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Accessory Cassiterite as an Indicator of Rare Metal Petrogenesis and Mineralization

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Abstract—This paper is a scientific overview of studies of accessory cassiterite from rare metal granites, pegmatites, and accompanying greisens in 1990–2021. The earlier and newest data on the morphology, physical and chemical features of accessory cassiterite, and its economic facility are summarized. The consolidated database includes 1759 cassiterite compositions from more than 100 publications. We have confirmed previous and identified new indicator features of cassiterite from rare metal granites, pegmatites, and greisens: concentrations of isomorphous components (Ta, Nb, Fe, Ti, Mn, W, Sc, In, Zr, Hf, U), informative ratios (Nb/Ta, Zr/Hf, Fe/Mn), and main substitution schemes (“tapiolite” and “hydrothermal”). The average trace element content in cassiterite from granites, pegmatites, and greisens is 6.68, 4.87, and 1.18 wt %, respectively. Based on the published data, the solubility limit of tapiolite (Fe,Mn)(Ta,Nb)₂O₆ in the structure of cassiterite is calculated. These limit is 0.1–11, 0.7–12.8, and 0.1–3.3% in granites, pegmatites, and greisens, respectively. The tapiolite endmember proportion in cassiterite ranges from 0.1 to 12.8%. It is noted that tantalum-bearing cassiterite is predominantly observed in Li–F plumasite granites and LCT lepidolite pegmatites with the high phosphorus concentration over the range of 0.12–2.50 wt % P₂O₅. The Ta₂O₅ content in accessory cassiterite reaches 17.9–18.4 wt % and promises additional economic prospects for rare metal pegmatites and granites. Cassiterite can be used as an alternative source of tantalum, indium, niobium, and scandium. Typical occurrences of accessory cassiterite have been identified in granites of the Beauvoir massif (France), in pegmatites of the Peerless (USA) and Varuträsk (Sweden) deposits, and in greisens of the Kester and Polyarnoe deposits (Yakutia). Accessory cassiterite is an advanced mineral geochronometer for rare metal granites and pegmatites, since it is not susceptible to radiation damage and disruption of the U–Pb isotope system.

Keywords: cassiterite, typomorphism, typochemistry, plumasite rare metal granite, rare metal pegmatite, greisen, rare metal deposits, petrogenesis, ore genesis, tantalum, isomorphism

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INTRODUCTION

Cassiterite has been known for more than 3000 years; as a major source of tin, it was one of the material foundations for the early development of human civilization. Scientific interest in this mineral has remained and intensified over the last 100 years. Cassiterite is stable in many environments, from granite and granite pegmatites to medium- and low-temperature greisen and other hydrothermal alterations. The simple composition and structure of the mineral conceal many physical and chemical features that make it an effective indicator of granite petrogenesis and economic deposits (Maksimiyuk and Voronina, 1989).

With the advent of high technology, cassiterite is becoming increasingly important as an economic source of rare metals, tantalum and indium (Nikishina and Drobot, 2014; Gaskov et al., 2017; Alfonso et al., 2020). Increasing recovery of high-tech metals from

cassiterite is equivalent to the discovery and production of new deposits (Sidorenko et al., 1992). It can be added that cassiterite from pegmatites and greisens is a popular collection and unconventional gemstone that increases the profitability of tin and rare metal deposits (Petrochenkov, 2018).

The interest in cassiterite as an informative mineral of petrogenesis and a rare element concentrator resulted in the scientific reviews in 1960s–1980s that systematized information about cassiterite of various genetic types (*Minerals* ..., 1965; Deer et al., 1962; Kuzmenko and Eskova, 1968; Dolomanova et al., 1969, 1975; Maksimiyuk, 1973; *Deposits* ..., 1980; Evzikova, 1984; Nekrasov, 1984; Möller et al., 1983, 1988; Ivanov et al., 1989; Maksimiyuk and Voronina, 1989). According to the Web of Science database, 1844 papers concerning the study and practical use of cassiterite have been published since 1990: 346 in 1990–

2000 and 1498 in 2001–2021. In this information stream, we have identified 432 publications with important data on accessory cassiterite¹ from rare-metal granites, pegmatites, and greisens. However, information about accessory cassiterite has not been reviewed since 1989.

The aim of this study is a modern scientific overview of the indicator features of cassiterite from rare-metal granites, pegmatites, and accompanying minerals, and estimating its capacity as a rock- and ore-forming process, as well as an economic source of rare metals. This overview covers period from 1990 to present.

MODERN STUDIES OF ACCESSORY CASSITERITE

Accessory cassiterite was identified in granites in the 1920s during prospecting for sources of tin placers in Nigeria and Malaysia (Falconer, 1921; Scrivenor, 1928). One of the areas was the Jos Plateau in Nigeria (Jacobson, 1945; Rushton, 1956; Williams et al., 1956; Maksimuk, 1973; Möller et al., 1988). Up to the 1970s, cassiterite from granites, pegmatites, and hydrothermal deposits was studied as an economic source of tin. A crisis in tantalum production in the 1970s forced the search for new sources of raw materials and spurred interest in magmatic cassiterite as a source of the high-tech metals.

Tin slags and metallurgical products of cassiterite from rare metal granites and pegmatites are increasingly used in the tantalum production worldwide (*Rare metal ...*, 1997; Nikishina and Drobot, 2014; Alfonso et al., 2020; Nambaje et al., 2020). Rare metal Li–F granites with associated Sn–Ta deposits are one of the most productive types of cassiterite-bearing rocks (*Atlas ...*, 1977; Nekrasov, 1984; Solodov et al., 1987). Pegmatites form high-grade complex deposits and most of tantalum in the world is recovered from tantalite, microlite, wodginite, and cassiterite from deposits related to rare metal granites and pegmatites (*Deposits ...*, 1980; Solodov et al., 1987). In Russia, economic tantalum-rich cassiterite was not discussed in the recent decade, although it was mentioned at the Etyka deposit in Transbaikalian Region and the Polyarnoe deposit in Yakutia (Kuzmenko and Eskova, 1968; Flerov, 1976; *Atlas ...*, 1977; Solodov et al., 1987). Cassiterite is also additional source of indium and probable source of scandium (Botelho and Moura, 1998; Briskey, 2005; Sinclair et al., 2006; Gaskov et al., 2017; Alekseev et al., 2019; Hu et al., 2021).

Accessory cassiterite is observed in non-rare metal tin-bearing leucogranites, and crystal and mica pegmatites, but it is especially relevant to lithium–fluorine granites, rare metal pegmatites, and accompanying ongonites and rare metal greisens in the Eastern Russia, Australia, Algeria, Angola, Argentina, Brazil,

Great Britain, Vietnam, Germany, Egypt, India, Spain, Canada, Kazakhstan, Kyrgyzstan, China, Malaysia, Morocco, Namibia, Nigeria, New Zealand, Portugal, Rwanda, Slovakia, USA, Thailand, Finland, France, Czechia, and other countries (Gotman, 1941; Boldyreva, 1941; Williams et al., 1956; Weibel, 1956; Lyakhovich, 1967; Burke et al., 1969; Kuzmenko and Eskova, 1968; Barsanov and Kuznetsov, 1971; *Atlas ...*, 1977; Beskin et al., 1979; Nekrasov, 1984; Černý and Ercit, 1985; Černý et al., 1986; Ollila, 1986; Solodov et al., 1987; Ixer et al., 1987; Wang et al., 1987; Möller et al., 1988; Cuney et al., 1992; Spilde and Shearer, 1992; Abella et al., 1995; Černý and Nemec, 1995; Suwimonprecha et al., 1995; Trumbull, 1995; Neiva, 1996; Haapala, 1997; Murciego et al., 1997; Botelho and Moura, 1998; Raimbault, 1998; Raimbault and Burnol, 1998; Roda-Robles et al., 1999; Costi et al., 2000; Masau et al., 2000; Huang et al., 2002; Kesraoui and Nedjari, 2002; Sosa et al., 2002; Groat et al., 2003; Černý et al., 2004; Saleh et al., 2008; Pal et al., 2007; Rao et al., 2009; Klomínský et al., 2010; Martins et al., 2011; Wise and Brown, 2011; Canosa et al., 2012; Llorens and Moro, 2012; Antunes et al., 2013; Pieczka et al., 2013; Nikishina and Drobot, 2014; Gaafar, 2014; Chicharro et al., 2015; Huang et al., 2015; Xie et al., 2015, 2018, 2019; Beskin and Marin, 2015; Zhu et al., 2015; Yan et al., 2016; Breiter et al., 2017; Fernandes and Moura, 2017; Hien-Dinh et al., 2017; Lerouge et al., 2017; Llorens et al., 2017; Zhang et al., 2017; Lerouge et al., 2017; Lopez-Moro et al., 2017; Simons et al., 2017; Singh et al., 2017; Alfonso et al., 2018; Broska and Kubis, 2018; Neymark et al., 2018; Fuchsloch et al., 2018; René, 2018; Cheng et al., 2019; Feng et al., 2019; Gonçalves et al., 2019; Neiva et al., 2019; Alekseev et al., 2020; Kigai, 2020; Alfonso et al., 2020; Barros Neto et al., 2020; Carr et al., 2020; Garate-Olave et al., 2020; Kendall-Langley et al., 2020; Liu et al., 2020a; Michaud et al., 2020; Soloviev et al., 2020; Hu et al., 2021; Lv et al., 2021). By the beginning of the review period, Ta-bearing cassiterite from rare metal pegmatites and granites firmly entered the list of the major economic minerals (Kuzmenko and Eskova, 1968; *Atlas ...*, 1977; Solodov et al., 1987; Nikishina and Drobot, 2014) and had acquired the status of an indicative mineral for rare metal petro- and ore genesis. Three main directions of cassiterite research development can be identified: constitutional (morphology, structure, and composition), genetic (formation conditions and indicator features), and topomineralogical (mineral variations in various rocks, deposits, regions, and environments). This paper is written in the line with the first two directions. Cassiterite from greisens genetically related to rare metal granites and pegmatites is also studied along with accessory cassiterite. Successes in genetic study of cassiterite rely heavily on experimental methods in mineralogy and physicochemical petrology. Physicochemical conditions of cassiterite crystallization in natural environments were

¹ Accessory cassiterite is formed during crystallization of host granites, pegmatites, or greisens.

studied (Quensel, 1941; Michel-Levy and Wyart, 1947; Kuzmina and Litvin, 1963; Fujiki and Suzuki, 1973; Zhilinsky et al., 1981; Nekrasov, 1984; Liu et al., 2020b). Trapping temperature of melt and fluid inclusions in cassiterite was estimated: 220–430°C in greisens, 300–620°C in pegmatites, and 450–570°C in granites (Little, 1960; Dolomanova et al., 1969; Giuliani, 1987; Kholmogorov, 1989; Tsareva et al., 1993; Trumbull, 1995; Borisova et al., 2012; Nambaje et al., 2020; Soloviev et al., 2020; Zhang et al., 2020). Experimental temperature of cassiterite crystallization is 400–850°C under pressure of 300–850 MPa (Michel-Lévy and Wyart, 1947; Liu et al., 2020b). According to the data of synthetic cassiterite, the fluid phase is required for mineral precipitating from the melt (Zhilinsky et al., 1981).

The high SnO₂ solubility in granite melts was experimentally established (>1000 ppm under reductive conditions at 700–800°C) and it was concluded that cassiterite could crystallize only from the K, Na, Al-rich rare metal granite melts during their oxidation (Nekrasov, 1984; Ryabchikov et al., 1984; Kholmogorov, 1989; Štemprok, 1990; Taylor and Wall, 1992; Linnen et al., 1996; Bhalla et al., 2005; Yang et al., 2016; Singh et al., 2017; Yao et al., 2018). The three-stage model of cassiterite formation was suggested: crystallization in silicate melt through metasomatic transformation under effect by aqueous–salt melt to hydrothermal precipitation (Borisova et al., 2012; Kaeter et al., 2021).

Topomineralogical observations show that variations in the cassiterite composition from magmatic bodies are governed by the fractionation crystallization (Huang et al., 2002; Martins et al., 2011; Lopez-Moro et al., 2017; Singh et al., 2017; Cheng et al., 2019; Feng et al., 2019). Tin is partitioned between cassiterite and syngentic minerals, biotite, titanite, ilmenite, and potassium feldspars. Melt temperature decreasing and water content increasing in the melt result in increased tin diffusion rate and decreased tin concentration (Ryabchikov et al., 1984; Yang et al., 2016). The important role of fluorine that increases cassiterite solubility in rare-metal magma has been noted. Tin forming fluoride SnF₄ is precipitated with the *f*(H₂O) increasing during magma ascending from deep chambers and decompression boiling: $\text{SnF}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{SnO}_2 + 4\text{HF}$. Probable crystallization of cassiterite immediately from the residual melt in the tin-bearing rare metal granites was shown by experiments (Zhilinsky et al., 1981; Nekrasov, 1984; Kholmogorov, 1989; Spilde and Shearer, 1992; Haapala, 1997; Raimbault and Burnol, 1998; Roda-Robles et al., 1999; Černý et al., 2004; Pal et al., 2007; Martins et al., 2011; Llorens and Moro, 2012; Xie et al., 2015; Zhu et al., 2015; Llorens et al., 2017; Simons et al., 2017; Kigai, 2020; Garate-Olave et al., 2020; Nambaje et al., 2020; Soloviev et al., 2020).

In recent decades, cassiterite from pegmatites and greisens is studied using cathodoluminescence, which reveals anatomy of the crystals, microdefects, and distribution of trace elements (Maksimiyuk et al., 1982; Farmer et al., 1991; Wight et al., 2010; Zhang et al., 2017; Wille et al., 2018; Cheng et al., 2019; Nambaje et al., 2020; Hu et al., 2021; Kaeter et al., 2021). The use of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) resulted in a new direction that is U–Pb dating of the mineral and the processes of rare metal–tin petro- and ore genesis (Gulson and Jones, 1992; Liu et al., 2007; Li et al., 2016; Zhang et al., 2017; Neymark et al., 2018; Deng et al., 2018; Rizvanova and Kuznetsov, 2020; Carr et al., 2020). Isotopic study of accessory cassiterite in the granites of the Yazov Pluton in Transbaikalian Region revealed cassiterite inheritance from the ancient protolith (Neymark et al., 2021).

MATERIALS

The information and conclusions given in this paper are based on a review of published scientific articles on cassiterite from rare metal deposits. The Russian Science Citation Index, All-Russian Institute for Scientific and Technical Information Russian Academy of Sciences, Web of Science, and Scopus abstract databases, and author data on rare metal–tin deposits in the Russian Far East were used.

A consolidated database of the chemical composition and physical properties of accessory cassiterite from rare metal granites, pegmatites and greisens has been established based on a review of all world publications in 1990–2021. The summary also includes the earlier overviews and selected articles on accessory cassiterite from 1931 to 1989. The consolidated database contains 442 compositions (28 references) of cassiterite from rare metal plumasite granites (GC); 501 compositions (41 references) of cassiterite from rare metal pegmatites (PC); and 816 compositions (31 references) of cassiterite from greisens accompanying rare metal granites and pegmatites (GrC). A total of 1759 compositions primarily measured with electron microprobe were used. The LA-ICP-MS data are given in 14 references of 2016–2021 and TIMS data are published in 7 references (Tables 1–3). It should be noted that the actual number of compositions forming the basis of the review is ten times higher than that number because most publications used only 2 to 9 representative analyses from analytical arrays containing 30–220 samples.

INDICATOR FEATURES OF ACCESSORY CASSITERITE

Cassiterite is a prime example of indicator mineral whose shape, composition, and physical properties reflect its origin. It was established from high- to low-temperature generations: changes in crystal habit and

Table 1. Chemical composition (wt %) of cassiterite from rare metal granites

No	Deposit	N	SnO ₂	Ta ₂ O ₅	Nb ₂ O ₅	FeO ⁺	TiO ₂	MnO	WO ₃	ZrO ₂	HfO ₂	Reference
1	Kester, Yakutia	148	85.72	10.78	1.24	1.86	0.07	0.11				Alekseev et al., 2020
2	Penouta, Spain	9	95.02	3.44	0.57	0.70	0.05	0.11	0.02			Alfonso et al., 2018
3	Podlesi, Czech Republic	6	93.86	2.54	1.19	0.80	0.95		0.11			Breiter et al., 2007
4	Greer Lake, Canada	2	94.20	4.80	0.00	0.85	0.00	0.13				Černý et al., 1986
5	Logrosán, Spain	2	94.03	2.71	1.38	1.01	0.41	0.23	0.10			Chicharro et al., 2015
6	Madeira, Brazil	4	93.92	0.35	1.73	1.16	0.08					Costi et al., 2000
7	Beauvoir, France	1	94.08	3.20	1.92	0.23	0.05	0.53				Cuney et al., 1992
8	Nuweibi, Egypt	2	91.90	2.00	2.39	1.14	0.00	0.16		0.28	0.22	Gaafar, 2014
9	Eurajoki, Finland	5	93.12	2.50	3.54	1.78	0.26					Haapala, 1997
10	Yichun, China	9	94.16	2.37	0.65	0.28	0.26	0.24	0.15			Huang et al., 2002
11	Xianghualing, China*	2	92.41	4.08	1.42	1.03	0.40	0.37	0.91			Huang et al., 2015
12	Ririwai, Nigeria	4	95.13	1.82	2.53	0.97	0.13	0.01	0.00			Ixer et al., 1987
13	Ebelekan, Algeria	2	88.97	7.04	0.48	1.41	0.74	0.10	0.29			Kesraoui and Nedjari, 2002
14	Beauvoir, France	46	99.96	0.15	0.25	0.03	0.05					Lerouge et al., 2017
15	Jalama, Spain	8	94.05	3.82	1.11	0.76	0.01	0.16				Llorens et al., 2017
16	Penouta, Spain	7	97.15	2.28	0.89	0.55	0.02	0.08				Lopez-Moro et al., 2017
17	Argemela, Portugal	6	93.61	3.72	2.00	1.00	0.18	0.08	0.00			Michaud et al., 2020
18	Penouta, Spain	55	95.93	1.32	0.81	1.11	0.58	0.12				Murciego et al., 1997
19	Golpejas, Spain	55	93.26	1.76	2.68	1.56	0.01	0.23				Murciego et al., 1997
20	Richemont, France	7	83.89	3.10	5.11	1.49	0.46	0.77	2.20	0.05		Raimbault and Burnol, 1998
21	Goebel Dihmit, Egypt	3	94.52	3.35	0.69	0.55	0.17	0.25	0.08			Saleh et al., 2008
22	Kougarok, USA	4	94.83	2.09	1.85	0.76	0.00	0.06	0.35			Soloviev et al., 2020
23	Separation Rapids, Canada	1	97.10	0.98	0.75	0.52		0.05				Tindle and Breaks, 1998
24	Beauvoir, France	13	96.64	2.05	1.18	0.43	0.22	0.04	0.10			Wang et al., 1987
25	Qiguling, China*	23	95.04	0.53	1.10	0.85	2.48	0.03	0.42			Xie et al., 2015
26	Laizilingn, China	5	92.79	2.58	2.04	1.34	0.62	0.04	0.14			Xie et al., 2018
27	Yifeng, China	6	90.78	4.53	1.90	0.73	0.02	0.40	0.10			Xie et al., 2019
28	Songshugang, China	7	88.52	8.52	1.04	1.77	0.47	0.09	0.14			Zhu et al., 2015

* Cassiterite from ongonites. Average contents based on references are given; *N* is number of analyses. The Ca, Mg, Al, Sc, In, As, Y, Sb, REE, and U contents are not given. Space denotes that the data are absent. FeO⁺ = FeO + Fe₂O₃.

elongation, decrease of color intensity, increasing resistance, and changes in the content of minor elements (*Minerals* ..., 1965; Deer et al., 1962; Dolomanova et al., 1969, 1975; Maksimuk, 1973; Evzikova, 1984; Nekrasov, 1984; Karyakin, 1985; Ivanov et al., 1989; Maksimuk and Voronina, 1989; Brodskaya and Marin, 2016).

