CQF greisens and veins (positive values of Factor 1) is enriched in Mn, F, and Li. The second group tourmaline from CSF tourmalinites and veins (negative values of Factor 1) is characterized by the association of Y, HREE, Zr, W, Ca, Cr, V, Ti, and Sn (Fig.2). Thus, the first factor shows the statistical difference in tourmaline of the studied formations, which occurs due to the

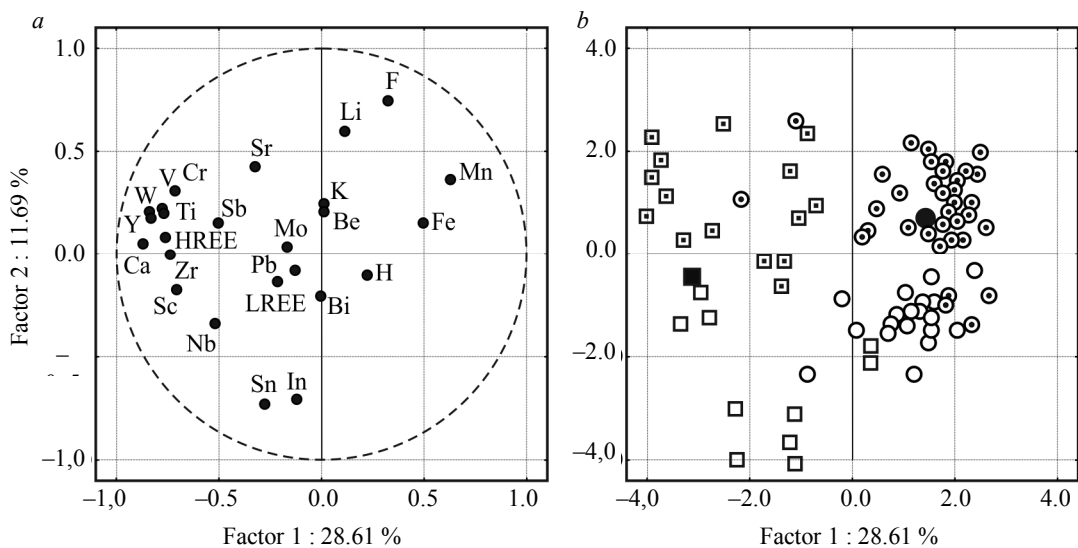


Fig.2. Typomorphic associations of trace elements in tourmaline from tin ore occurrences of the Verkhneurmisky ore cluster on factor loadings plots (a) and eigenvalues of the first and second factors (b)

Legend, see fig.1. Based on 139 SIMS analyses. The threshold value of the loading of trace elements content on the factors is 0.167 (significance value is 0.05). The axes indicate the factors share in the total variance

chemical composition of the mineral-forming fluids and the crystal-chemical features of schorl from greisens and the schorl-dravite from tourmalinites. The second factor reveals the differences in tourmaline from different ore occurrences. Positive values of Factor 2 are characteristic of tourmaline from sublateral ore-bearing structures (Pravourmiyskoe, Dvoinoe, Alenushkino, Sulfidnoe, and Wolfram-Makit) with typomorphic association of trace elements F–Li–Sr–Mn–Cr–V. Negative values of Factor 2 are observed in the tourmaline from submeridional zones (Dozhdlivoe, Vysokoye, and Wolframitovoe) with association of trace elements Sn–In–Nb–Bi–Sc–LREE (Fig.2). This factor, apparently, characterizes the redox conditions of ore formation, since the highest values of iron oxidation number are characteristic of tourmaline from submeridional ore bodies, regardless of their formational identity (Table 1).

An electron microscopic study of tourmaline with a high tin content was carried out with a resolution of 6 nm. In more than ten tourmaline crystals with Sn content of 900-7000 ppm, no inclusions of tin-bearing minerals were detected. The impurities of cassiterite, stannoidite, and tin-bearing titanite with a size of 3-130  $\mu\text{m}$  were found in crystals of tourmaline from CQF (Pravourmiyskoe, Sulfidnoe) and CSF (Dvoinoe). Electron and ion microprobe analysis of tourmaline in areas free from inclusions in some cases showed a low Sn content of  $\approx 100$ -150 ppm, and in others  $\approx 500$ -1000 ppm, up to the maximum value of 8049.88 ppm.

There is not enough published data to make reasonable conclusions about the REE content in tourmaline. Some researchers suggest the dependence of the REE concentration in tourmaline on the crystallization temperature, the composition of the host rocks and mineral inclusions, as well as pH and Eh of source solutions. According to published data, the total REE content in tourmaline from greisens is 0.28-5.24 ppm, while hydrothermal tourmaline contains 0.35-119.00 ppm of REE [10]. Other authors provide information on 10-23 ppm of REE in tourmaline [5]. Hydrothermal schorl-dravite is characterized as an REE concentrator (18.9-85.8 ppm) with minimum MREE content and a variable Eu-anomaly [14, 16].