Association with quartz and lithium micas (Li-bearing muscovite, lepidolite, and zinnwaldite) is an essential feature of cassiterite. Albite, topaz, fluorite, amblygonite—montebrazite, tourmaline, and petalite are intergrown with accessory cassiterite. Accessory minerals of rare metal granites and pegmatites, tantaloniobates, ilmenorutile, strüverite, ferberite, zircon, thorite, monazite, allanite, and ilmenite coexist with cassiterite or observed as inclusions in it.

Accessory GC and PC are distinguished by their dark brown almost black color and resinous or submetallic luster on fracture. Magnetic susceptibility increases in the darkest grains. The density is elevated, 6.90–7.12 g/cm³. Researchers note perfect and simple faceting of accessory cassiterite, its dipyrnidal habit, rare twins, and dull faces (Scrivenor, 1928; Gotman, 1941; Boldyreva, 1941; Williams et al., 1956; Deer et al., 1962; Dolomanova et al., 1969; Grubb and Hannaford, 1966; Flerov, 1976; *Atlas* ..., 1977; *Deposits* ..., 1980; Ollila, 1986; Giuliani, 1987; Wang et al., 1987; Ivanov et al., 1989; Maksimuk and Voronina, 1989; Spilde and Shearer, 1992; Tsareva et al., 1993; Trumbull, 1995; Neiva, 1996; Murciego et al., 1997; Rub et al., 1998; Roda-Robles et al., 1999; Costi et al., 2000; Gavrilenko and Panova, 2001;

Table 2. Chemical composition (wt %) of cassiterite from rare metal pegmatites

	Deposit	N	SnO ₂	Ta ₂ O ₅	Nb ₂ O ₅	FeO ⁺	TiO ₂	MnO	WO ₃	ZrO ₂	HfO ₂	Reference
1	Eastern Sayan, Siberia	15	96.30	2.41	0.22	0.23	0.14	0.15				Belozerova and Makagon (2005)
2	Karavshin, Kyrgyzstan	1	91.57	2.62	1.63	0.74	0.06	0.08	0.00		0.08	Gerasimov (2015)
3	Pegmatite, Central Asia ¹⁾	6	95.96	1.79	1.45	0.52	0.15	0.09	0.01	0.04		Gotman (1941)
4	Malo-Kulindinskoe, Transbaikalian Region	1	93.69	2.17	1.75	0.87	0.14	0.04	0.32	0.12		Dolomanova et al., 1969
5	Pegmatites, Central Asia ²⁾	3	94.43	1.69	0.94	0.59	0.03	0.09	0.09			Maksimov (1973)
6	Otboinoe, Eastern Sayan	21	91.57	6.01	1.04	0.93	0.15					Sokolov and Nechelyustov (2017)
7	Priiskatel, Kolyma	1	97.59	1.19	0.53	0.43	0.09		0.17			Flerov (1976)
8	Segura, Portugal	6	96.44	1.21	2.00	0.05	0.02	0.20	0.17			Antunes et al., 2013
9	Seridózinho, Brazil	9	73.30	21.50	1.80	3.70	0.03	0.30				Burke et al., 1969
10	Peerless, USA	6	94.68	3.83	0.48	0.52	0.06	0.06				Černý et al., 1985
11	Greer Lake, Canada	1	93.00	3.30	1.30	0.90	0.00	0.00				Černý et al., 1986
12	Jihlava, Czech Republic	2	97.05	0.23	0.83	0.25	0.18	0.04	0.08	0.01	0.00	Černý, Nemeček, 1995
13	Varuträsk, Sweden	4	94.68	3.38	0.66	0.23	0.03	0.37	0.00	0.03		Černý et al., 2004
14	Mogok, Burma	1	83.34	13.67	0.51	2.27	0.04	0.17				Clark et al., 1976
15	Dahongliutan, China	32	93.73	2.05	1.07	0.51	0.07	0.13	0.06	0.10	0.02	Feng et al., 2019
16	Macainhas, Portugal	2	91.66	6.97	0.00	1.38	0.00	0.00				Fernandes, Moura, 2017
17	Cross-Uis, Namibia	6	97.48	2.17	0.49	0.44	0.10	0.02	0.06			Fuchsloch et al., 2018
18	Tres Arroyos, Spain	6	94.42	3.13	1.41	0.72	0.33	0.15	0.06			Garate-Olave et al., 2020
19	Giraúl, Angola	9	96.95	2.12	0.31	0.58	0.30	0.04	0.12			Gonçalves et al., 2019
20	Little Nahanni, Canada	6	96.07	2.58	1.17	0.13	0.11	0.30	0.03	0.07		Groat et al., 2003
21	Pegmatites from Ireland ³⁾	5	96.52	1.82	0.52	0.39	0.02	0.05	0.01			Kaeter et al., 2021

Table 2. (Contd.)

	Deposit	N	SnO ₂	Ta ₂ O ₅	Nb ₂ O ₅	FeO ⁺	TiO ₂	MnO	WO ₃	ZrO ₂	HfO ₂	Reference
22	Pegmatites from Australia ⁴⁾	4	96.05	2.13	0.73	0.55	0.18	0.03	0.00		0.04	Kendall-Langley et al., 2020
23	Pusila, China	3	96.88	1.35	0.67	0.37	0.29	0.01	0.00			Liu et al., 2020
24	Jalama, Spain	4	94.33	3.12	1.02	0.58	0.19	0.14	0.00	0.00		Llorens and Moro, 2012
25	Barroso-Alvão, Portugal ⁵⁾	2	96.32	1.94	0.44	0.40	0.21	0.18	0.10			Martins et al., 2011
26	Annie Claim, Canada	3	91.14	6.45	0.69	0.11	0.00	0.83	0.08	0.14	0.00	Masau et al., 2000
27	Pegmatites from Spain ⁶⁾	220	94.22	1.70	1.78	0.78	0.63	0.20				Murciego et al., 1997
28	Karagwe Ankole, Rwanda	36	95.17	2.67	1.28	0.45	0.06	0.18	0.00	0.14	0.03	Nambaje et al., 2020
29	Pegmatites from Portugal ⁷⁾	7	92.68	5.30	1.04	1.24	0.14	0.04	0.04			Neiva, 1996
30	Gravanho, Portugal	3	93.75	4.01	1.35	0.08	0.08	0.61	0.09			Neiva et al., 2019
31	Malkangiri, India	4	90.70	6.80	0.92	0.76	0.00	0.42	0.01			Pal et al., 2007
32	Pilawa Gorna, Poland	8	92.85	4.26	0.84	1.07	0.29		0.25			Pieczka et al., 2013
33	Chedeville, France	3	91.00	5.65	1.89	0.11	0.08	0.80	0.00			Raimbault, 1998
34	Nanping, China	4	84.93	11.62	1.14	2.20	0.02	0.11	0.11			Rao et al., 2009
35	Fregeneda, Spain	10	96.90	1.79	0.49	0.37	0.09	0.03				Roda-Robles et al., 1999
36	Kawadgaon, India	5	91.70	4.40	3.90							Singh et al., 2017
37	Pegmatites from USA ⁸⁾	7	96.15	2.31	0.69	0.32		0.31	0.21			Spilde and Shearer, 1992
38	Phuket, Thailand	4	95.43	2.78	0.55	0.47	0.13	0.19	0.07			Suwimonprecha et al., 1995
39	Separation Rapids, Canada	8	95.84	2.91	0.40	0.58		0.09				Tindle and Breaks, 1998
40	Sinceni, Swaziland	4	98.75	0.66	0.33	0.27	0.11	0.03	0.02			Trumbull, 1995
41	Dahongliutan, China	19	97.15	1.52	0.29	0.62	0.15	0.01	0.03			Yan et al., 2016

1) Verkhe-Baimurzinskoe and Urankhaiskoe in Kazakhstan, Bilyagi-Don in Northern Osetia, and Novo-Durulgueskoe and Zavitaya in Transbaikai Region; 2) Bakemnoe in Kazakhstan, Malokulindinskoe in Transbaikai Region, and Pamir; 3) Aclare and Moylisha; 4) Moolyella, Mount Francisco, Siffleete's Reward, and Greenbushes; 5) Portugal; 6) Las Navas, Sando, Barkila, and Fregeneda; 7) Cabrãço, Fental, and Vieiros; 8) Bob Ingersoll and Tin Mountain.

Table 3. Chemical composition (wt %) of cassiterite from rare-metal greisens

	Deposit	N	SnO ₂	Ta ₂ O ₅	Nb ₂ O ₅	FeO ⁺	TiO ₂	MnO	WO ₃	ZrO ₂	HfO ₂	Reference
1	Urmi, Amur Region	95	99.50	0.00	0.05	0.04	0.34	0.01	0.06			Alekseev et al. (2019)
2	Greisens, Yakutia ¹⁾	4	98.61	0.11	0.27	0.25	0.16	0.11		0.03	0.01	Amichba and Vorontsova (1978)
3	Iultin, Chukotka	1	98.12	0.14	0.22	0.29	0.28	0.17	0.03	0.10		Gotman (1941)
4	Greisens, Siberia ²⁾	7	96.26	0.09	0.14	0.99	0.30	0.02	0.11			Maksimiyuk (1973)
5	Greisens, Yakutia ³⁾	2	99.01	0.10	0.14	0.30	0.03		0.06			Flerov (1976)
6	Cap de Creus, Spain	2	96.68	1.71	0.01	0.45	0.00	0.00	0.00			Abella et al., 1995
7	Mokambo, Brazil	7	98.69	0.00	0.10	0.44	0.24	0.01	0.17			Barros Neto et al., 2020
8	Podlesi, Czech Republic	1	97.00	0.01	0.00	1.47	0.16		0.08			Breiter et al., 2007
9	Logrosán, Spain	5	98.64	0.20	0.21	0.14	0.69	0.00	0.03			Chicharro et al., 2015
10	Madeira, Brazil	1	99.54	0.02	0.08	0.09	0.48					Costi et al., 2000
11	Cross-Uis, Namibia	5	96.15	1.43	1.39	0.77	0.17	0.02	0.00			Fuchsloch et al., 2018
12	Sokhret Allal, Morocco	21	99.40	0.01	0.06	0.12	0.43		0.01			Giuliani, 1987
13	Eurajoki, Finland	5	99.08	0.00	0.30	0.16	0.44					Haapala, 1997
14	Yinyan, China	28	96.51	0.10	0.31	1.71	0.88	0.01	0.33	0.11	0.01	Hu et al., 2021
15	Ririwai, Nigeria	4	98.56	0.81	0.29	0.28	0.12	0.01	0.00			Ixer et al., 1987
16	Greisens, France ⁴⁾	292	99.12	0.31	0.20	0.16	0.47					Lerouge et al., 2017
17	Greisens, Spain ⁵⁾	102	99.46	0.39	0.18	0.09	0.57					Lerouge et al., 2017
18	Jálama, Spain	4	98.86	0.00	0.21	0.09	0.46	0.02	0.03	0.00		Llorens, Moro, 2012
19	Lumbrals, Spain	55	97.66	0.01	0.64	0.42	1.24	0.01				Murciego et al., 1997
20	Greisens, England ⁶⁾	17	98.93	0.03	0.09	0.18	0.03		0.34			Moore, Howie, 1979
21	Karagwe Ankole, Rwanda	20	98.64	0.14	0.11	0.05	0.19	0.01	0.00	0.01	0.00	Nambaje et al., 2020
22	Greisens, Portugal ⁷⁾	26	99.24	0.08	0.07	0.63	0.51	0.03	0.08			Neiva et al., 1996, 2008
23	Malkangiri, India	4	98.57	0.86	0.05	0.92	0.00	0.03	0.00			Pal et al., 2007
24	Hub Stock, Czechia	8	99.57	0.01	0.02	0.09	0.05	0.01	0.11			Rene, 2018
25	Kougarok, USA	2	98.36	0.26	0.13	0.36	0.00	0.01	0.69			Soloviev et al., 2020
26	Bom Futuro, Brazil	25	98.45	0.18	0.16	0.16	1.03		0.10			Souza, Botelho, 2009
27	Greisens, Spain ⁸⁾	2	97.50	0.36	0.30	0.65	0.85					Weibel, 1956
28	Montbelleux, France	45	98.97	0.71	0.56	0.33	0.44					Wille et al., 2018
29	Black Mountain, USA	7	97.31	1.53	0.80	0.49	0.02	0.07				Wise and Brown, 2011
30	Qiguling, China	17	98.50	0.09	0.04	0.35	0.77	0.01	0.28			Xie et al., 2015
31	Songshugang, China	2	95.23	1.25	1.06	0.57	1.07	0.05	0.22			Zhu et al., 2015

¹⁾ Kester, Polymoe, Oidinokoe, and Ytyr-Khalan; ²⁾ Onon and Etyka in Transbaikai Region, Chapaevskoe in Primorsky Krai, and Iultin in Chukotka; ³⁾ Kester, Polymoe; ⁴⁾ Montbelleux, La Villeder, and Saint-Renan; ⁵⁾ Magros and Marcofan; ⁶⁾ St Michael's Mount and Cligga Head; ⁷⁾ Filharoso, Carris, Lombo de Boi, Linhares, Fonte Figueira, Vale das Gatas, Muralha, Carvalhal, Panasqueira, Montezinho, and Argozelo; ⁸⁾ Trasquilón and Logrosán.

Groat et al., 2003; Černý et al., 2004; Saleh et al., 2008; Rao et al., 2009; Chicharro et al., 2015; Zhu et al., 2015; Sokolov and Nechelyustov, 2017; Llorens et al., 2017; Petrochenkov, 2018; Fuchsloch et al., 2018; Xie et al., 2018; Cheng et al., 2019; Feng et al., 2019; Xie et al., 2019; Garate-Olave et al., 2020; Michaud et al., 2020; Soloviev et al., 2020; Lv et al., 2021; Kaeter et al., 2021). Pseudoprismatic individuals with anomalous parallel dipyrarnidal faces (111) are observed (Artem'ev, 1933; Boldyreva, 1941).

The average size of the GC grains is microscopic, 0.8 mm (range of 0.002–12 mm), whereas that of the PC and GrC is macroscopic, 4.8 and 3.7 mm (0.01–110 and 0.001–135 mm), respectively (Ahlfeld, 1931; Artem'ev, 1933; Amichba and Vorontsova, 1978; Roda-Robles et al., 1999; Costi et al., 2000; Gerasimov, 2015; Chicharro et al., 2015; Petrochenkov, 2018; Alfonso et al., 2018, 2020; Cheng et al., 2019). It is interesting that cassiterite from greisens is comparable in its crystal size with that from pegmatites, reaching 10–13.5 cm in length (Dolomanova et al., 1969; Petrochenkov, 2018). In our view, this is due to the tendency of GrC to grow as twins. The finest cassiterite was observed in ongonite groundmass, 8–50 μm (Raimbault and Burnol, 1998; Huang et al., 2015; Xie et al., 2015).

Microscopically, accessory cassiterite is distinguished by its reddish brown color (very rare dirty-green in pegmatites), which is frequently zoned and drastically variable depending on axis: from cherry-brown, chocolate-brown or bottle-green along γ to yellow-brown and greenish yellow along β . The refractive and birefringence indices of cassiterite from pegmatites are higher than those from greisens. γ and $\gamma-\beta$ in PC vary from 2.06 to 2.10 and from 0.082 to 0.099, whereas those in GrC range from 1.98 to 2.07 and from 0.060 to 0.090, respectively; PC is frequently abnormal biaxial with $2V$ up to 21° (Gotman, 1941; Grigoriev and Dolomanova, 1951; *Minerals ...*, 1965; Deer et al., 1962; Dolomanova et al., 1969).

High-temperature cassiterite is characterized by oscillatory zoning observed in cathode rays. The intensity of luminescence is strongly correlated with the Ta and Nb contents and to less extent with Fe and U (dark zones), and W and Ti (light zones) (Farmer et al., 1991; Cheng et al., 2019; Hu et al., 2021). Microhardness of accessory cassiterite, 824–1220 kg/mm², is less than that of hydrothermal cassiterite, 1069–1506 kg/mm² (Barsanov and Kuznetsov, 1971; Bykovsky et al., 1972).

The rutile-type structure of cassiterite is stable. Previously, it was considered that the unit-cell parameters of cassiterite are independent on its genesis, minor elements, and mineral impurities: $a = 4.71\text{--}4.74\text{ \AA}$, $c = 3.17\text{--}3.19\text{ \AA}$ (Boldyreva, 1941; *Minerals ...*, 1965; Dolomanova et al., 1969; Ivanov et al., 1989). It has been now determined that cassiterite from pegmatite and greisen deposits is distinguished by its X-ray

diffraction pattern and the lowest parameter $c = 3.181\text{--}3.185\text{ \AA}$ that correlates with the Nb₂O₅ and Ta₂O₅, and TiO₂ contents in the mineral, respectively. Pegmatitic cassiterite has the highest parameter $a = 4.738\text{--}4.739\text{ \AA}$ and tapiolite-mossite blocks irregular distributed in the structure, whereas in GrC, rutile layers with parameter $a = 4.734\text{--}4.737\text{ \AA}$ were identified (Amichba and Vorontsova, 1978; Krivokoneva and Sirina, 2005). Experiments have shown that the structure parameters of synthetic cassiterite are a function of temperature and pH of mineral-forming medium (Sidorenko et al., 1992).

Cassiterite from greisens is lighter (brown, yellow, pink) and is colorless, semitransparent with vitreous or strong adamantine luster on the faces and greasy, on fracture. Microscopically, cassiterite is slightly pleochroic; zoned coloration is rare, whereas mottled is frequent. The alternated dark and light zones in cassiterite have allochromatic nature and reflect variations in minor element and mineral impurity contents (Gotman, 1941; Boldyreva, 1941; Grigoriev and Dolomanova, 1951; Weibel, 1956; Flerov, 1976; Amichba and Vorontsova, 1978; Karyakin, 1985; Giuliani, 1987; Ixer et al., 1987; Abella et al., 1995; Murciego et al., 1997; Costi et al., 2000; Schneider, 2008; Chicharro et al., 2015; Fuchsloch et al., 2018; Alekseev et al., 2019; Barros Neto et al., 2020; Hu et al., 2021; Nambaje et al., 2020). Slightly magnetic colored GrC with wolframite inclusions is observed (Dolomanova et al., 1969; Moore and Howie, 1979).

Postmagmatic cassiterite is diverse in its morphology that is a basis for crystal morphological estimation of tin prospects (Evzikova, 1984). In greisens accompanying rare metal granites and pegmatites, cassiterite is anhedral and short-prismatic (100), (110), and less frequent dipyrarnidal (111), (101). The crystal shape is complicated by additional faces of prisms, acute dipyrarnids (hkl), and pinacoid (001), and irregular developed similar faces and diverse twins, simple, polysynthetic, and complex (Gotman, 1941; Boldyreva, 1941; Flerov, 1976; Evzikova, 1984; Vdovina, 1987).

TYPOCHEMISTRY OF ACCESSORY CASSITERITE

Despite cassiterite is the major source of tin, its chemical composition in rare metal granites and pegmatites is gaining a growth interest in view of trace elements with practical and genetic importance. Accessory cassiterite is associated with tantaloniobates, which are columbite, tantalite, tapiolite, wodginite, ixiolite, microlite, wolframixiolite, and ilmenorutile; tantalum dominates niobium in this cassiterite (Kuzmenko and Eskova, 1968; Maksimuk, 1973; Khvostova et al., 1983; Černý and Ercit, 1985; Klementova and Rieder, 2005). Granitic and pegmatitic cassiterite is enriched in Ta during compositional evolution that is determined by the Ta accumulation during differen-

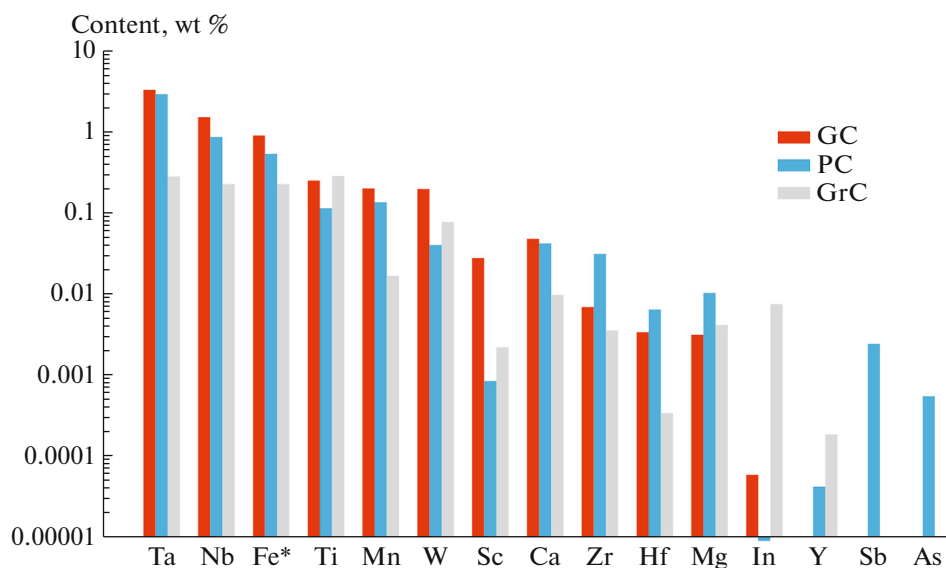


Fig. 1. Average contents of minor and trace elements in cassiterite from rare-metal granites (GC), pegmatites (PC) and greisens (GrC) in the world (summary data, 1759 compositions). Oxide contents are given. Fe* = FeO + Fe₂O₃.

tiation of rare metal granite magma and selective isomorphous capacity of cassiterite.

The major minor elements in cassiterite (≥ 0.1 wt %) are Ta, Nb, Fe, Mn, Ti, and W; rare trace elements (50–500 ppm) are Ca, Sc, Zr, Hf, and In; and very rare trace elements (< 50 ppm) are Mg, Sb, U, As, Y, and REE (Fig. 1). Total content of minor and trace elements in GC reaches 27.10 wt % (average 6.68 wt %); this value in PC is up to 27.33 wt % (average 4.87 wt %); and that in GrC is up to 6.23 wt % (average 1.18%) (Table 4). The set of minor and trace elements is due to the crystal chemical affinity of some of them to the Sn⁴⁺ ion. Tantalum, Mn, and Hf are typical traces in accessory cassiterite from granites and pegmatites. This is reflected in the low Nb/Ta, Fe/Mn, and Zr/Hf ratios (Table 4) and is noted in overview papers (Möller and Dulski, 1983; Cheng et al., 2019; Feng et al., 2019).

Tanatalum and niobium in accessory cassiterite.

Substantial minor Ta and Nb are specific feature of cassiterite from rare metal granites and pegmatites (Gotman, 1941; Quensel, 1941; Hutton, 1950; Deer et al., 1962; Barsanov and Kuznetsov, 1971; Flerov, 1976; Nekrasov, 1984; Černý et al., 1986; Solodov et al., 1987; Wang et al., 1987; Möller et al., 1988; Sidorenko et al., 1992; Cuney et al., 1992; Spilde and Shearer, 1992; Tsareva et al., 1993; Černý and Nemec, 1995; Suwimonprecha et al., 1995; Trumbull, 1995; *Rare-metal ...*, 1997; Haapala, 1997; Murciego et al., 1997; Roda-Robles et al., 1999; Masau et al., 2000; Huang et al., 2002; Kesraoui and Nedjari, 2002; Groat et al., 2003; Klementova and Rieder, 2005; Wise and Brown, 2011; Antunes et al., 2013; Gaafar, 2014; Chicharro et al., 2015; Yan et al., 2016; Breiter et al., 2017; Lopez-Moro et al., 2017; Singh et al., 2017;

Broska and Kubis, 2018; Xie et al., 2018, 2019; Gonçalves et al., 2019; Neiva et al., 2019; Alekseev et al., 2020; Alfonso et al., 2020; Nambaje et al., 2020; Soloviev et al., 2020; Kaeter et al., 2021; Lv et al., 2021) (Fig. 2). Accessory cassiterite from tin-bearing leucogranites does not have this feature (Kuzmenko and Eskova 1968; Maksimiyuk, 1973; Maksimiyuk and Voronina, 1989).

The reviewed literature shows that accessory cassiterite contains, wt %: 3.06 (21.50) Ta₂O₅ and 1.14 (12.02) Nb₂O₅.² The highest Ta₂O₅ and Nb₂O₅ contents are measured in GC, average 3.42 and 1.58 wt %, respectively (Table 4); frequently they reach 5.88–12.35 and 1.58–12.02 wt %, respectively (*Deposits ...*, Raimbault and Burnol, 1998; Kesraoui and Nedjari, 2002; Chicharro et al., 2015; Huang et al., 2015; Llorens et al., 2017; Michaud et al., 2020; Soloviev et al., 2020) (Table 1). The extremely high Ta₂O₅ concentration was measured in cassiterite from rare metal granites in Russia and China, 17.9 wt % (Alekseev et al., 2020) and 18.4 wt % (Zhu et al., 2015), respectively. Tantalum always dominates niobium. The Nb/Ta ratio ranges from 0.3 to 0.5. The exception is cassiterite from ongonite: 1.23–1.59 wt % Nb₂O₅ and 0.34–0.66 wt % Ta₂O₅ in the Qiguling dike, South China (Xie et al., 2015), and 6.24–12.02 wt % Nb₂O₅ and 3.64–7.43 wt % Ta₂O₅ in the Richemont dike, France (Raimbault and Burnol, 1998) (Tables 1, 4; Fig. 2).

In PC, the Ta₂O₅ and Nb₂O₅ concentrations are 3.03 and 0.90 wt %, respectively (Table 4) and reach

² The average concentration and the highest content in parentheses are here and below.

Table 4. Average chemical composition (wt %) of cassiterite from rare metal granites, pegmatites and greisens worldwide

Component	Cassiterite from granites		Cassiterite from pegmatites		Cassiterite from greisens	
	Av. (442)	Max	Av. (501)	Max	Av. (816)	Max
SnO ₂	93.17		94.98		98.57	
Ta ₂ O ₅	3.42	18.28	3.03	21.50	0.29	3.07
Nb ₂ O ₅	1.58	12.02	0.90	4.10	0.23	2.40
FeO*	0.93	5.02	0.55	5.27	0.24	3.22
TiO ₂	0.26	2.48	0.12	1.64	0.30	1.50
MnO	0.21	3.55	0.14	1.41	0.02	0.35
WO ₃	0.20	6.86	0.04	1.05	0.08	1.61
Sc ₂ O ₃	0.03	0.95	0.00	0.07	0.00	0.09
CaO	0.05	0.37	0.04	0.59	0.01	0.53
ZrO ₂	0.01	0.40	0.03	0.41	0.00	0.11
HfO ₂	0.00	0.24	0.01	0.08	0.00	0.04
MgO	0.00	0.40	0.01	0.20	0.00	0.10
In ₂ O ₃	0.00	0.01	0.00	0.00	0.01	0.08
Y ₂ O ₃	0.00	0.00	0.00	0.01	0.00	0.03
Sb ₂ O ₃	—	—	0.00	0.12	—	—
As ₂ O ₃	—	—	0.00	0.03	—	—
Σ	6.68	27.10	4.87	27.33	1.18	6.23
Nb/Ta	0.5		0.3		0.8	
Fe/Mn	4.5		4.0		13.6	
Zr/Hf	2.1		4.8		10.5	

Average cassiterite composition (Av., number of analyses in parentheses) and the highest contents (Max.) are given. Σ denotes total of trace elements. Dash denotes that the data are absent; FeO* is FeO + Fe₂O₃.

6.28–13.67 and 0.90–4.10 wt %, respectively (Clark et al., 1976; Khvostova et al., 1983; Černý et al., 1985; Neiva, 1996; Raimbault, 1998; Tindle and Breaks, 1998; Masau et al., 2000; Belozero and Makagon, 2005; Pal et al., 2007; Rao et al., 2009; Pieczka et al., 2013; Sokolov and Nechelyustov, 2017; Fernandes and Moura, 2017; Alfonso et al., 2018; Neiva et al., 2019; Xie et al., 2019) (Table 2). Cassiterite from the Seridózinho rare metal pegmatite in Brazil contains 20.1–22.4 wt % Ta₂O₅ (Burke et al., 1969). Dark red, brown, and orange color of accessory cassiterite is traditionally associated with minor Ta and Nb as a few percent, as well as Fe, Ti, and W (Neuhaus and Noll, 1949; Khvostova et al., 1983; Neiva, 1996; Gavrilenko and Panova, 2001; Nascimento and Souza, 2017; Alekseev et al., 2020).

Tantalum-bearing cassiterite variety named as “ainalite” was described for the first time in 1863 from pegmatite in Finland (Quensel, 1941; Khvostova et al., 1983). The elevated contents of minor Ta, Nb, and Fe in cassiterite from rare-metal pegmatites in Brazil and Eastern Siberia resulted in attempt to define individual mineral species starringite (Burke et al., 1969; Khvo-

stova et al., 1974) that now is considered as mixed cassiterite and tapiolite-(Fe) (Krivovichev, 2008).

The Ta and Nb average concentrations decrease from GC through PC to GrC (Fig. 1). The minor element ratio also evolves: the Nb/Ta ratio decreases from ongonites through granite to pegmatites (Figs. 2, 3). The Ta and Nb concentrations in GrC are one order lower than those in GC and PC, and the Nb/Ta ratio is close to 1.0 (Table 4). It is worth noting the Ta content sustainably increased from core to rim in the GC and PC crystals.

The increased Ta concentration results in increased Mn concentration in accessory cassiterite, with most publications noting primarily Fe-rich nature of PC and GC, Mn/(Mn + Fe) < 0.4 (Masau et al., 2000; Černý et al., 2004; Rao et al., 2009; Wise and Brown, 2011; Llorens et al., 2017; Alfonso et al., 2018; Fuchsloch, et al., 2018; Xie, et al., 2018). Correlation between Mn/(Mn + Fe) and Ta/(Ta + Nb) is supported by the review of consolidated database. However, it should be noted that Mn-rich cassiterite is quite common in rare-metal pegmatites, granites, and ongonites (Fig. 3).

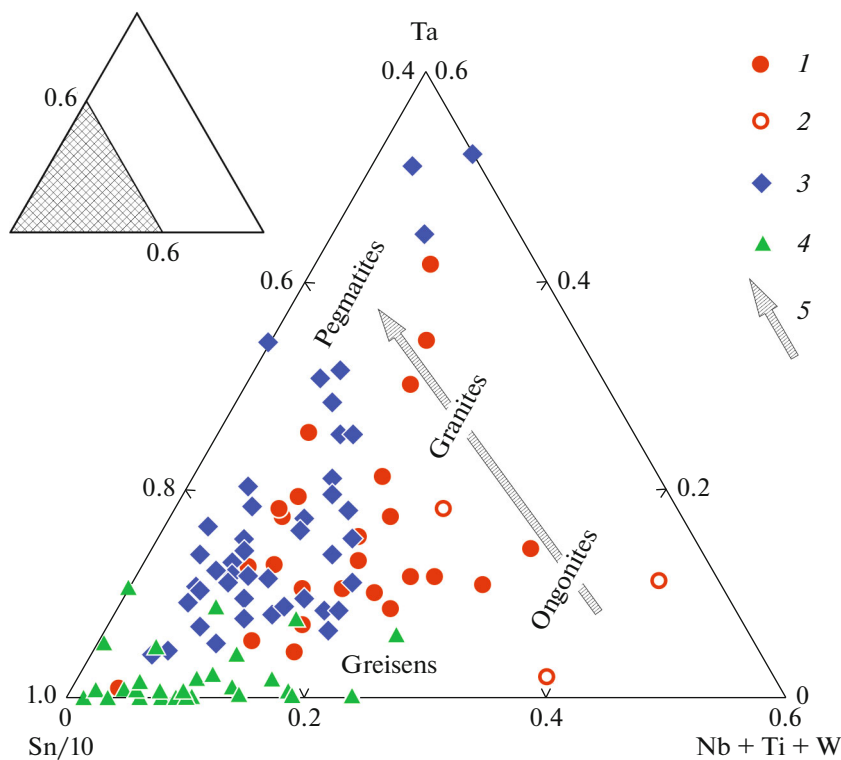


Fig. 2. Ternary plot in terms of atomic quantities of Sn, Ta and (Nb + Ti + W) in cassiterite from (1) rare-metal granites, (2) ongonites, (3) pegmatites, and (4) greisens over the world. The arrow (5) shows the trend of Ta/(Nb + Ti + W) modal values in accessory cassiterite.

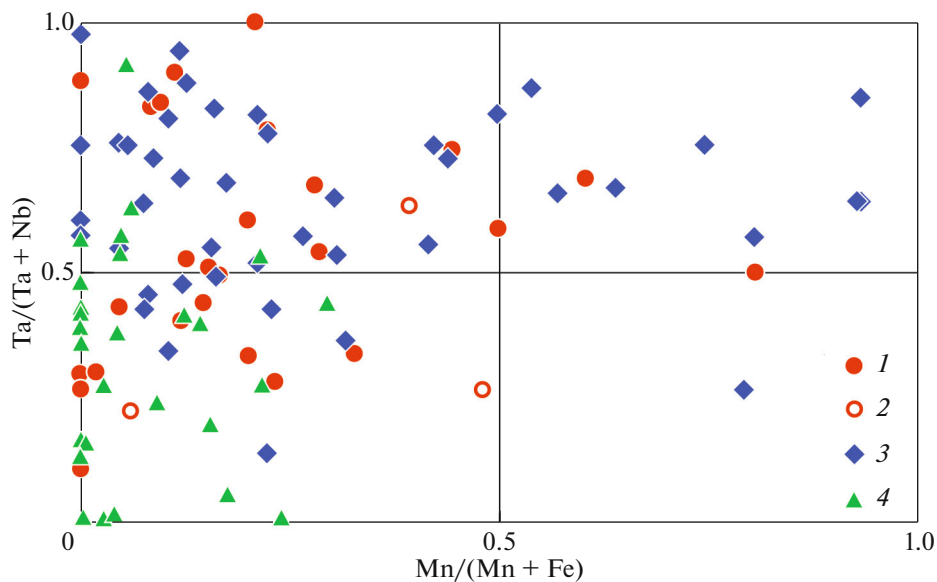


Fig. 3. Ta/(Ta + Nb) versus Mn/(Mn + Fe) binary plot (columbite quadrilateral, Černý and Ercit, 1985) illustrating ratios of Ta, Nb, Mn, Fe atomic quantities in cassiterite from (1) rare-metal granites, (2) ongonites, (3) pegmatites, and (4) greisens worldwide.

Titanium and tungsten in accessory cassiterite. Minor titanium is the most characteristic of GrC (Weibel, 1956; Amichba and Vorontsova, 1978; Giuliani, 1987; Haapala, 1997; Rub et al., 1998;

Gavrilenko and Panova, 2001; Souza and Botelho, 2009; Llorens and Moro, 2012; Chicharro et al., 2015; Lerouge et al., 2017; Fuchsloch et al., 2018; René, 2018; Wille et al., 2018; Soloviev et al., 2020) and is

0.30 (1.50) wt % TiO_2 mac. % (Tables 3, 4; Fig. 1). The greisen cassiterite generation, in which Ti dominates Ta, is frequent in rare metal granites and pegmatites: 0.26 (2.48) wt % TiO_2 in GC and 0.12 (1.64) wt % TiO_2 in PC (Tables 1, 2, 4; Fig. 2). Such an admixture is resulted from isomorphous substitution Ti^{4+} for Sn^{4+} , which limited in cassiterite by 1–2 wt % TiO_2 (Krivokoneva and Sirina, 2005).

Minor tungsten in accessory GC and PC is insignificant, 0.20 and 0.004 wt %, respectively (Table 4). The exception is cassiterite from ongonites, where cassiterite has extremely high WO_3 , wt %: 1.82–5.13 at Laizilingn, China (Huang et al., 2015); 0.62–6.86 at Richemont, France (Raimbault and Burnol, 1998); and 0.1–0.42 at Qiguling, South China (Xie et al., 2015) (Table 1; Fig. 2). Such anomalies are rare in rare metal pegmatites, for example, PC from Tin Mountain in the USA contains up to 1.05 wt % WO_3 (Spilde and Shearer, 1992) and that from Pilawa Gorna in Poland contains up to 0.57 wt % WO_3 (Piecicka et al., 2013) (Table 2). Tungsten is typical element of greisens accompanying rare metal granites (Maksimiyuk, 1973; Dolomanova et al., 1975; Flerov, 1976; Moore and Howie, 1979; Giuliani, 1987; Möller et al., 1988; Maksimiyuk and Voronina, 1989; Neiva, 1996, 2008; Gavrilenko and Panova, 2001; Fuchsloch et al., 2018; René, 2018; Alekseev et al., 2019; Barros Neto et al., 2020; Hu et al., 2021). However, the WO_3 content in GrC is highly variable from 0.01 to 1.61 wt % (Table 3) and its average of 0.08 wt % is comparable with that in GC and PC (Table 4; Fig. 2).

Scandium and indium in accessory cassiterite. Scandium is rare trace in GC, 0.03 (0.95) wt % Sc_2O_3 . For example, GC from Transbaikalian Region, Altay, and Northeastern Russia contains 10–200 ppm Sc (Bykhovskiy et al., 1972). Scandium is less frequent in PC and GrC, 0.001 (0.07) and 0.002 (0.09) wt % Sc_2O_3 , respectively (Table 4). Cassiterite from pegmatites in Yakutia contains 9–100 ppm Sc (Flerov, 1976). Elevated Sc concentration was measured in zwitter cassiterite from Yinyan, China (55–474 ppm) (Hu et al., 2021) and deposits in the Eastern Russia (12–1660 ppm) (Bykhovskiy et al., 1972; Maksimiyuk, 1973; Flerov, 1976; Amichba and Vorontsova, 1978; Maksimiyuk and Voronina, 1989; Gavrilenko and Panova, 2001; Alekseev et al., 2019).

Indium in accessory cassiterite is measured using neither electron microprobe nor ICP-MS, because its content in GC and PC is $n \times 0.001$ ppm (Plimer et al., 1991). The exception is rare metal granites in the Eastern Russia and Montebbras in France, where cassiterite contains 3–190 and 63 ppm In (Lerouge et al., 2017; Bykhovskiy et al., 1972; Maksimiyuk and Voronina, 1989). Substantial In (0.01–1.23 wt %) is observed in cassiterite from greisens, most frequently, from zwitter (Bykhovskiy et al., 1972; Flerov, 1976; Amichba and Vorontsova, 1978; Moore and Howie, 1979; Nikulin, 1981; Maksimiyuk and Voronina, 1989;

Botelho and Moura, 1998; Gavrilenko and Panova, 2001; Briskey, 2005; Sinclair et al., 2006; Schneider, 2008; Gaskov et al., 2017; Alekseev et al., 2019; Nambaje et al., 2020) (Table 4). It is suggested that high In in GrC is partially due to interfered electron clouds of the mineral matrix and inclusions of In minerals (roquesite, dzhallindite, sakuraiite) and In-bearing sulfides (sphalerite, chalcocopyrite, stannite, and kesterite). The X-ray mapping of the GC and GrC grains from Massif Central and Armorican Massif revealed isomorphous nature of trace In (Lerouge et al., 2017). The In content in GrC measured using the accurate neutron activation method is 38–90 ppm (Sinclair et al., 2006).