We have studied REE distribution in tourmaline from VUOC using SIMS analysis. REE demonstrate uneven concentration: tourmaline from CQF concentrate LREE, ppm: La 3.55, Ce 7.87, Pr 0.82, Nd 2.78, and Sm 0.45; while tourmaline from CSF is relatively enriched in HREE, Y, and Eu, ppm: Y 8.11, Gd 0.54, Dy 0.95, Er 1.18, Yb 1.94, Lu 0.29, and Eu 0.20 (see table 1). At the same time, tourmaline of different genesis shows a similar accumulation of HREE and LREE, reflected in the U-shaped REE spectra. CQF schorl differs from CSF schorl-dravite in a steeper downward La-Sm trend ( $\text{Sm}_N/\text{La}_N$  values are 0.2 and 0.4, respectively) and a flatter Gd-Lu trend ( $\text{Lu}_N/\text{Gd}_N$  values are 4.4 and 2.4, respectively) (Fig.3).

The difference in the REE spectra of the tourmaline under study is also in the Eu-anomaly: which is negative in schorl from greisens and positive in hydrothermal schorl-dravite ( $\text{Eu}/\text{Eu}^* = 0.7$  and 1.3). The paradox is that schorl-dravite formed under oxidizing conditions should be depleted in Eu due to the loss of its protoxide form. In contrast to this, tourmaline under study is characterized by Ce-step and positive Eu-anomaly, previously described in tourmaline from the Amur River region [5, 10]. However, variations in the Eu content and  $\text{Eu}/\text{Eu}^*$  values are occasional: tourmalines from CQF show not only with negative but also positive Eu-anomaly (Wolfram-Makit, Sulfidnoe). Schorl from greisen is characterized by a low content of HREE accompanied by positive Gd-anomaly:  $\text{Gd}/\text{Gd}^*$  ratio is 1.6 and 0.7 in schorl from greisen and schorl-dravite from tourmalinite, respectively (Fig.3).

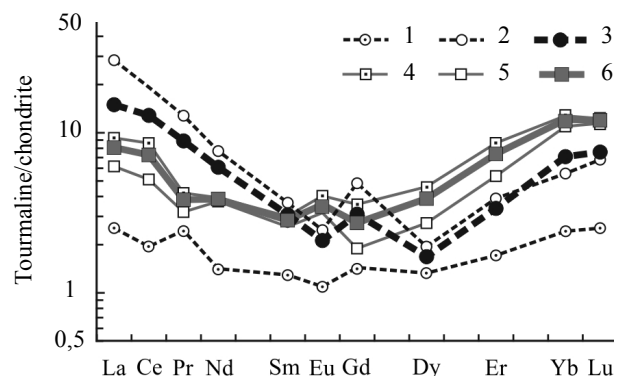


Fig.3. REE spectra in tourmaline from tin ore occurrences of Verkhneurmisky ore cluster

1-3 – the average composition of tourmaline from cassiterite-quartz formation: 1 – Pravourmiyskoe (47 analyses); 2 – Vysokoe (15 analyses); 3 – Verkhneurmisky ore cluster in whole (113 analyses.); 4-6 – the average composition of tourmaline from cassiterite-silicate formation: 4 – Dvoinoe (16 analyses); 5 – Dozhdlivoe (10 analyses); 6 – Verkhneurmisky ore cluster in whole (26 analyses)

**Discussion.** The obtained results confirm and complement the concept of tourmaline features from tin-ore rocks [2, 7, 11, 14]. Tourmaline from VUOC is schorl-dravite. Schorl from CQF is distinguished by its high iron content, weak iron oxidation ( $K_o = 0.03$ ), the following type of isomorphic substitution,  ${}^Y\text{Al}^{3+} + {}^W\text{O}^{2-}(\square) \leftrightarrow {}^Y(\text{Fe}^{2+}) + {}^W\text{OH}^-$ , high content of Al, Mn, and, sometimes, K. Schorl-dravite from CSF is characterized by the strong oxidation of iron ( $K_o = 0.17$ ) and the presence of Ti and Ca. Typical isomorphic substitution in schorl-dravite is:  ${}^Y\text{Mg}^{2+} \leftrightarrow {}^Y\text{Fe}^{2+}$ ;  ${}^Z\text{Al}^{3+} \leftrightarrow {}^Z\text{Fe}^{3+}$ ;  $\text{K}^+ \leftrightarrow \text{Ca}^{2+} + \square$  (Table 1, 2). An important tourmaline feature is the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio and iron distribution in the crystal lattice. It was revealed that oxidation of iron in the tourmaline of CSF ore occurrences is noticeably higher than in greisen ones (Table 1). Consequently, hydrothermal ore formation in tourmalinites occurred under more oxidative conditions than in greisens. This is reflected in the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  occupation of Y- and Z-sites in CSF tourmaline (Fig.2), which is indicative to the «ferric iron tourmaline» [7] or povondraite [13, 15].