Zirconium and hafnium in accessory cassiterite. The systematic information about Zr and Hf in cassiterite is not accumulated. It has been experimentally established that Zr for Sn substitution results in increased unit cell parameters: $a = 4.759$ and $c = 3.201$ Å at 20 wt % ZrO_2 (Deer et al., 1962). The Zr and Hf contents are, wt %: 0.01 (0.40) and 0.003 (0.24) in GC, and 0.03 (0.41) and 0.01 (0.08) in PC (Tables 1, 2, 4).

There are published data on substantial Zr and Hf traces in accessory cassiterite. Pegmatitic cassiterite from the Dahongliutan deposit in China contains 104–4903 ppm Zr and 49–959 ppm Hf (Feng et al., 2019); cassiterite from Annie in Canada contains 666–1555 ppm Zr (Masau et al., 2000); the Zr and Hf contents in cassiterite from Karagwe Ankole in Rwanda are 460–1900 and 62–500 ppm, respectively (Nambaje et al., 2020); cassiterite from the Karavshin deposit in Kyrgyzstan and the Upper Baimurza deposit in Kazakhstan contains 700 ppm Hf (Gerasimov, 2015) and 1110 ppm Zr (Gotman, 1941), respectively; the Zr concentration in cassiterite from the Novo-Durulgui deposit in the Transbaikalian Region is 590 ppm (Gotman, 1941); cassiterite in pegmatites from the Eastern Siberia, Transbaikalian Region, and Central Asia contains up to 1000 ppm Zr and 240 ppm Hf (Maksimiyuk, 1973). The Zr and Hf contents in GC from the Nuweibi Pluton in Egypt are 1185–2961 and 1696–2035 ppm, respectively (Gaafar, 2014). Greisen cassiterite from the Karagwe Ankole deposits in Rwanda contains 5.5–239 and 0.2–15 ppm Zr and Hf, respectively (Nambaje et al., 2020); from Yinyan in China, 372–1098 and 37–161 ppm (Hu et al., 2021); and from the Gejiu district in China, 34.6–77.2 and 0.54–1.12 ppm (Zhang et al., 2020) (Tables 1, 2, 3). The study of cassiterite from 16 pegmatite deposits in Africa and South America revealed that it contains 16–510 ppm Zr and 1.4–180 ppm Hf (Möller and Dulski, 1983).

Judging from the consolidated data, Ta and Zr, and Ta and Hf pairs are directly correlated (Table 1). Rare metal melts are fractionated with the substantial increasing Zr/Hf ratio from GC (2.1) through PC (4.8) to GrC (10.5) (Table 4). This compositional evolution of cassiterite is reported in some publications:

0.7–1.5 in granites, 1.4–7 in pegmatites, and 5–17 in greisenized granites (Maksimyuk and Voronina, 1989; Jiang et al., 2004; Gaafar, 2014; Cheng et al., 2019; Feng et al., 2019; Zhang et al., 2020; Hu et al., 2021).

Comparison of the given Zr/Hf values with those in hydrothermally synthesized cassiterite (~30) and rock-forming minerals (~43) (Möller and Dulski, 1983) allows conclusion that accessory cassiterite is enriched in Hf (Fig. 1). The Zr/Hf ratio is indicative for cassiterite genesis. In particular, the predominance of pegmatitic cassiterite in some placers has been proven (Möller and Dulski, 1983). The Nb/Ta and Zr/Hf ratios are correlated. The geochemical behavior of Hf paired with Zr is similar to that of Ta paired with Nb: the Hf and Ta concentrations increase during evolution of rare metal magmatism and from core to rim in cassiterite crystals (Feng et al., 2019; Kaeter et al., 2021).

REE in accessory cassiterite. The study of REE and Y traces in cassiterite has commenced in recent years, and it is premature to generalize. Pegmatitic cassiterite from Western Kunlun in China contains 0.23–0.88 ppm Σ REE and 0–0.05 ppm Y (Feng et al., 2019); in cassiterite from the Mole pegmatites in Australia contains 0.3 ppm Σ REE (Plimer et al., 1991). The published data indicate the higher REE and Y concentrations in GrC from some deposits, ppm: 1.68–1.83 and 1.26–1.31 at Yunlong in China (Jiang et al., 2004); 2.7–9.2 and 0.1–0.8 in the Gejiu district in China (Zhang et al., 2020); 4.59–15.60 Σ REE at Emerald in Australia (Plimer et al., 1991); and 1.80–2.30 Y at Pravouriiskoe in the Amur Region (Gavrilenko and Panova, 2001).

The REE distribution patterns are gentle, almost flat and are complicated by the negative Eu anomalies (0.13–0.76 Eu/Eu*). Similar REE composition in GrC and host rocks proves magmatic nature of greisenizing fluids. Difference in the REE distribution pattern in GC and GrC indicates the elevated oxygen fugacity during greisenization (Zhang et al., 2020). Variations in the LREE/HREE ratio in cassiterite reflect the REE distribution during crystallization of syngentic micas, topaz, tourmaline, fluorite, and monazite. The low REE content in PC indicates that these elements are predominantly partitioned into those minerals (Plimer et al., 1991).

Uranium in accessory cassiterite. The U^{4+} ion may substitute Sn^{4+} in the crystal structure of cassiterite. The range of the U and Pb contents in GC, PC, and GrC is, ppm: 0.5–30.0 and 2.5–4.4; 0.1–26.9 and 0.01–5.3; and 0.09–46.6 and 0.01–7.5, respectively (Maksimyuk, 1973; Gulson and Jones, 1992; Costi et al., 2000; Chen et al., 2014; Li et al., 2016; Yan et al., 2016; Zhang et al., 2017, 2020; Neymark et al., 2018; Cheng et al., 2019; Feng et al., 2019; Carr et al., 2020; Kendall-Langley et al., 2020; Lehmann et al., 2020; Moscati, Neymark, 2020; Nambaje et al., 2020; Zhang and Jiang, 2021). Uncommonly high U 37–481

ppm was determined in cassiterite from zwitter at the Yinyan deposit in China (Hu et al., 2021).

ISOMORPHISM IN ACCESSORY CASSITERITE

Isomorphism in cassiterite and its limits have been discussed up to now. First, it is necessary to objectively consider the relationship between Ta, Nb, Fe, Mn, Ti, W isomorphous admixtures and the mineral inclusions of these elements in cassiterite crystals of various genesis; secondly, to develop criteria for distinguishing between inclusions trapped during the growth and exsolved microminerals (Neuhaus and Noll, 1949; *Minerals ...*, 1965; Deer et al., 1962; Barsanov and Kuznetsov, 1971; Maksimyuk, 1973; Amichba and Vorontsova, 1978; Maksimyuk et al., 1982; Černý and Ercit, 1985).

The high-resolution scanning electron microscopy indicates that homogeneous cassiterite crystals without tantaloniobate inclusions contain up to 5 and more wt % Ta_2O_5 . Ta, Nb, Fe, Mn, Ti, and W are isomorphous constituents in cassiterite (Khvostova et al., 1983; Murciego et al., 1997; Makagon et al., 2001; Saleh et al., 2008; Rao et al., 2009; Fuchsloch et al., 2018; Feng et al., 2019; Nambaje et al., 2020). Possible polar isomorphism cannot be ruled out (Popov, 1966; Dolomanova et al., 1969, 1975). The detailed in situ studies of GC and PC and crystal chemical modeling support heterovalent substitution of Sn^{4+} by Ta^{5+} , Nb^{5+} , Fe^{2+} , and Ti^{4+} (Dolomanova et al., 1969, 1975; Wang et al., 1987; Suwimonprecha et al., 1995; Neiva, 1996; Haapala, 1997; Murciego et al., 1997; Tindle and Breaks, 1998; Sosa et al., 2002; Černý et al., 2004; Klementova and Rieder, 2005; Breiter et al., 2007; Wise and Brown, 2011; Llorens and Moro, 2012; Lerouge et al., 2017; Feng et al., 2019; Gonçalves et al., 2019; Garate-Olave et al., 2020). For example, Belozero and Makagon (2005) reported isomorphous incorporation of Ta (0.37–6.35 wt % Ta_2O_5) and Nb (0.34–1.23 wt % Nb_2O_5) into the structure of cassiterite from rare metal pegmatites of the Eastern Sayan.

Substitutions in cassiterite have been studied using the X-ray diffraction. Substitution of Sn by Ta, Nb, Fe, and Mn was supported by variations in the unit-cell volume of pegmatitic cassiterite depending on the admixture concentration (Dolomanova et al., 1975). Irregular arranged tapiolite layers were identified in the cassiterite structure (Krivokoneva and Sirina, 2005).

Ion radii of Ta (0.68 Å) and Sn (0.74 Å) are sufficiently close for probable partial substitution $Ta^{6+} \leftrightarrow Sn^{4+}$ without any structure distortion and with compensation by divalent cations. Electron spin resonance study revealed similar Fe spectra in rutile and cassiterite and isomorphous incorporation of iron into the structure of the latter (Sherbakova et al., 1970). The most abundant isomorphous constituent in accessory cassiterite is (Fe,Mn)(Ta,Nb) $_2O_6$ (Groat et al., 2003).

According to V.A. Kornetova, the rutile-type structure may contain up to 25 mol % FeNb_2O_6 or FeTa_2O_6 (*Minerals ...*, 1965).

In the case of Ta, Nb, Fe, Mn, Ti, and W micro-minerals in cassiterite, attempts for distinguishing primary inclusions and exsolved products and their segregations are occasional (Dolomanova et al., 1969, 1975; Barsanov and Kuznetsov, 1971; Maksimuk, 1973; Černý and Ecrít, 1985; Spilde and Shearer, 1992; Suwimonprecha et al., 1995; Neiva, 1996; Tindle and Breaks, 1998; Sokolov and Nechelyustov, 2017; Llorens et al., 2017; Fuchsloch et al., 2018; Feng et al., 2019). Tantalite and tapiolite microinclusions in cassiterite from the Peerless pegmatites in the USA were considered as exsolutions (Černý and Ecrít 1985). Tapiolite, columbite, tantalite, wodginite, and Ta-rich rutile are reported as products of the cassiterite structure transformation. For example, cassiterite with exsolution textures and secondary grains of Zr–Hf-bearing wodginite was described from the Annie pegmatites in Canada (Masau et al., 2000).

Clusters of anhedral Ta–Nb oxide micrograins ($<1\ \mu\text{m}$) confined to crystal zones and growth sectors in cassiterite are widely considered as exsolutions (Grigoriev and Dolomanova, 1951; Dolomanova et al., 1969, 1975; Maksimuk, 1973). Morphology of the tantalite-niobate inclusions and dependence of their number and mineral species (tapiolite-(Fe), and columbite, wodginite, and rutile group minerals) on concentration and set of trace elements in the matrix of primary cassiterite (Barsanov and Kuznetsov, 1971; Dolomanova et al., 1975; Wang et al., 1987; Rao et al., 2009).

Secondary nature of microinclusions is proved by the decreased content of Ta, Nb, Fe, and Mn around them resulted from exsolution and generation of secondary tantalite-niobates (Spilde and Shearer, 1992; Neiva, 1996; Sokolov and Nechelyustov, 2017). Depletion in the Ta, Nb, Fe, and Mn content around exsolutions reaches 5 and more wt % $(\text{Mn,Fe})(\text{Ta,Nb})_6$. Both decoloration and darker color reflect change in the cassiterite composition. Zones of changed color around tantalite-niobate grains look like pleochroic halos and are frequently elongated parallel to the certain crystallographic directions (Grigoriev and Dolomanova, 1951; Dolomanova et al., 1969).

The exsolution textures are verified by the study of crystallographic orientation of the inclusions. The X-ray and electron diffraction shows that corresponding crystallographic axes of tantalite-niobates in cassiterite are roughly parallel to one of them in host mineral, [101], [011], and other. Segregations are formed at the late exsolution featured by coarsening and slightly rotating boundaries of the newly formed phases (Klementova and Rieder, 2005).

It was established that chemical and mineral admixtures are selectively concentrated in the growth sectors of the main cassiterite faces (100), (111), (101),

(110) (Grigoriev and Dolomanova, 1951; Dolomanova et al., 1969). In hydrothermal cassiterite, W, Nb, and Fe are preferably captured by dipyrimal, whereas In and Sc, by prismatic crystals; the concentration gradient between faces reaches $n \times 100\%$ (Evezikova, 1984). The similar pattern in accessory cassiterite has not been studied.

The tapiolite substitution scheme in magmatic cassiterite $(\text{Fe,Mn})^{2+} + 2(\text{Nb,Ta})^{5+} \leftrightarrow 3(\text{Sn,Ti})^{4+}$ suggested by Černý and Ecrít (1985) has been recognized worldwide (Spilde and Shearer, 1992; Neiva, 1996; Costi et al., 2000; Neiva, 2008; Rao et al., 2009; Souza and Botelho, 2009; Wise and Brown, 2011; Llorens and Moro, 2012; Antunes et al., 2013; Chicharro et al., 2015; Lerouge et al., 2017; Nascimento and Souza, 2017; Alfonso et al., 2018; Fuchsloch et al., 2018; Gonçalves et al., 2019; Neiva et al., 2019; Alekseev et al., 2020; Hu et al., 2021). Previously, Kuzmenko and Eskova (1968) suggested the following scheme $2\text{Ta}^{5+} + (\text{Mn,Fe})^{2+} \leftrightarrow 3\text{Sn}^{4+}$. Tapiolite substitution is characteristic of magmatic systems with Fe^{2+} and it was examined with charge balance constraints and Mössbauer spectroscopy (Feng et al., 2019). The scheme provides cation exchange ($\text{Fe}^{2+} \leftrightarrow \text{Mn}^{2+}$) and ($\text{Sn}^{4+} \leftrightarrow \text{Ti}^{4+}$). Tapiolite substitution in GC and PC without Ti^{4+} ($3\text{Sn}^{4+} \leftrightarrow 2(\text{Nb,Ta})^{5+} + (\text{Fe,Mn})^{2+}$) was established in (Möller et al., 1988; *Rare-metal ...*, 1997; Murciego et al., 1997; Tindle and Breaks, 1998; Makagon et al., 2001; Kesraoui and Nedjari, 2002; Pal et al., 2007; Pieczka et al., 2013; Chicharro et al., 2015; Huang et al., 2015; Xie et al., 2015, 2018; Sokolov and Nechelyustov, 2017; Breiter et al., 2017; Llorens et al., 2017; René, 2018; Xie et al., 2019; Garate-Olave et al., 2020; Michaud et al., 2020).

More complex substitutions in GC and PC are identified in abnormal geochemical environments. For example, possible Sn substitution with lack of divalent cations to form vacancies $5\text{Sn}^{4+} \leftrightarrow 4\text{Ta}^{5+} + \square$ cannot be ruled out (Möller et al., 1988; *Rare metal ...*, 1997; Makagon et al., 2001). Tungsten admixture in GC and PC is associated with substitution $2(\text{Sn,Ti})^{4+} \leftrightarrow \text{W}^{6+} + \text{Fe}^{2+}$ (Souza and Botelho, 2009; Nascimento and Souza, 2017; Barros Neto et al., 2020). In PC from Massif Central, France and Iberian Massif, Spain, the substitution $3(\text{Nb}^{5+}, \text{Ta}^{5+}) + \text{Li}^+ \leftrightarrow 4\text{Sn}^{4+}$ is suggested at the presence of Li^+ in magma and lack of other charge compensators, Fe^{2+} and Mn^{2+} (Raimbault, 1998; Garate-Olave et al., 2020). The cation exchange in cassiterite from rare metal pegmatites in the presence of In, Sc, Nb, and Ta is $(\text{Sn,Ti})^{4+} + \text{In}^{3+} \leftrightarrow \text{Fe}^{2+} + (\text{Nb,Ta})^{5+}$ (Lerouge et al., 2017) and $(\text{Sn,Ti})^{4+} + \text{Sc}^{3+} \leftrightarrow \text{Fe}^{2+} + (\text{Nb,Ta})^{5+}$ (Barsanov and Kuznetsov, 1971).

The example of greisenized rare metal pegmatite was used to show that in oxidative mineral-forming environment hydrothermal, substitution $2\text{Sn}^{4+} \leftrightarrow (\text{Ta,Nb})^{5+} + \text{Fe}^{3+}$ (Kuzmenko and Eskova, 1968; *Rare metal ...*, 1997; Murciego et al., 1997; Tindle and

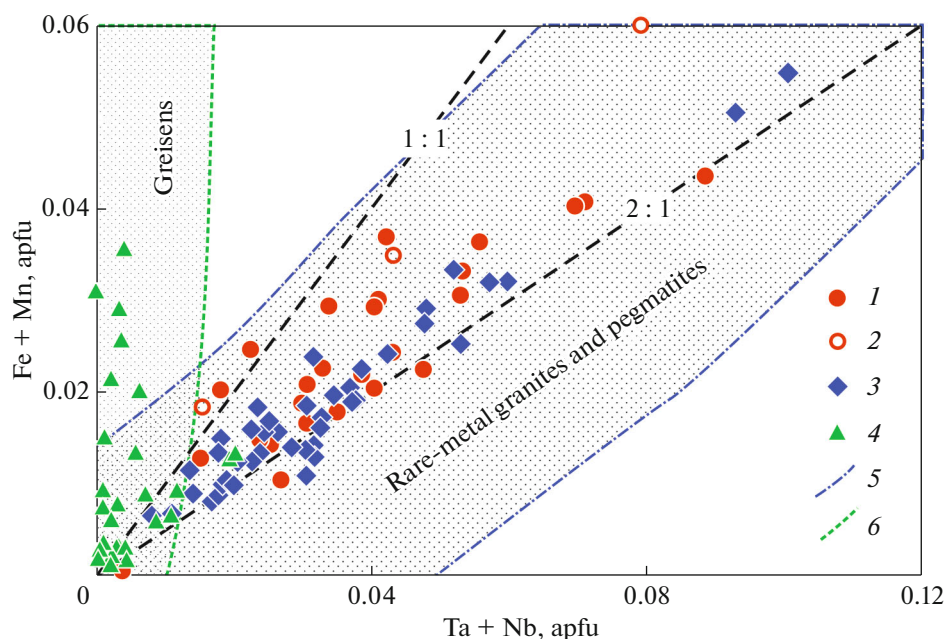


Fig. 4. (Fe + Mn) versus (Ta + Nb) plot for cassiterite from (1) rare-metal granites, (2) ongonites, (3) pegmatites, and (4) greisens over the world. The average compositions of cassiterite from various regions are shown (1759 analyses according to Tables 1–3). Fields of cassiterite from (5) rare-metal pegmatites and (6) greisens are plotted according to Tindle and Breaks (1998). Staringite is not shown (Burke et al., 1969).

Breaks, 1998; Lerouge et al., 2017; Breiter et al., 2017; Xie et al., 2015, 2018; Yan et al., 2016; Hu et al., 2021) or $\text{Sn}^{4+} + \text{O}^{2-} = \text{Fe}^{3+} + \text{OH}^-$ (Dolomanova et al., 1975; Solodov et al., 1987; Möller et al., 1988; Murciego et al., 1997; Rub et al., 1998; Makagon et al., 2001; Souza and Botelho, 2009) is possible in GrC.

Under these conditions, GrC is being enriched in Ti and W: $2\text{Sn}^{4+} + \text{O}^{2+} \leftrightarrow \text{Ti}^{4+} + \text{Fe}^{3+} + \text{OH}^-$ (Souza and Botelho, 2009; Lerouge et al., 2017; Nascimento and Souza, 2017); $\text{W}^{6+} + 2\text{Fe}^{3+} \leftrightarrow 3\text{Sn}^{4+}$ (Moore and Howie, 1979; Möller et al., 1988; Hu et al., 2021); or $2(\text{Sn}, \text{Ti})^{4+} \leftrightarrow \text{W}^{6+} + \text{Fe}^{2+}$ (Barros Neto et al., 2020). GrC is characterized by substitution $\text{Sn}^{4+} \leftrightarrow \text{Ti}^{4+}$ (Costi et al., 2000; Llorens and Moro, 2012; Chicharro et al., 2015; Lerouge et al., 2017; Llorens et al., 2017). In greisens of Massif Central and Armorican Massif, cassiterite contains $(\text{Fe}, \text{In})^{3+}$ substituting Sn: $(\text{Fe}, \text{In})^{3+} + (\text{Nb}, \text{Ta})^{5+} \leftrightarrow 2(\text{Sn}, \text{Ti})^{4+}$ (Lerouge et al., 2017). Many admixtures determined with LA-ICP-MS in GrC suggest complex substitution: $(2 - n)(\text{Nb}, \text{Ta}, \text{V})^{5+} + (1 - n)(\text{Fe}, \text{Mn}, \text{Ca}, \text{Mg})^{2+} + n(\text{Al}, \text{Sc}, \text{Fe})^{3+} \leftrightarrow (3 - n)\text{Sn}^{4+}$, where $0 \leq n \leq 1$ (Nambaje et al., 2020).

Statistical analysis of the consolidated database has supported tapiolite-type substitution in GC and PC and shown clear distinguishing magmatic and pneumatolytic cassiterite due to a different substitution mechanism. On the Tindle–Breaks diagram (Tindle and Breaks, 1998), these cassiterite varieties are characterized by trends $(\text{Ta} + \text{Nb})/(\text{Fe} + \text{Mn})$ of 2 : 1 (tapiolite substitution) and 0 : n (hydrothermal substitu-

tion). Some compositions of GrC in the pegmatite field correspond to relict protolith cassiterite (GC or PC) in greisens (Fig. 4).

However, part of the GrC compositions and all compositions from ongonite cassiterite deviate from the tapiolite trend 2 : 1 toward 1 : 1 (Fig. 4). An unbalanced increase in (Fe + Mn) can be attributed to a sharp increase in the Mn/(Mn + Fe) ratio in Ta-rich cassiterite, previously noted in rare-metal pegmatites (Fuchsloch et al., 2018; Garate-Olave et al., 2020). As is seen, this tendency is more common of ongonite and granite cassiterite (Murciego et al., 1997; Raimbault, 1998; Huang et al., 2015; Xie et al., 2015; Lerouge et al., 2017). The increased oxygen fugacity at the late stage of crystallization (Ryabchikov et al., 1984; Yang et al., 2016) and enforced hydrothermal substitution $2\text{Sn}^{4+} \leftrightarrow (\text{Ta}, \text{Nb})^{5+} + \text{Fe}^{3+}$ in GC may explain the deviation from the 2 : 1 trend. It follows that PC is more stable in terms of crystal chemistry than GC.

Limit of cassiterite isomorphous capacity. The question of the limit of the cassiterite isomorphous capacity with respect to Ta and Nb is of great theoretical and practical importance. The study of natural cassiterite shows that the high isomorphous capacity is achieved under high-temperature magmatic conditions. It has long been assumed that the cassiterite–tapiolite solid solution can be formed with the tapiolite content up to 3.86 wt % (Hutton, 1950) and up to 10.4 wt % (Quensel, 1941).

In the 1960–1980s, it was believed that the isomorphous capacity of the cassiterite structure was limited

to $n \times 0.1$ wt % $(\text{Ta}, \text{Nb})_2\text{O}_5$, and high concentrations of trace elements are associated with mineral inclusions (Kuzmenko and Eskova, 1968; Zubkov, 1971; Maksimuk, 1973; Černý and Ercit, 1985). These ideas were facilitated by the inadequacy of local analytical techniques, the small number of the samples studied, and the predominance of hydrothermal cassiterite, which is characterized by a low isomorphous capacity and abundance of mineral inclusions. Later, I.E. Maksimuk changed her opinion and gave the limit of Ta for Sn substitution in PC as up to 3 wt % Ta_2O_5 (Maksimuk et al., 1982). V.E. Zagorsky et al. noted a substitution limit up to 1.5 wt % Ta for PC from the Eastern Sayan (*Rare metal ...*, 1997).

The probable wide isomorphism of Ta, Nb, Fe in cassiterite is supported by its isostructurality with rutile, which may contain a solid solution up to 25 wt % $\text{Fe}(\text{Ta}, \text{Nb})_2\text{O}_6$ (*Minerals ...*, 1965; Sokolov and Nechelyustov, 2017). Over the past 20 years, the high miscibility of cassiterite and tapiolite has been suggested: up to 9 wt % (Masau et al., 2000), up to 10 wt % (Breiter et al., 2007; *Geochemistry ...*, 1964), up to 15 wt % (Wise and Brown, 2011), and up to 16.1 wt % (Aleksseev et al., 2020). The consolidated database makes it possible to estimate the isomorphous capacity of cassiterite to tapiolite as follows, wt %: 0.1–11.0 GC, 0.7–12.8 PC, and 0.1–3.3 GrC.

Thus, the isomorphous capacity limit of accessory cassiterite requires further investigation and ranges from 0.1 to 12.8 wt % $(\text{Fe}, \text{Mn})(\text{Ta}, \text{Nb})_2\text{O}_6$. Temperature is the main factor of the Ta and Nb solubility in cassiterite. Concentration of isomorphous admixtures in cassiterite regularly decreases by two to four orders of magnitude from accessory cassiterite to pneumatolytic and hydrothermal. At the postmagmatic stage, the facility of trace elements to incorporate into the crystal structure of the mineral decreases with temperature decreasing. High-temperature accessory cassiterite with tapiolite molecule exsolved into cassiterite and secondary inclusions of tapiolite, tantalite, and columbite when temperature drops (*Geochemistry ...*, 1964; Kuzmenko and Eskova 1968; Dolomanova et al., 1975; *Deposits ...*, 1980; Wang et al., 1987; Neuhäus and Noll, 1949; Hutton, 1950; Neiva, 1996; Tindle and Breaks, 1998; Fuchsloch et al., 2018).

Mineral inclusions in accessory cassiterite. Inclusions of Nb, Ta, Fe, Ti, and Zr minerals are one form of the trace element concentration in cassiterite. Pegmatitic cassiterite frequently contains a small number of columbite, tantalite, tapiolite, wodginite, ixiolite, and microlite grains ranging from 0.01–1 to 20 μm in size, less frequent 40–400 μm . Inclusions of rutile, ilmenorutile, strüverite, ferberite, zircon, thorite, monazite, allanite and other are also reported (Grigoriev and Dolomanova, 1951; *Minerals ...*, 1965; Kuzmenko and Eskova 1968; Barsanov and Kuznetsov, 1971; Maksimuk, 1973; Maksimuk et al., 1982; Ivanov et al., 1989; Sidorenko et al., 1992; Spilde and Shearer,

1992; *Rare-metal ...*, 1997; Tindle and Breaks, 1998; Singh et al., 2017; Petrochenkov, 2018; Kaeter et al., 2021). Cassiterite from rare metal granites is inclusion-free as usual and is saturated in isomorphous minor and trace elements (Ollila, 1986; Murciego et al., 1997; Saleh et al., 2008; Zhu et al., 2015; Breiter et al., 2017; Lerouge et al., 2017; Llorens et al., 2017; Xie et al., 2018; Cheng et al., 2019; Michaud et al., 2019; Soloviev et al., 2020; Lerouge et al., 2017). The precession scanning electron microscopy did not reveal the Ta-bearing phases even in the cassiterite crystals containing extremely high Ta, 17.9 and 18.4 wt % Ta_2O_5 , from the Kester deposit in Russia and Sungshugang deposit in China, respectively (Aleksseev et al., 2020; Zhu et al., 2015).

Many researchers observe microinclusions in accessory cassiterite without distinguishing primary minerals, exsolved products, and segregations (Amichba and Vorontsova, 1978; Černý and Ercit, 1985; Trumbull, 1995; Martins et al., 2011; Antunes et al., 2013; Singh et al., 2017; Petrochenkov, 2018; Alfonso et al., 2018). In fact, tantalite-niobate inclusions in GC and PC are resulted from the elevated Ta and Nb contents showing morphological and crystal chemical features of postmagmatic exsolutions $[\text{SnO}_2-(\text{Ta} + \text{Nb})_2\text{O}_5]$ rather than reason for these elevated concentrations (Dolomanova et al., 1969, 1975; Barsanov and Kuznetsov, 1971; Černý et al., 1985; Spilde and Shearer, 1992; Suwimonprecha et al., 1995; Neiva, 1996; Tindle and Breaks, 1998; Makagon et al., 2001; Sokolov and Nechelyustov, 2017; Llorens et al., 2017; Fuchsloch et al., 2018; Feng et al., 2019). Sidorenko et al. (1992) identified specific blocky isomorphism in cassiterite demonstrated by epitactic microintgrowths with tapiolite and columbite-(Fe).

Inclusions of early tantalite–columbite generations captured during the crystallization of GC and PC are undoubted. Such inclusions are distinguished by proper faces in combination with reabsorption and complex growth zoning reflecting compositional evolution, $\text{Ta}/(\text{Ta} + \text{Nb})$ and $\text{Mn}/(\text{Mn} + \text{Fe})$. The composition of early and secondary tantalite-niobates is clearly different: in exsolution products, the Ta/Nb ratio is usually elevated, whereas the Mn/Fe ratio is lowered (Černý and Ercit, 1985; Neiva, 1996; Sosa et al., 2002; Wise and Brown, 2011; Chicharro et al., 2015; Alfonso et al., 2018; Fuchsloch et al., 2018). The columbite inclusions in cassiterite are enriched in Sn, W, Zr, and Bi with respect to early accessory columbite, but contain less Ti, U, Y, and Ca in Varuträsk pegmatite, in Sweden, where ainalite was discovered (Černý et al., 2004). The problem of estimating the proportion of primary and secondary tantalite-niobate inclusions remains unresolved. The solution to this problem is complicated by the presence of late hydrothermal Ta and Nb oxides replacing accessory minerals (Wise and Brown, 2011).

Cassiterite from rare metal greisens as compared to GC and PC contains abundant microinclusions of wolframixiolite, wolframite, rutile, tapiolite, ilmenite, Fe-hydrostannates and Fe-stannates, which are exsolved at temperature decreasing (Grubb and Hannaford, 1966; Amichba and Vorontsova, 1978; Moore and Howie, 1979; Giuliani, 1987; Maksimuk and Voronina, 1989; Neiva, 1996, 2008; Souza and Botelho, 2009; Fuchsloch et al., 2018). Characteristically, the Ta–Nb mineral inclusions (columbite, ixiolite) in GrC contain minor W (Maksimuk et al., 1982; Maksimuk and Voronina, 1989).

ACCESSORY CASSITERITE AS A GEOCHRONOMETER

The U–Pb cassiterite age was determined for the first time in 1992. The relatively low U content requires the high-precession isotope dilution method ID-TIMS, which presupposes the complete decomposition of cassiterite for the chromatographic separation of U and Pb fractions (Gulson and Jones, 1992; Liu et al., 2007; Li et al., 2016; Deng et al., 2018). Difficult sample preparation makes it necessary to study the U–Pb system using leaching products in assumption of congruent dissolution and absence of Pb and U fractionation (Rizvanova et al., 2017). The problem of the cassiterite chemical decomposition was addressed in Russia and Australia (Rizvanova and Kuznetsov, 2020; Carr et al., 2020).

Lack of material and irregular distributed U in the structure of accessory cassiterite make it necessary to use in situ methods, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) (Chen et al., 2014; Du, 2015; Li et al., 2016; Deng et al., 2018; Cheng et al., 2019; Liu et al., 2020a; Moscati and Neymark, 2020; Zhang et al., 2020; Hu et al., 2021; Zhang and Jiang, 2021) or SIMS (Carr et al., 2017). It was established that in contrast to isostructural rutile, the isotope composition of cassiterite does not depend on the sample crystallographic orientation and can be studied in situ in random sections (Carr et al., 2017). The laboratory verification of the LA-ICP-MS data with the ID-TIMS method shows their reliability even in the case of the high Pb concentration in cassiterite (Deng et al., 2018).

Hydrothermal cassiterite is primarily dated by the U–Pb method, whereas accessory cassiterite is dated less frequent, both GC (Zhang et al., 2017; Neymark et al., 2018; Lehmann et al., 2020; Zhang and Jiang, 2021) and PC (Yan et al., 2016; Kendall-Langley et al., 2020; Liu et al., 2020a). Rare metal rocks are dated using more abundant accessory minerals, zircon, baddeleyite, allanite, and monazite, or rock-forming minerals. Nevertheless, the cassiterite dating of rare metal granites and pegmatites is promising owing to excessive enrichment of traditional mineral geochronometers in U and Pb and errors in dating of young rocks (<250 Ma). Cassiterite of the any age may

be dated, from 1500 to 23 Ma (Neymark et al., 2018; Liu et al., 2020a; Hu et al., 2021; Zhang and Jiang, 2021). For example, the stable nature of the U–Pb system in cassiterite versus that in zircon made it possible to date the tin mineralization to the Paleoproterozoic (1838 ± 34 Ma), whereas zircon from rare-metal granites of the Yazov Pluton yielded a Neoproterozoic age (719 ± 15 Ma) (Neymark et al., 2021).

ACCESSORY CASSITERITE AS AN ISOTOPIC INDICATOR OF GENESIS

In addition to the U–Pb isotope system, there were attempts to study oxygen isotopic composition of cassiterite. For example, there was an attempt to identify the source of tin-bearing fluids, which greisenized rare-metal pegmatites in the Kurnamona Province, Australia. The dependence of the $\delta^{18}\text{O}$ value on crystallographic orientation of the analyzed grains hampered the measurements (Carr et al., 2017).

The low $\delta^{18}\text{O}$ value (1.6–2.0‰) registered in cassiterite from greisenized rare metal granites of the Rondônia Province is interpreted as mixing of magmatic and meteoric water. Oxygen isotopic composition in cassiterite–quartz paragenetic assemblage was used as geothermometer: pneumatolytic cassiterite is crystallized at 420–500°C (Souza and Botelho, 2009; Nascimento and Souza, 2017). In greisen cassiterite from the Gejiu district in China the $\delta^{18}\text{O}$ is 3.17–7.67‰; i.e., it is lower than that in magmatic fluid testifying to the oxidation of pneumatolytic solutions (Zhang et al., 2020).

Owing to the Lu–Hf isotope system, cassiterite is a potential indicator of host rock genesis. For example, in cassiterite from rare metal pegmatites of Australia the Hf content reaches 243–407 ppm; the average Lu/Hf ratio is 0.0001; and the $^{176}\text{Yb}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios are very low, average values of 0.00046 ± 4 and 0.000018 ± 1 , respectively. The $^{176}\text{Hf}/^{177}\text{Hf}$ in cassiterite is 0.280885 ± 42 ; parameter $\epsilon_{\text{Hf}}(t)$ ranges from –4.0 to –0.7. This made it possible to prove comagmatic origin of LCT pegmatites and postorogenic monzogranites of the Western Australia, whose protolith was the Paleoproterozoic granites. In cassiterite from Siffleete's Reward, the $\epsilon_{\text{Hf}}(t)$ value is 2.2 that reflects pegmatite magma contaminated by radiogenic mantle matter (Kendall-Langley et al., 2020).

As mentioned above, tin occurs in rare metal magma as reduced form (Sn^{2+}) and precipitates as accessory cassiterite (Sn^{4+}O_2) during melt oxidation (Linnen et al., 1996; Bhalla et al., 2005; Yang et al., 2016). The increasing oxygen fugacity in transition to pneumatolytic and hydrothermal stages results in isotope fractionation and increasing proportion of heavy tin ^{124}Sn . In this case, the $\delta^{124}\text{Sn}$ of cassiterite is a better indicator of redox mineral-forming conditions than the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio depending on the Fe distribution

over phase and redistribution during alteration and supergene processes. The isotope composition of tin is the basis for assessing the genesis of cassiterite: magmatic, greisen, or hydrothermal, even with strong weathering. In GC of Cornwall, England, and the Ore Mountains, Czech Republic, the average $\delta^{124}\text{Sn}$ value is $0.48 \pm 0.62\text{‰}$, $n = 50$ (Yao et al., 2018).

CASSITERITE FROM RARE-METAL DEPOSITS IN EASTERN RUSSIA

Russia has the largest tin reserves, 95% of which are concentrated at deposits in the East. Greisen deposits accompanying rare metal granites and containing by-product W, Ta, In, and Sc are the largest of them. Pravourmiiskoe, Pyrkakai, Voznesenka, Tigrinoe, Odinskoe, Polyarnoe, and Kester are tin–rare metal deposits (Alekseev et al., 2019, 2020). Multiple changes in geodynamic regime resulted in advance evolution of granitoid magmatism and tin-bearing alteration are one of factors of the deposit complexity in the region (Khanchuk et al., 2004).

Special features of cassiterite from rare metal–tin deposits in the Russian Far East are similar to those of the described above GC and GrC. The major genetic features are associated with the mineral composition: species and concentration of trace elements are determined by the regional geochemical conditions, and geological type and denudation level of the deposits (Amichba and Vorontsova, 1978; Vdovina, 1987; Gavrilenko and Panova, 2001; Alekseev et al., 2019, 2020). Statistical analysis of the trace element concentration in cassiterite from the Russian Far East made it possible to establish element assemblages inherent in various deposit types formed in different geodynamic environments. Thus, mineralogical base of prognostic-genetic evaluation of tin deposits and geodynamic conditions of their formation have been improved. In particular, two indicator trace-element assemblages were identified in cassiterite from rare metal greisens of cassiterite–quartz deposits: W–Be–Sc and Be–W–In–Fe (Khanchuk et al., 2004; Gorelikova et al., 2008).

Typical features of cassiterite are widely used in exploration in Eastern Russia. The Mn/Fe and Ti/Fe, and Nb/In ratios are used to assess the denudation level of greisen (Amichba, Vorontsova, 1978) and pegmatite (Maksimyuk and Voronina, 1989) deposits, respectively. The highest Mn/Fe ratio reflects the deepest denudation, whereas the Ti/Fe reflects the shallow erosion. The Nb/Ta and Nb/In ratios are genetic proxies of cassiterite: 0.04–1.2 and >10000 in pegmatites, 0.2–4.3 and 100–600 in granites, and 15–60 and 20–30 in greisens (Bykhovsky et al., 1972; Nikulin, 1981). The Nb/In ratio regularly increases in cassiterite from top to bottom of tin bodies that allow estimation of deposit denudation level. The In content in GrC depends on the crystallization depth of ore-

bearing intrusion: it is 10–200 and 1–10 ppm in greisens associated with shallow (1.5–2 km) and deeper (2–4 km) intrusions, respectively (Nikulin, 1981).

It should be noted that associated production of rare metal at the greisens deposits of the Eastern Russia is prospective. Alekseev et al. (2020) reported the extremely high Ta content in GC from the Kester deposit in Yakutia, 5.3–17.9 wt % Ta_2O_5 . At the deposits of the Verkhneurmiskiy cluster in the Amur Region, GrC contains economic Nb, Sc, and In (Alekseev et al., 2019).