The trace element composition in tourmaline from VUOC is similar to that of other tin ore areas. However, new regional typomorphic features of tourmaline have been identified and can be used as indicators of tin-ore formations. Tourmaline of CQF concentrates some rare metals (Nb, LREE, Be, and Li), as well as Bi, Mn, K, and F. The revealed correlation of hydroxyl hydrogen with iron confirms that it is schorl (Fig.2). The group of typomorphic elements of the CQF schorl includes (in order of importance): Nb, LREE (La, Ce, Pr), Be, Bi, F, Li, Mn, K, Al, and Fe. The concentration of the majority of tin ore trace elements in the CSF schorl-dravite of VUOC should be considered as its typomorphic feature. The group of typomorphic elements of CSF tourmaline is geochemically inhomogeneous, but in the studied area it is shown steadily: Zr, Y, Ca, Cr, V, Sn, In, Pb, W, Mo, Ti, HREE, Eu, Sr, Sb, Sc, and Mg. Let's also note the accumulation of tungsten and rare metals in schorl-dravite, excluding Li, Be and LREE (Table 1, Fig.2).

The principal components analysis showed that the tourmaline of the submeridional ore zones formed under oxidative conditions, regardless of its formation, is characterized by increased concentrations of tin and rare metals (In, Nb, Bi, Sc, and LREE). Such tourmaline has a geological exploration value, as it is associated with the CSF ore occurrences with the highest tin concentrations. Studies by local methods have shown that tourmaline with a high tin content does not contain inclusions of tin-bearing minerals and, conversely, there are low tin concentrations in tourmaline saturated with cassiterite inclusions. The obtained data allow us to dispose of the assumption of a low tin accumulation limits in tourmaline:  $\approx 250$  ppm [2, 7]. Probably, the content of isomorphic tin impurity in tourmaline can reach  $\approx 8000$  ppm.

The presence of LREE in tourmaline is, apparently, its common feature in the tin provinces. There is a decrease in the LREE content in tourmaline along with the transition from greisens to hydrothermal veins. The variations in Eu content in tourmaline are occasional and cannot serve as indicative signs [5, 10, 14, 16]. High content of LREE ( $> 9$  ppm) and a positive Gd-anomaly are characteristic of the CQF schorl. Increased content of Y ( $> 2$  ppm), HREE ( $> 3$  ppm), Eu ( $> 0.1$  ppm) are indicative of schorl-dravite from CSF (Table 1, Fig.3). This feature of hydrothermal tourmaline can be explained by the presence of HREE-bearing mineral inclusions [5, 14] or the presence of REE fluoride complexes in mother solutions [16]. The results of a local tourmaline study and correlation between HREE and isomorphic impurities (Fig.2) indicate the enrichment of tin-bearing solutions with HREE associated with rare metals (Y, Zr, In, Eu, Sr, and Sc).

The described features of the tourmaline from tin ore occurrences of a VUOC are confirmed by the prospecting works in the ore regions of the Far East and can serve as criteria for distinguishing CQF and CSF ore objects.

## Conclusions

1. Tourmaline from tin ore occurrences of the Verkhneurmisky ore cluster is characterized by typomorphic features of cassiterite-quartz and cassiterite-silicate formations.

2. Signs of tourmaline from cassiterite-quartz formation: schorl ( $\text{Mg}/(\text{Mg} + \text{Fe}) = 0.06$ ) with a high content of Al and K;  $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+}) = 0.03$ ;  ${}^Z\text{Fe}^{3+} = 1\%$ ; typomorphic impurities: Nb,



LREE (La, Ce, Pr), Be, Bi, F, Li, and Mn; LREE content is >9 ppm; positive Gd-anomaly; tourmaline from cassiterite-silicate formation: schorl-dravite ( $Mg/(Mg + Fe) = 0.22$ ) with a high Ca content;  $Fe^{3+}/(Fe^{3+} + Fe^{2+}) = 0.17$ ;  ${}^ZFe^{3+} = 9\%$ ; typomorphic impurities: Zr, Y, Cr, V, Sn, In, Pb, W, Mo, Ti, HREE, Eu, Sr, Sb, and Sc; Y content is >2 ppm, HREE is >3 ppm, Eu > 0.1 ppm.

3. Ore occurrences of cassiterite-silicate formation were formed under more oxidative conditions than cassiterite-quartz one, and contain tourmaline with such trace elements, as Sn, In, Nb, Bi, Sc, and LREE; the content of tin isomorphous impurity in tourmaline reaches  $\approx 8000$  ppm.

**Acknowledgments.** *The work was carried out within the framework of the State Program of the Ministry of Education and Science of the Russian Federation in the field of scientific activities № 5.9248.2017/6.7, 2017-2019. We are grateful to I.M.Gembitskaya AND V.G.POVAROV (Saint-Petersburg Mining University, Saint-Petersburg), N.M.Korolev (IPGG RAS, Saint-Petersburg), S.G.Simakin (Institute of Physics and Technology, RAS, Yaroslavl) for the analytical studies.*

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The paper was received on 4 September, 2018.

The paper was accepted for publication on 27 September, 2018.