DISCUSSION

The survey shows that accessory cassiterite from rare metal pegmatites and granites is characterized by a set of common physical features: relatively large size (0.8 mm GC and 4.8 mm PC), dipyratidal habit, dark zoned coloration, dull luster, drastic pleochroism, and high density. The main features of accessory cassiterite are governed by its compositions. It is strongly enriched in Ta, Nb, Fe, Ti, Mn, and W and contains Sc, Zr, Hf and In. Tantalum, Mn, and Hf are typical admixtures. Informative ratios are Nb/Ta = 0.3–0.5, Zr/Hf = 2.1–4.8, and Fe/Mn = 4.0–4.5. The review of consolidated database highlighted differences in cassiterite features from rare metal granite, rare metal pegmatite, and greisens deposits (Tables 1–4; Figs. 1–4). It can be concluded that accessory cassiterite from granites and pegmatites is an informative mineral for the rare-metal petrogenesis and ore formation and can be considered as an economic alternative source of rare metals, tantalum, indium, and scandium. Let us highlight the most significant new results of the last thirty years in the study of accessory cassiterite.

Occurrence of typical cassiterite in rare-metal rocks. The main result of this period is the accumulation of new information on the composition and origin of accessory cassiterite, obtained with precision analytical techniques for the study of the mineral composition and structure. The obtained information made it possible to construct a consolidated database of characteristic features of high-temperature cassiterite, which helps to determine average cassiterite composition from rare metal granites, pegmatites, and greisens. Based on these data, occurrences of typical³ cassiterite of various genetic types were identified. The Beauvoir Massif in France is an occurrence of typical cassiterite. Cassiterite from the Penouta, Logrosán, and Jalama granites in Spain; Argemela Pluton in Portugal; Gebel Dihmit granite in Egypt; and Laiziling and Yifeng plutons in China is sufficiently close to typical (cf. Tables 1 and 4). The Peerless, USA and Varuträsk, Sweden complexes are occurrences of typi-

³ The tapiolite molecule content in cassiterite from various deposits has been compared with its average content in GC, PC, and GrC (Table 4) using *t*-test (reliability 95%).

cal cassiterite in rare metal pegmatites. Cassiterite from pegmatite deposits Separation Rapids in Canada, Tres Arroyos and Jalama in Spain, Karavshin in Kyrgyzstan, Dahongliutan in China, Phuket in Thailand, and Karagwe Ankole in Rwanda is close to typical PC (cf. Tables 2 and 4). The most typical cassiterite of rare metal greisens is observed at the Kester and Polyarnoe deposits in Yakutia. The Logrosán deposit in Spain, Karagwe Ankole in Rwanda, Ririwai in Nigeria, Bom Futuro in Brazil, and Montbelleux in France are comparable with occurrences of typical cassiterite (cf. Tables 3 and 4).

Rare metal rocks with Ta-bearing cassiterite.

Recent decades have brought many discoveries in the study of cassiterite-bearing rare metal rocks. The identified geochemical association of Sn with F, Li, and P (Nekrasov, 1984) is clearly reflected in relation of Ta-rich cassiterite to rare metal granites and pegmatites, among which the Li–F plumasite granites (Beskin et al., 1979; Solodov et al., 1987; Beskin and Marin, 2015) and LCT-type lepidolite pegmatites (Černý et al., 1985, 2004; Solodov et al., 1987; Raimbault, 1998; Masau et al., 2000) are predominant. Decreasing Ta and Nb contents and increasing W concentration are observed in cassiterite from spodumene pegmatites (Spilde and Shearer, 1992). Cassiterite from granites has the highest concentration of rare metals (excluding Zr and Hf) (Fig. 1).

The apparent difference in cassiterite from low- and high-phosphorus rare metal granites requires separation into lithium–fluorine and lithium–phosphorous (Taylor and Wall, 1992). Cassiterite enriched in Ta and Nb was found primarily in rare metal granites and pegmatites with the high phosphorous content ranging from 0.12 to 2.50 wt % P_2O_5 in association with amblygonite–montebrasite, fluorapatite, and lithiophilite–triphylite (Gotman, 1941; *Atlas ...*, 1977; *Deposits ...*, 1980; Černý et al., 1985; Solodov et al., 1987; Cuney et al., 1992; Spilde and Shearer, 1992; Abella et al., 1995; Raimbault, 1998; Raimbault and Burnol, 1998; Tindle and Breaks, 1998; Roda-Robles et al., 1999; Huang et al., 2002; Groat et al., 2003; Belozerovala and Makagon, 2005; Pal et al., 2007; Saleh et al., 2008; Rao et al., 2009; Martins et al., 2011; Wise and Brown, 2011; Canosa et al., 2012; Llorens and Moro, 2012; Antunes et al., 2013; Gerasimov, 2015; Chicharro et al., 2015; Yan et al., 2016; Fernandes and Moura, 2017; Hien-Dinh et al., 2017; Simons et al., 2017; Broska and Kubis, 2018; Feng et al., 2019; Goñcalves et al., 2019; Neiva et al., 2019; Xie et al., 2019; Garate-Olave et al., 2020; Michaud et al., 2020). Rare metal cassiterite is the basis of the tin–phosphorous–fluorine geochemical type of tin–rare metal mineralization (Nekrasov, 1984).

Accessory cassiterite as a rock-forming indicator.

Two generations of cassiterite are frequently observed in rare metal granites and pegmatites. Early accessory cassiterite enriched in Ta, Sc, Zr, and Hf is associated

with columbite–tantalite and tapiolite. Late greisen cassiterite enriched in Nb, Ti, and W is associated with wolframite, wolframixiolite, and sulfides. The compositional evolution accessory cassiterite followed by pneumatolytic cassiterite is established: the average Ta and Nb concentration decreases follows $GC \rightarrow PC \rightarrow GrC$ (Fig. 1) and the Nb/Ta ratio decreases from ongonites through granites to pegmatites (Figs. 2, 3).

Accessory cassiterite could be an indicator of parental rocks when identifying placer sources: (1) the Ta_2O_5 content, wt %: 0.10–18.28 GC, 0.18–21.50 PC, and 0–3.07 GrC; (2) the Fe/Mn ratio: 1.5 GC < 4.0 PC < 13.6 GrC; (3) the Nb/Ta ratio: 0.3 PC < 0.5 GC < 0.8 GrC; (4) the Zr/Hf ratio: 2.1 GC < 4.8 PC < 10.5 GrC. Ongonites are special category of cassiterite-bearing rocks, in which cassiterite is microscopic (8–50 μm) and highly enriched in Nb (Nb > Ta), W, Ti, and Sc.

Some chemical features of accessory cassiterite.

The main minor elements in accessory cassiterite are, ≥ 0.1 wt %: Ta, Nb, Fe, Mn, Ti, W; trace elements are, 50–500 ppm: Ca, Sc, Zr, Hf, In (Fig. 1). Total admixtures in cassiterite are, wt %: 6.68 (27.10) GC, 4.87 (27.33) PC, and 1.18 (6.23) GrC. Tantalum, Mn, and Hf are typical admixtures; the low Nb/Ta, Fe/Mn, and Zr/Hf ratio are characteristic. The highest Ta_2O_5 and Nb_2O_5 content are measured in GC: on average 3.42 and 1.58 wt %, respectively; they frequently increase up to 5.88–12.35 and 1.58–12.02 wt %, respectively. Tantalum dominates niobium, Nb/Ta 0.3–0.5. The Ta_2O_5 and Nb_2O_5 concentrations in PC are 3.03 and 0.90 wt % and reach 6.28–13.67 and 0.90–4.10 wt %, respectively (Tables 1, 2, 4).

Most researchers noted the high Fe content in accessory cassiterite, but the consolidated database shows that Mn-rich cassiterite is quite common in rare metal pegmatites, granites, and ongonites (Fig. 3). Minor Ti is the most characteristic of GrC (0.30 wt % TiO_2). Substantial TiO_2 in GC (up to 2.48 wt %) and PC (up to 1.64 wt %) may indicate greisen cassiterite in the sample. The Ti for Sn substitution is limited by 1–2 wt % TiO_2 . The W concentration in cassiterite from ongonites, greisens, and greisenized granites reaches 6.86, 1.61, and 1.05 wt % WO_3 , respectively (Fig. 2). If GC contains tapiolite molecule then cassiterite from greisens and ongonites probably contains molecule close to wolframixiolite molecule.

Scandium is rare in GC, 0.03 (0.95) wt % Sc_2O_3 and is much rarer in PC and GrC, 0.001 (0.07) and 0.002 (0.09) wt % Sc_2O_3 , respectively. The indium concentration in accessory cassiterite is $n \times 0.001$ g/t; GrC contains more In (0.01–1.23 wt %) (Tables 1–4). The X-ray mapping of the GC and GrC grains revealed isomorphous nature of In admixture. Zirconium and Hf are typical of accessory cassiterite, wt %: 0.01 (0.40) and 0.003 (0.24) in GC, and 0.03 (0.41) and 0.01 (0.08) in PC, respectively (Fig. 1; Tables 1, 2, 4).

Isomorphism in cassiterite and its limits. The review of the world literature suggests that high-temperature cassiterite crystallized from melt is homogeneous and is enriched in isomorphous Ta, Nb, Fe, Mn, Ti, W, Sc, Zr, and Hf. Excess Ta and Fe in the structure of accessory cassiterite or temperature decreased at postmagmatic stage of mineral-forming process results in the exsolution to form mixture of cassiterite and tantaloniobates, tapiolite, tantalite, and columbite. Microscopic and crystallographic oriented inclusions, around which cassiterite matrix is depleted in Ta, Nb, and Fe are the features of exsolved accessory cassiterite.

The consolidated database supports the major tapiolite substitution in accessory cassiterite, $3(\text{Sn}, \text{Ti})^{4+} \leftrightarrow 2(\text{Nb}, \text{Ta})^{5+} + (\text{Fe}, \text{Mn})^{2+}$. It was established that PC is more stable in term of crystal chemistry than GC, which may show trend of hydrothermal isomorphism common in GrC: $2\text{Sn}^{4+} \leftrightarrow (\text{Ta}, \text{Nb})^{5+} + \text{Fe}^{3+}$ or $\text{Sn}^{4+} + \text{O}^{2-} = \text{Fe}^{3+} + \text{OH}^-$ (Fig. 4). According to calculations, cassiterite has a high isomorphous capacity, wt % $(\text{Fe}, \text{Mn})(\text{Ta}, \text{Nb})_2\text{O}_6$: 0.1–11.0 GC, 0.7–12.8 PC, and 0.1–3.3 GrC. The limit of the cassiterite isomorphous capacity requires further research and is over the range of 0.1 to 12.8 wt % of tapiolite endmember. An extremely high Ta_2O_5 content was measured in cassiterite from rare metal pegmatites in Russia and China, 17.9 and 18.4 wt %, respectively.

Accessory cassiterite as mineral geochronometer. U^{4+} substitutes Sn^{4+} in the crystal structure of accessory cassiterite and is typomorphically important. The range of the U and Pb contents in GC is 0.5–30.0 and 2.5–4.4 ppm; in PC, 0.1–26.9 and 0.01–5.3 ppm, and in GrC, 0.09–46.6 and 0.01–7.5 ppm, respectively. A new direction of geochronology is a direct dating of mineralization and reconstruction of the of ore genesis using the U–Pb isotope system of cassiterite, which has been actively developed since 2007. Abundant cassiterite in the ores of rare metal–tin and other deposits, trace U in the mineral (0.1–50 ppm), limited isomorphous exchange of Sn^{4+} for Pb^{2+} , and physical and chemical resistance of cassiterite are prerequisites for this (Gulson and Jones, 1992; Liu et al., 2007; Li et al., 2016; Deng et al., 2018; Rizvanova and Kuznetsov, 2020; Carr et al., 2020).

Since cassiterite is formed in granites and pegmatites during transition from the late magmatic to pneumatolytic stage (Breiter et al., 2007), its dating makes it possible to estimate age of one of the earliest stages of rare metal–tin mineralization (Yan et al., 2016; Zhang et al., 2017; Neymark et al., 2018; Kendall-Langley et al., 2020; Lehmann et al., 2020). Other directions in the isotope-geochemical study of cassiterite (oxygen and tin isotopes, $^{176}\text{Lu}/^{177}\text{Hf}$) are prospective for evaluation of its origin and formation conditions, but further experiments are necessary.

Accessory cassiterite as an economic rare metal mineral. Over the past 50 years, cassiterite was

accepted as economic source of tantalum. Recently, cassiterite from greisens accompanying rare metal granites and pegmatites is considered as associated source of indium at tin deposits in Brazil, Canada, USA, and Great Britain. Value of the In-bearing cassiterite ores is increasing because host zwitterites contain additional sources of In as sulfides (roquesite, sakuraiite, sphalerite, chalcopyrite, stannite, kesterite, and other).

The recovery of rare metals (Ta, Nb, In, Sc) from cassiterite produced at greisen deposits in the Eastern Russia is promising. At the Kester deposit in Yakutia, cassiterite contains 5.3–17.9 wt % Ta_2O_5 ; at the deposits of the Verkhneurmitsky cluster in the Amur Region, cassiterite contains Nb, Sc, and In as by-products.

CONCLUSIONS

Accessory cassiterite from rare metal granites and pegmatites is dramatically different from that in greisen and hydrothermal assemblages. It is distinguished by its size, morphology, density, color, and optical and other parameters. The major indicator feature of accessory cassiterite is its chemical composition, which is determined by isomorphous admixture of Ta, Nb, Fe, Ti, Mn, W, Sc, Zr, and Hf (average 5.39 wt %) and exsolved tapiolite, tantalite, and columbite. Tantalum, Mn, and Hf are the main minor and trace elements in accessory cassiterite. Cassiterite from rare metal granites and pegmatites is characterized by the following ratios of admixtures: $\text{Nb}/\text{Ta} = 0.3\text{--}0.5$, $\text{Zr}/\text{Hf} = 2.1\text{--}4.8$, and $\text{Fe}/\text{Mn} = 4.0\text{--}4.5$.

The review of the consolidated database showed differences in cassiterite from rare metal granite, pegmatite, and greisen deposits. Thus, accessory cassiterite from granites and pegmatites is an indicator of rare metal petro- and ore genesis. The compositional evolution of cassiterite is evolved in order from granites through pegmatites to greisens: decreasing average Ta_2O_5 content ($3.42 > 3.03 > 0.29$ wt %); increasing Fe/Mn ratio ($1.5 < 4.0 < 13.6$); and increasing Zr/Hf ratio ($2.1 < 4.8 < 10.5$). The Nb/Ta ratio decreases from ongonites through granite to pegmatites. Ongonite cassiterite is drastically enriched in Nb ($\text{Nb} > \text{Ta}$) and W.

Occurrences of typical cassiterite are identified in rare metal rocks: Beauvoir granites in France; pegmatites of the Peerless and Varuträsk deposits in the US and Sweden, respectively; and greisens of the Kester and Polymoe deposits in Yakutia.

The consolidated database support the tapiolite substitution scheme in accessory cassiterite $3(\text{Sn}, \text{Ti})^{4+} \leftrightarrow 2(\text{Nb}, \text{Ta})^{5+} + (\text{Fe}, \text{Mn})^{2+}$. The calculated isomorphous capacity of the cassiterite structure is high, wt % $(\text{Fe}, \text{Mn})(\text{Ta}, \text{Nb})_2\text{O}_6$: 0.1–11.0 in rare metal granites, 0.7–12.8 in pegmatite, and 0.1–3.3 in greisens. The limit of the cassiterite isomorphous requires further

investigation and is over the range of 0.1–12.8 wt % tantalite endmember.

Tantalum-bearing cassiterite predominantly observed in rare-metal granites and pegmatites with the high P content is a basis for tin–phosphorous–fluorine type of the tin–rare metal mineralization. The content of minor Ta₂O₅ in cassiterite may reach 17.9–18.4 wt % and defines economic prospects of rare-metal granites and pegmatites. Cassiterite can be used as alternative economic source of rare metals, tantalum, indium, and scandium.

A new direction of geochronology, direct U–Pb dating of cassiterite mineralization and reconstruction of the ore-forming history, has been actively developed since 2007. Accessory cassiterite may help in dating of rare-metal granites and pegmatites, because it is not susceptible to radiation damage and disruption of the U–Pb isotope system.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

- Abella, P.A., Corbella, I., Cordon, I.M., Melgarejo, I., and Draper, J.-C., Nb–Ta-minerals from the Cap de Creus pegmatite field, eastern Pyrenees: distribution and geochemical trends, *Mineral. Petrol.*, 1995, vol. 55, pp. 53–69.
- Ahlfeld, F., Über tracht und genesis des zinnsteines, *Fortschr. Miner.*, 1931, vol. 16, p. 47–69.
- Alekseev, V.I., Marin, Yu.B., and Gavrilenko, V.V., Rare-metal mineralization of Sn occurrences in the area of Li–F granites, Verkhneurmisky ore cluster, Amur Region, *Russ. J. Pac. Geol.*, 2019, vol. 13, no. 2, pp. 120–131.
- Alekseev, V.I., Marin, Yu.B., and Galankina, O.L., An extreme concentration of isomorphic tantalum in cassiterite from lithium–fluoride granites (Arga–Ynnakh–Khayskii Massif, Yakutia), *Dokl. Earth Sci.*, 2020, vol. 490, no. 2, pp. 65–67.
- Alfonso, P., Hamid, S.A., Garcia-Valles, M., Llorens, T., Moro, F.J.L., Tomasa, O., Calvo, D., Guasch, E., Anticoi, H., Oliva, J., Parcerisa, D., and Polonio, F.G., Textural and mineral-chemistry constraints on columbite-group minerals in the Penouta deposit: evidence from magmatic and fluid-related processes, *Mineral. Mag.*, 2018, vol. 82, pp. 199–S222.
- Alfonso, P., Hamid, S.A., Anticoi, H., Garcia-Valles, M., Oliva, J., Oriol, T., López-Moro, F.J., Bascompta, M., Llorens, T., Castro, D., and Polonio, F.G., Liberation characteristics of Ta–Sn ores from Penouta, NW Spain, *Minerals*, 2020, vol. 10, no. 6.
- Amichba, T.M. and Vorontsova, L.A., Cassiterites of the tin ore deposits of Northeast Yakutia, In: *Novye dannye o mineralakh SSSR* (New Data on the Minerals of the USSR), Moscow: Nauka, 1978, vol. 26, pp. 3–14 (in Russian).
- Antunes, I.M.H.R., Neiva, A.M.R., Ramos, J.M.F., Silva, P.B., Silva, M.M.V.G., and Corfu, F., Petrogenetic links between lepidolite-subtype aplite-pegmatite, aplite veins and associated granites at Segura (central Portugal), *Chem. Erde. Geochem.*, 2013, vol. 73, no. 3, pp. 323–341.
- Artemyev, B.N., Materials on the mineralogy of cassiterite and some other pegmatite and pneumatolytic minerals, *Izv. Akad. Nauk SSSR. Otd. Matemat. Estestv. Nauk*, 1933, no. 8, pp. 1125–1144.
- Atlas mineralov I rud redkikh elementov* (Atlas of Minerals and Ores of Rare Elements), Zdorik T.B., Gorzhetskaya S.A., Kupriyanova I.I., Eds., Moscow: Nedra, 1977.
- Barros Neto, R.S.B., Lamarao, C.N., Marques, G.T., and Pinto-Coelho, C.V., Morphological and compositional study of quartz and cassiterite of the Mocambo Granite, South Para Tin Province, Amazonian Craton, *Brazilian J. Geol.*, 2020, vol. 50, no. 4, p. e20190096.
- Barsanov, G.P. and Kuznetsov, K.M., Features of cassiterite from granite pegmatites of the Central Caucasus, In: *Novye dannye o mineralakh SSSR* (New Data on the Minerals of the USSR), Moscow: Nauka, 1971, vol. 20, pp. 14–24.
- Belozeroval, O.Yu. and Makagon, V.M., Study of inclusions of tantalite-niobates in cassiterites of rare metal pegmatites by the method of electron probe microanalysis, *Analytika i Kontrol'*, 2005, vol. 9, no. 1, pp. 41–49.
- Beskin, S.M. and Marin Yu.V., Comprehensive systematics of tantalum and tantalum–niobium deposits, *Zap. Ross. Mineral. O-va*, 2015, no. 3, pp. 45–54.
- Beskin, S.M., Larin, V.N., and Marin, Yu.B., *Redkometal'nye granitovye formatsii* (Rare Metal Granite Formations), Leningrad: Nedra, 1979.
- Bhalla, P., Holtz, F., Linnen, R.L., and Behrens, H., Solubility of cassiterite in evolved granitic melts: Effect of T, fO₂, and additional volatiles, *Lithos*, 2005, vol. 80, pp. 387–400.
- Borisova, A.Y., Thomas, R., Salvi, S., Candaudap, F., Lanzanova, A., and Chmeleff, J., Tin and associated metal and metalloid geochemistry by femtosecond LA-ICP-QMS microanalysis of pegmatite–leucogranite melt and fluid inclusions: New evidence for melt–melt–fluid immiscibility, *Mineral. Mag.*, 2012, vol. 76, pp. 91–113.
- Botelho, N.F. and Moura, M.A., Granite-ore deposit relationships in Central Brazil, *J. South Am. Earth Sci.*, 1998, vol. 11, no. 5, pp. 427–438.
- Breiter, K., Škoda, R., and Uher, P., Nb–Ta–Ti–W–Sn-oxide minerals as indicators of a peraluminous P- and F-rich granitic system evolution: Podlesi, Czech Republic, *Mineral. Petrol.*, 2007, vol. 91, pp. 225–248.
- Breiter, K., Korbelová, Z., Chládek, Š., Uher, P., Knésl, I., Rambousek, P., Honig, S., and Šešulka, V., Diversity of Ti–Sn–W–Nb–Ta oxide minerals in the classic granite related magmatic–hydrothermal Cínovec/Zinnwald Sn–W–Li deposit (Czech Republic), *Eur. J. Mineral.*, 2017, vol. 29, pp. 727–738.
- Briskey, J.A., Indium in zinc–lead and other mineral deposits: a reconnaissance survey of 1118 indium analyses published before 1985, *U.S. Geol. Surv. Open-File Rept.*, 2005, no. 1209, pp. 2005–1209.
- Brodskaya, R.L. and Marin, Yu.B., Ontogenetic analysis of mineral individuals and aggregates at micro and nanolevel

- for the restoration of ore-forming conditions and assessment of mineral raw technological properties, *J. Mining Inst.*, 2016, vol. 219, pp. 369–376.
- Broska, I. and Kubis, M., Accessory minerals and evolution of tin-bearing S-type granites in the western segment of the Gemeric Unit (Western Carpathians), *Geologica Carpathica*, 2018, vol. 69, no. 5, pp. 483–497.
- Burke, E.A.J., Kieft C., Felius R.O., and Adusumili, M.S., Staringite, a new Sn-Ta mineral from northeastern Brasil, *Mineral. Mag.*, 1969, vol. 37, no. 288, pp. 447–452.
- Bykhovsky, L.Z., Novikov, V.P., and Sveshnikova, V.I., Typomorphic features of cassiterites and wolframites and their importance in the search and evaluation of ore deposits, In: *Typomorfizm mineralov i ego prakticheskoe znachenie* (Typomorphism of Minerals and its Practical Significance), Moscow: Nedra, 1972, pp. 162–168.
- Canosa, F., Martin-Izard, A., and Fuertes-Fuente, M., Evolved granitic system as a source of rare-element deposits: The Ponte Segade case (Galicia, NW Spain), *Lithos*, 2012, vol. 153, pp. 165–176.
- Carr, P.A., Norman, M.D., and Bennett, V.C., Assessment of crystallographic orientation effects on secondary ion mass spectrometry (SIMS) analysis of cassiterite, *Chem. Geol.*, 2017, vol. 467, pp. 122–133.
- Carr, P.A., Zink, S., Bennett, V., Norman, M.D., Amelin, Yu., et al., A new method for U-Pb geochronology of cassiterite by ID-TIMS applied to the Mole Granite polymetallic system, eastern Australia, *Chem. Geol.*, 2020, vol. 539, p. 119539.
- Černý, P. and Ercit, T.S., Some recent advances in the mineralogy and geochemistry of Nb and Ta in rare element granitic pegmatites, *Bull. Mineral.*, 1985, vol. 108, pp. 499–532.
- Černý, P. and Nemec, D., Pristine vs contaminated trends in Nb, Ta-oxide minerals of the Jihlava pegmatite district, Czech-Republic, *Mineral. Petrol.*, 1995, vol. 55, no. 1–3, pp. 117–129.
- Černý, P., Roberts, W.L., Ercit, T.S., and Chapman, R., Wodginite and associated oxide minerals from the Peerless pegmatite, Pennington County, South Dakota, *Am. Mineral.*, 1985, vol. 70, nos. 9–10, pp. 1044–1049.
- Černý, P., Goad, B.E., Hawthorne, F.C., and Chapman, R., Fractionation trends of the Nb- and Ta-bearing oxide minerals in the Greer Lake pegmatitic granite and its pegmatite aureole, southeastern Manitoba, *Am. Mineral.*, 1986, vol. 71, pp. 501–517.
- Černý, P., Chapman, R., Ferreira, K., and Smeds, S.-A., Geochemistry of oxide minerals of Nb, Ta, Sn, and Sb in the Varutrask granitic pegmatite, Sweden: the case of an “anomalous” columbite–tantalite trend, *Am. Mineral.*, 2004, vol. 89, pp. 505–518.
- Chen, X.-C., Hu, R.-Z., Bi, X.-W., Li, H.-M., Lan, J.-B., Zhao, C.-H., and Zhu, J.-J., Cassiterite LA-MC-ICP-MS U/Pb and muscovite $^{40}\text{Ar}/^{39}\text{Ar}$ dating of tin deposits in the Tengchong-Lianghe tin district, NW Yunnan, China, *Mineral. Deposita*, 2014, vol. 49, no. 7, pp. 843–860.
- Cheng, Y., Spandler, C., Kemp, A., Mao, J., Rusk, B., Hu, Y., and Blake, K., Controls on cassiterite (SnO_2) crystallization: Evidence from cathodoluminescence, trace-element chemistry, and geochronology at the Gejiu Tin District, *Am. Mineral.*, 2019, vol. 104, pp. 118–129.
- Chicharro, E., Martín-Crespo, T., Gómez-Ortiz, D., López-García, J.A., Oyarzun, R., and Villaseca, C., Geology and gravity modeling of the Logrosan Sn-(W) ore deposits (Central Iberian Zone, Spain), *Ore Geol. Rev.*, 2015, vol. 65, pp. 294–307.
- Clark, A.M., Fejer, E.E., Donaldson, O.J., and Silver, J., The ^{119}Sn Mössbauer spectra, cell dimensions, and minor element contents of some cassiterites, *Mineral. Mag.*, 1976, vol. 40, pp. 895–898.
- Costi, H.T., Horbe, A.M.C., Borges, R.M.K., Dall’Agnol, R., Rossi, A., and Sighinolh, G.P., Mineral chemistry of cassiterites from Pitinga Province, Amazonian craton, Brazil, *Revista Brasileira de Geociencias*, 2000, vol. 30, no. 4, pp. 775–782.
- Cuney, M., Marignac, C., and Weisbrod, A., The Beauvoir topaz–lepidolite albite granite (Massif Central, France): the disseminated magmatic Sn–Li–Ta–Nb–Be mineralization, *Econ. Geol.*, 1992, vol. 87, pp. 1766–1794.
- Deer, W.A., Howie, R.A., and Zussman, J., *Rock-Forming Minerals. Volume 5. Non-Silicates*, London–New York: Longman, 1962.
- Deng, X.-H., Chen, Y.-J., Bagas, L., Zhou, H.-Y., Zheng, Z., Yue, S.-W., Chen, H.-J., Li, H.-M., Tu, J.-R., and Cui, Y.-R., Cassiterite U–Pb geochronology of the Kekekaerde W–Sn deposit in the Baiganhu ore field, East Kunlun Orogen, NW China: Timing and tectonic setting of mineralization, *Ore Geol. Rev.*, 2018, vol. 100, pp. 534–544.
- Dolomanova, E.I., Boyarskaya, R.V., Rakcheev, A.D., Yakovlevskaya, T.A. Cassiterite and its typomorphic features. In: *Typomorfizm mineralov* (Typomorphism of Minerals), Moscow: Nauka, 1969, pp. 128–184.
- Dolomanova, E.I., Podolsky, A.M., Dobrovolskaya, H.V., Loseva, T.I., Savinsky, I.D., and Rabinovich, S.G. On the question of isomorphism in cassiterite. In: *Izomorfizm v mineralakh* (Isomorphism in Minerals), Moscow: Nauka, 1975, pp. 61–79.
- Du, S., Wen, H., Qin, C., Yan, Y., Yang, G., Fan, H., Zhang, W., Zhang, L., Wang, D., Li, H., Geng, J., and Meng, G., Caledonian ore-forming event in the Laojunshan mining district, SE Yunnan Province, China: in situ LA-MC-ICP-MS U–Pb dating on cassiterite, *Geochem. J.*, 2015, vol. 49, pp. 11–21.
- Evzikova, N.Z., *Poiskovaya kristallomorfologiya* (Prospecting Crystal Morphology) Moscow: Nedra, 1984.
- Falconer, J.D., The geology of the plateau tin deposit, *Bull. Geol. Surv. Dep. Nigeria*, 1921, no. 1, pp. 17–42.
- Farmer, C.C., Searl, A., and Halls, C., Cathodoluminescence and growth of cassiterite in the composite lodes at South Crofty Mine, Cornwall, England, *Mineral. Mag.*, 1991, vol. 55, pp. 447–458.
- Feng, Y., Liang, T., Yang, X., Zhang, Z., and Wang, Y., Chemical evolution of Nb–Ta oxides and cassiterite in phosphorus-rich albite–spodumene pegmatites in the Kangxiwa–Dahongliutan pegmatite field, Western Kunlun Orogen, China, *Minerals*, 2019, vol. 9.
- Fernandes, J. and Moura, A., Metallographic and in situ compositional study on columbite–tantalite mining concentrates from placers at Macainhas (Central-East Portugal): insights for tantalum exploration, *J. Iberian Geol.*, 2017, vol. 43, no. 3, pp. 439–450.

- Flerov, B.L., *Olovorudnye mestorozhdeniya Yano-Kolymskoi skladchatoi oblasti* (Tin Ore Deposits of the Yana–Kolyma Fold Belt), Novosibirsk: Nauka, 1976.
- Fuchsloch, W.C., Nex, P.A.M., and Kinnaird, J.A., The geochemical evolution of Nb–Ta–Sn oxides from pegmatites of the Cape Cross–Uis pegmatite belt, Namibia, *Mineral. Mag.*, 2018, vol. 83, no. 2, pp. 161–179.
- Fujiki, Y. and Suzuki, Y., Hydrothermal and flux growth of cassiterite (SnO₂) crystals, *J. Jap. Assoc. Min., Petrol. Econ. Geol.*, 1973, vol. 68, pp. 277–283.
- Gaafar, I., Geophysical mapping, geochemical evidence and mineralogy for Nuweibi rare metal albite granite, Eastern Desert, Egypt, *Open J. Geol.*, 2014, vol. 4, pp. 108–136.
- Garate-Olave, I., Roda-Robles, E., Gil-Crespo, P.P., Pesquera, A., and Errandonea-Martin, J., The Tres Arroyos granitic aplite-pegmatite field (Central Iberian Zone, Spain): Petrogenetic constraints from evolution of Nb–Ta–Sn oxides, whole-rock geochemistry and U–Pb geochronology, *Minerals*, 2020, vol. 10, no. 11, p. 1008.
- Gaskov, I.V., Vladimirov, A.G., Khanchuk, A.I., Pavlova, G.A., and Gvozdev, V.I., Features of the distribution of indium in the ores of some base metal and tin-sulfide deposits in Siberia and the Russian Far East, *Geol. Ore Deposits*, 2017, vol. 59, no. 1, pp. 62–74.
- Gavrilenko, V.V. and Panova, E.G., *Geokhimiya, genesis, i tipomorfizm mineralov mestorozhdenii olova i vol'frama*, (Geochemistry, Genesis and Typomorphism of the Minerals of Tin and Tungsten Deposits), St Petersburg: Nevsky courier, 2001.
- Geokhimiya, mineralogiya, i geneticheskie tipy mestorozhdenii redkikh metallov. T. 1. Geokhimiya redkikh elementov* (Geochemistry, Mineralogy and Genetic Types of Rare Metal Deposits. Volume 1. Geochemistry of Rare Elements), Moscow: Nauka, 1964.
- Gerasimov, V.K., Typomorphism of columbite pegmatites of the Karavshinsky field. In: *Problemy geologii i osvoeniya nedr* (Problems of Geology and Interior Exploration), Tomsk: Tomsk. Politekhn. Univ., 2015, vol. 1, pp. 95–96.
- Giuliani, G., La cassitérite zonée du gisement de Sokhret Allal (Granite des Zaër; Maroc Central): composition chimique et phases fluides associées, *Mineral. Deposita*, 1987, vol. 22, pp. 253–261.
- Gonçalves, A.O., Melgarejo, J.-C., Alfonso, P., Amores, S., Paniagua, A., Neto, A.B., Morais, E.A., and Camprubi, A., The distribution of rare metals in the LCT pegmatites from the Giraul Field, Angola, *Minerals*, 2019, vol. 9, pp. 580.
- Gorelikova N.V., Chizhova I.A., Gonevchuk V.G. Paragenesis of trace elements of cassiterite as indicators of the tin mineralization. In: *Tikhookeanskii rudnyi pojas: Materialy novykh issledovaniy* (Pacific Ore belt: New Data), Vladivostok: Dalnauka, 2008, pp. 369–382.
- Gotman, Ya.D., Typomorphic features of cassiterite of USSR tin ore deposits, *Tr. IGK Akad. Nauk SSSR*, 1941, vol. 46, no. 9, pp. 63–92.
- Grigoryev, Iv.F. and Dolomanova, E.I., New data on crystal chemistry and typomorphic features of cassiterite of different genesis, *Tr. Mineral. Muzeya Akad. Nauk SSSR*, 1951, vol. 3, pp. 73–92.
- Groat, L.A., Mulja, T., Mauthner, M.H.F., Ercit, T.S., Raudsepp, M., Gault, R.A., and Rollo, H.A., Geology and mineralogy of the little Nahanni rare-element granitic pegmatites, Northwest Territories, *Can. Mineral.*, 2003, vol. 41, pp. 139–160.
- Grubb, P.L.C. and Hannaford, P., Magnetism in cassiterite, *Mineral. Deposita*, 1966, vol. 2, pp. 148–171.
- Gulson, B.L. and Jones, M.T., Cassiterite: Potential for direct dating of mineral deposits and a precise age for the Bushveld Complex granites, *Geology*, 1992, vol. 20, no. 4, pp. 355–358.
- Haapala, I., Magmatic and postmagmatic processes in tin-mineralized granites: Topaz-bearing leucogranite in the Eurajoki Rapakivi granite stock, Finland, *J. Petrol.*, 1997, vol. 38, no. 12, pp. 1645–1659.
- Hien-Dinh, T.T., Dao, D.A., Tran, T., Wahl, M., Stein, E., and Giere, R., Lithium-rich albite-topaz–lepidolite granite from Central Vietnam: a mineralogical and geochemical characterization, *Eur. J. Miner.*, 2017, vol. 29, no. 1, pp. 35–52.
- Hu, P.C., Zhu, W.G., Zhong, H., Zhang, R.Q., Zhao, X.Y., and Mao, W., Late Cretaceous granitic magmatism and Sn mineralization in the giant Yinyan porphyry tin deposit, South China: constraints from zircon and cassiterite U–Pb and molybdenite Re–Os geochronology, *Mineral. Deposita*, 2021, vol. 56, pp. 743–765.
- Huang, F.-F., Wang, R.-C., Xie, L., Zhu, J.-C., Erdmann, S., Che, X.-D., and Zhang, R.-Q., Differentiated rare-element mineralization in an ongonite-topazite composite dike at the Xianghualing tin district, Southern China: An electron-microprobe study on the evolution from niobium-tantalum-oxides to cassiterite, *Ore Geol. Rev.*, 2015, vol. 65, pp. 761–778.
- Huang, X.L., Wang, R.C., Chen, X.M., Hu, H., and Liu, C.S., Vertical variations in the mineralogy of the Yichun topaz-lepidolite granite, Jiangxi Province, southern China, *Can. Mineral.*, 2002, vol. 40, pp. 1047–1068.
- Hutton S.O. Studies of heavy detrital minerals, *Bull. Geol. Soc. Amer.*, 1950, vol. 61, no. 7, pp. 635–710.
- Ivanov, O.P., Kushparenko, Yu.S., and Marshukova, N.K., *Tekhnologicheskaya mineralogiya olovyannykh rud* (Technological Mineralogy of Tin Ores), Leningrad: Nauka, 1989.
- Ixer, R.A. and Ashworth, J.R., and Pointer, C.M., Accessory mineralogy of the Ririwai biotite granite, Nigeria, and its albitized and greisenized facies. *Geol. J.*, 1987, vol. 22, no. S2, pp. 403–427.
- Jacobson, R.R., Notes on the occurrence of columbite in the younger granites, *Ann. Rept. Geol. Surv. Dept. Nigeria*, 1945, vol. 16, p. 26.
- Jiang, S.-Y., Yu, J.-M., and Lu, J.-J., Trace and rare-earth element geochemistry in tourmaline and cassiterite from the Yunlong tin deposit, Yunnan, China: implication for migmatitic-hydrothermal fluid evolution and ore genesis, *Chem. Geol.*, 2004, vol. 209, pp. 193–213.
- Kaeter, D., Barros, R., and Menuge, J.F., Metasomatic high field strength element, tin, and base metal enrichment processes in lithium pegmatites from Southeast Ireland, *Econ. Geol.*, 2021, vol. 116, no. 1, pp. 169–198.
- Karjakin, I.A., The nature of the variability in the properties of placer cassiterite, *J. Mining Inst.*, 1985, vol. 104, pp. 84–91.
- Kendall-Langley, L.A., Kemp, A.I.S., Grigson, J.L., and Hammerli, J., U–Pb and reconnaissance Lu–Hf isotope analysis of cassiterite and columbite group minerals from

- Archean Li–Cs–Ta type pegmatites of Western Australia, *Lithos*, 2020, vol. 352, p. 105231.
- Kesraoui, M. and Nedjari, S., Contrasting evolution of low-P rare metal granites from two different terranes in the Hoggar area, Algeria, *J. Afr. Earth Sci.*, 2002, vol. 34, pp. 247–257.
- Khanchuk, A.I., Gorelikova, N.V., Pavlovskaya-Glen, V., and Tolozana-Delgado, R., New data on the distribution of trace elements in the cassiterite of tin deposits of the Far East, *Dokl. Earth Sci.*, 2004, vol. 399, no. 1, pp. 100–103.
- Kholmogorov, A.I., Tin-bearing greisens of the North-East Yakutia (Elementary ore-igneous systems), Olovonosnye magmaticheskie I rudnye formatsii Vostochnoi Yakutii (Tin-Bearing Igneous and Ore Formations of Eastern Yakutia), Yakutsk: YaSC SB Akad. Nauk SSSR, 1989, pp. 44–56.
- Khvostova, V.A., Slesarchuk, V.S., and Laputina, I.P., The first find of staurolite in the Soviet Union, *Tr. Mineral. Muz. In. A.E. Fersmana*, 1974, vol. 23, pp. 226–228.
- Khvostova, V.A., Lebedeva, S.I., and Maksimova, N.V., Tin-bearing tantaloniobates and their typomorphic features. Rare minerals of the tin-bearing tantaloniobate group, *Int. Geol. Rev.*, 1983, vol. 25, no. 8, pp. 922–932.
- Kigai, I.N., *Problemy gidrotermal'nogo rudoobrazovaniya* (Problems of Hydrothermal Ore Formation), Moscow: MAKSS Press, 2020.
- Klementova, M. and Rieder, M., Tantaloniobates in cassiterite: inclusions or exsolutions? *Materials Structure*, 2005, vol. 12, no. 2, pp. 104–108.
- Klomínský, J., Jarchovský T., and Rajpoot, G.S., Atlas of Plutonic Rocks and Orthogneisses in the Bohemian Massif, Prague: Czech Geological Survey, 2010.
- Krivokoneva, G.K. and Sirina, T.N., X-ray signs of cassiterite affiliation, *Razved. Okhr. Nedr*, 2005, no. 4, pp. 40–45.
- Krivovichev, V.G., *Mineralogicheskii slovar'* (Glossary of Mineralogy), St. Petersburg: St. Petersburg Gos. Univ., 2009.
- Kuzmenko, M.V. and Yeskova, E.M., *Tantal i niobii* (Tantalum and Niobium), Moscow: Nauka, 1968.
- Kuzmina, I.P. and Litvin, B.N., Crystallization of cassiterite (SnO₂) under hydrothermal conditions, *Kristallografiya*, 1963, vol. 8, no. 3, pp. 478–480.
- Lehmann, B., Zoheir, B.A., Neymark, L.A., Zeh, A., Emam, A., Radwan, A.M., Zhang, R.Q., and Moscati, R.J., Monazite and cassiterite U–Pb dating of the Abu Dabbab rare-metal granite, Egypt: Late Cryogenian metalliferous granite magmatism in the Arabian-Nubian Shield, *Gondwana Res.*, 2020, vol. 84, pp. 71–80.
- Lerouge, C., Gloaguen, E., Wille, G., and Bailly, L., The distribution of In and other rare metals in cassiterite and associated minerals in Sn ± W ore deposits of the Western Variscan Belt, *Eur. J. Mineral.*, 2017, vol. 29, pp. 739–753.
- Li, C.Y., Zhang, R.Q., Ding, X., Ling, M.X., Fan, W.M., and Sun, W.D., Dating cassiterite using laser ablation ICP-MS, *Ore Geol. Rev.*, 2016, vol. 72, pp. 313–322.
- Linnen, R.L., Pichavant, M., and Holtz, F., The combined effect of $f(\text{O}_2)$ and melt composition on SnO₂ solubility and tin diffusivity in haplogranitic melts, *Geochim. Cosmochim. Acta*, 1996, vol. 60, pp. 4965–4976.
- Little, W.M., Inclusions in cassiterite and associated minerals, *Econ. Geol.*, 1960, vol. 55, no. 3, pp. 485–509.
- Liu, Y., Li, Z.-X., Li, H.-M., Guo, L.-G., Xu, W., Ye, L., Li, C.-Y., and Pi, D.-H., U–Pb geochronology of cassiterite and zircon from the Dulong Sn–Zn deposit: Evidence for Cretaceous large-scale granitic magmatism and mineralization events in southeastern Yunnan province, China, *Acta Petrol. Sinica*, 2007, vol. 23, no. 5, pp. 967–976.
- Liu, C., Wang, R.-C., Wu, F.-Y., Xie, L., Liu, X.-C., Li, X.-K., Yang, L., and Li, X.-J., Spodumene pegmatites from the Pusila pluton in the higher Himalaya, South Tibet: Lithium mineralization in a highly fractionated leucogranite batholith, *Lithos*, 2020a, vol. 358–359.
- Liu, Y., Li, J., and Chou, I.-M., Cassiterite crystallization experiments in alkali carbonate aqueous solutions using a hydrothermal diamond-anvil cell, *Am. Mineral.*, 2020b, vol. 105, no. 5, pp. 664–673.
- Llorens, T. and Moro, M.C., Oxide minerals in the granitic cupola of the Jalama Batholith, Salamanca, Spain. Part I: accessory Sn, Nb, Ta and Ti minerals in leucogranites, aplites and pegmatites, *J. Geosci.*, 2012, vol. 57, pp. 25–43.
- Llorens, G.T., Polonio, F.G., Moro, F.J.L., Fernandez, A.F., Contreras, J.L.S., and Moro, M.C.B., Tin-tantalum-niobium mineralization in the Penouta deposit (NW Spain): Textural features and mineral chemistry to unravel the genesis and evolution of cassiterite and columbite group minerals in a peraluminous system, *Ore Geol. Rev.*, 2017, vol. 81, pp. 79–95.
- Lopez-Moro, F.J., Polonio, G.F., Llorens, G.T., Contreras, J.L.S., Fernandez, A.F., and Benito, M.C.M., Ta and Sn concentration by muscovite fractionation and degassing in a lens-like granite body: The case study of the Penouta rare-metal albite granite (NW Spain), *Ore Geol. Rev.*, 2017, vol. 82, pp. 10–30.
- Ly, Z.-H., Chen, J., Zhang, H., and Tang, Y., Petrogenesis of Neoproterozoic rare metal granite-pegmatite suite in Jiannan Orogen and its implications for rare metal mineralization of peraluminous rock in South China, *Ore Geol. Rev.*, 2021, vol. 128, p. 103923.
- Lyakhovich, V.V., *Aktsessornye mineral v granitoidakh* (Accessory Minerals in the Granitoids of the Soviet Union), Moscow: Nauka, 1967.
- Makagon, V.M., Chokan, V.M., Belozeroval, O.Yu., Shmakina, B.M. Forms of entry of tantalum and niobium into cassiterites in rare metal pegmatites of the Eastern Sayan, *Obogashchenie rud*, 2001, no. 3, pp. 21–26.
- Maksimuk, I.E. and Voronina, L.B., Cassiterite, In: *Tipomorfizm mineralov* (Typomorphism of Minerals), Moscow: Nedra, 1989, pp. 204–218.
- Maksimuk, I.E., Filippova, Yu.I., and Laputina, I.P., *On the heterogeneity of the cassiterite composition. Redkie elementy v geologii* (Rare Elements in Geology), Moscow: Nauka, 1982.
- Maksimuk, I.E., *Kassiterity i vol'framity* (Cassiterites and Wolframites), Moscow: Nedra, 1973.
- Martins, T., Lima, A., Simmons, W.B., Falster, A.U., and Noronha, F., Geochemical fractionation of Nb–Ta oxides in Li-bearing pegmatites from the Barroso–Alvao pegmatite field, Northern Portugal, *Can. Mineral.*, 2011, vol. 49, pp. 777–791.
- Masau, M., Černý, P., and Chapman, R., Exsolution of zirconian–hafnian wadginite from manganoan–tantalian cassiterite, Annie Claim #3 granitic pegmatite, Southeast-

- ern Manitoba, Canada, *Can. Mineral.*, 2000, vol. 38, pp. 685–694.
- Mestorozhdeniya litofil'nykh redikh elementov* (Deposits of Lithophilic Rare Elements), Borisenko, L.F., Burkov, V.V., Kapustin, Yu.L., Eds. Moscow: Nedra, 1980.
- Michaud, J.A.S., Gumiaux, C., Pichavant, M., Gloaguen, E., and Marcoux, E., From magmatic to hydrothermal Sn–Li–(Nb–Ta–W) mineralization: The Argemela area (central Portugal), *Ore Geol. Rev.*, 2020, vol. 116, p. 103215.
- Michel-Lévy, A. and Wyart, J., Sur la production artificielle simultanee de la cassiterite, de la topaze et de la cryolite, *Bull. Soc. Franc. Min.*, 1947, vol. 70, nos. 1–6, pp. 164–167.
- Mineraly. Spravochnik. T. 2. Vyp. 2. Prostye oksidy* (Minerals. Reference Book. Vol. 2. Iss. 2. Simple Oxides, Moscow: Nauka, 1965.
- Möller, P. and Dulski, P., Fractionation of Zr and Hf in cassiterite, *Chem. Geol.*, 1983, vol. 40, pp. 1–12.
- Möller, P., Dulski, P., Szacki, W., Malow, G., and Riedel, E., Substitution of tin in cassiterite by tantalum, niobium, tungsten, iron and manganese, *Geochem. Cosmochim. Acta*, 1988, vol. 52, pp. 1497–1503.
- Moore, F. and Howie, R.A., Geochemistry of some Cornubian cassiterites, *Mineral. Deposita*, 1979, vol. 14, pp. 103–107.
- Moscatti, R.J. and Neymark, L.A., U–Pb geochronology of tin deposits associated with the Cornubian Batholith of southwest England: Direct dating of cassiterite by in situ LA-ICPMS. *Mineral. Deposita*, 2020, vol. 55, pp. 1–20.
- Murciego, A., Garcia, Sanchez A., Dusauso, Y., Martin, Pozas J.M., and Ruck, R., Geochemistry and EPR of cassiterites from the Iberian Hercynian Massif, *Mineral. Mag.*, 1997, vol. 61, no. 3, pp. 357–365.
- Nambaje, C., Eggins, S.M., Yaxley, G.M., and Sajeev, K., Micro-characterisation of cassiterite by geology, texture and zonation: A case study of the Karagwe Ankole Belt, Rwanda, *Ore Geol. Rev.*, 2020, vol. 124, p. 103609.
- Nascimento, T.M.F. and Souza, S.V., Mineralogy, stable isotopes ($\delta^{18}\text{O}$ and $\delta^{34}\text{S}$) and ^{40}Ar – ^{39}Ar geochronology studies on the hydrothermal carapace of the Igarape Mantega W–Sn Deposit, Rondonia, *Brazilian J. Geol.*, 2017, vol. 47, no. 4, pp. 591–613.
- Neiva, A.M.R., Geochemistry of cassiterite and its inclusions and exsolution products from tin and tungsten deposits in Portugal, *Can. Mineral.*, 1996, vol. 34, no. 4, pp. 745–768.
- Neiva, A.M.R., Geochemistry of cassiterite and wolframite from tin and tungsten quartz veins in Portugal, *Ore Geol. Rev.*, 2008, vol. 33, nos. 3–4, pp. 221–238.
- Neiva, A.M.R., Gomes, C.L., Silva, P.B., Gomes, M.E.P., and Santos, A.C.T., Geochemistry of granitic aplite–pegmatite dykes and sills and their minerals from the Gravano-Gouveia area in Central Portugal, *Geochemistry*, 2019, vol. 79, no. 2, pp. 221–234.
- Nekrasov, I.Ya., *Olovo v magmaticheskoy i postmagmaticheskoy protsessakh* (Tin in Magmatic and Post-Magmatic Processes), Moscow: Nauka, 1984.
- Neuhaus, A. and Noll, W., Zur Kristallchemie des Zinnsteins, *Die Naturwissenschaften*, 1949, vol. 36, no. 1, pp. 26–27.
- Neymark, L.A., Holm-Denoma, Ch.S., and Moscati, R.J., In situ LA-ICPMS U–Pb dating of cassiterite without a known-age matrix-matched reference material: Examples from worldwide tin deposits spanning the Proterozoic to the Tertiary, *Chem. Geol.*, 2018, vol. 483, pp. 410–425.
- Neymark, L.A., Holm-Denoma, C.S., Larin, A.M., Moscati, R.J., and Plotkina, Y.V., LA-ICPMS U–Pb dating reveals cassiterite inheritance in the Yazov granite, Eastern Siberia: Implications for tin mineralization, *Mineral. Deposita*, 2021, vol. 56, pp. 1177–1194.
- Nikishina, E.E. and Drobot, D.V., Niobium and tantalum: the state of the world market, applications, raw materials sources. Part 2, *Izv. Vyssh. Ucheb. Zaved., Tsvetnaya Metallurgiya*, 2014, no. 1, pp. 29–41.
- Nikulin, N.N., Some features of the chemical typomorphism of cassiterite and their use in the applied aspect. In: *Mineralogiya metamorficheskikh i rudnykh obrazovaniy Dal'nego Vostoka* (Mineralogy of Metamorphic and Ore Formations of the Far East), Vladivostok: Dal'nevost. Nauchn. Ts. Akad. Nauk SSSR, 1981, pp. 109–118.
- Ollila, J.T., Origin of colour zoning in cassiterites from tin deposits within the Bushveld complex, South Africa, *Bull. Geol. Soc. Finland*, 1986, vol. 58, no. 2, pp. 3–11.
- Pal, D.C., Mishra, B., and Bernhardt, H.-J., Mineralogy and geochemistry of pegmatite-hosted Sn, Ta–Nb–, and Zr–Hf-bearing minerals from the southeastern part of the Bastar–Malkangiri pegmatite belt, Central India, *Ore Geol. Rev.*, 2007, vol. 30, no. 1, pp. 30–55.
- Petrochenkov, D.A., Collection and jewelry cassiterites; mining prospects, *Otechestvennaya Geol.*, 2018, no. 3, pp. 68–77.
- Pieczka, A., Szuszkiewicz, A., Szeleg, E., Nejbert, K., Lodzinski, M., Ilnicki, S., Turniak, K., Banach, M., Holub, W., Michalowski, P., and Rozniak, R., (Fe,Mn)–(Ti,Sn)–(Nb,Ta) oxide assemblage in a little fractionate portion of a mixed (NYF plus LCT) pegmatite from Pilawa Gorna, the Sowia Mts. block, SW Poland, *J. Geosci.*, 2013, vol. 58, no. 2, pp. 91–112.
- Plimer, I.R., Lu, J., and Kleeman, J.D., Trace and rare earth elements in cassiterite – sources of components for the tin deposits of the Mole Granite, Australia, *Mineral. Deposita*, 1991, vol. 26, no. 4, pp. 267–274.
- Popov, S.D., The role of geoenergetic indicators Th, Nb, Zr, W and Ti in isomorphic substitutions in the crystal lattices of sphene and cassiterite, In: *Ocherki geokhimii endogennykh i gipergennykh protsessov* (Essays on the Geochemistry of Endogenous and Supergene Processes), Moscow: Nauka, 1966, pp. 39–51.
- Quensel, P., *Minerals of the Varutrask pegmatite. XXX. cassiterite and stanniferous columbite. geologiska foreningen i, Stockholm: Förhandlingar*, 1941, p. 3.
- Raimbault, L., Composition of complex lepidolite-type granitic pegmatites and of constituent columbite–tantalite, Chedeville, Massif Central, France, *Can. Mineral.*, 1998, vol. 36, pp. 563–583.
- Raimbault, L. and Burnol, L., The Richemont rhyolite dyke, Massif Central, France: A subvolcanic equivalent of rare-metal granites, *Can. Mineral.*, 1998, vol. 36, pp. 265–282.
- Rao, C., Wang, R.C., Hu, H., and Zhang, W.L., Complex internal textures in oxide minerals from the Nanping, No. 31 dyke of granitic pegmatite, Fujian province, South-eastern China, *Can. Mineral.*, 2009, vol. 47, no. 5, pp. 1195–1212.

- Redkometall'nye pegmatity* (Rare-Metal Pegmatites), Zagorsky, V.E., Makagon, V.M., Shmakin, B.M., Eds., Novosibirsk: Nauka, 1997.
- René, M., Petrology, geochemistry and mineralogy of greisens associated with tin-tungsten mineralisation: Hub stock deposit at Krasno-Horní Slavkov Ore District, Czech Republic, *Contributions to Mineralization* (IntechOpen, 2018), pp. 1–22.
- Rizvanova, N.G. and Kuznetsov, A.B., A new approach to ID-TIMS U-Pb dating of cassiterite on example of the Pitkyaranta tin deposit, *Dokl. Earth Sci.*, 2020, vol. 491, no. 1, pp. 47–51.
- Rizvanova, N.G., Skublov, S.G., and Cheremazova, E.V., Age of hydrothermal processes in the Central Iberian zone (Spain) according to U-Pb dating of cassiterite and apatite, *J. Mining Inst.*, 2017, vol. 225, pp. 275–283.
- Roda-Robles, E., Pesquera-Perez, A., Velasco-Roldan, F., and Fontan, F., The granitic pegmatites of the Fregeneda area (Salamanca, Spain): characteristics and petrogenesis, *Mineral. Mag.*, 1999, vol. 63, no. 4, pp. 535–558.
- Rub, A.K., Stempok, M., and Rub, M.G., Tantalum mineralization in the apical part of the Cinovec (Zinnwald) granite stock, *Mineral. Petrol.*, 1998, vol. 63, pp. 199–222.
- Rushton, H.G., Economic geology of the decomposed columbite-bearing granites, Jos Plateau, Nigeria, *Econ. Geol.*, 1956, vol. 51, no. 4, pp. 528–544.
- Ryabchikov, I.D., Durasova, N.A., Barsukov, V.L. Physical and chemical analysis of igneous sources of tin. In: *Istochniki veshchestva i usloviya lokalizatsii olovorudnykh mestorozhdenii* (Sources of Matter and Conditions of Localization of Tin Ore Deposits), Moscow: Nauka, 1984, pp. 57–71.
- Saleh, G.M., El Galy, M.M., and Obeid, M.A., Geochemical characteristics and spectrometric prospecting in the muscovite-bearing pegmatites and granites, southeastern Aswan, Egypt, *Chinese J. Geochem.*, 2008, vol. 27, no. 1, pp. 9–20.
- Schneider, A.A., Typomorphic properties of minerals - indicators of rich mineralization, In: *Tipomorfnyye mineraly i mineral'nye assotsiatsii—indikatory masshtabnosti prirodnnykh i tekhnogennykh mestorozhdenii i kachestva rud* (Typomorphic Minerals and Mineral Associations as Indicators of the Scale of Natural and Man-Made Deposits and the Ore Quality) Yekaterinburg: Inst. Geol. Geokhim. Ural'sk Otd. Ross. Akad. Nauk, 2008, pp. 152–154.
- Scrivenor, J.B., *The Geology of Malayan Ore Deposits*, London: Macmillan and Co, 1928.
- Shcherbakova, M.Ya., Purvinsky, O.F., and Gilinskaya, L.G., Study of natural cassiterite by electronic paramagnetic resonance. In: *Issledovanie strukturnykh osobennostei mineralov sovremennymi fiziko-khimicheskimi metodami* (Study of Structural Features of Minerals by Modern Physicochemical Methods), Novosibirsk: Nauka, 1970, pp. 104–107.
- Sidorenko, G.A., Alexandrova, I.T., and Petrova, N.V., *Tekhnologicheskaya mineralogiya redkometallnykh rud* (Technological Mineralogy of Rare Metal Ores), St. Petersburg: Nauka, 1992.
- Simons, B., Andersen, Jens C.O., Shail, R.K., and Jenner, F., Fractionation of Li, Be, Ga, Nb, Ta, In, Sn, Sb, W and Bi in the peraluminous Early Permian Variscan granites of the Cornubian Batholith: Precursor processes to magmatic-hydrothermal mineralization, *Lithos*, 2017, vol. 278, pp. 491–512.
- Sinclair, W.D., Kooiman, G.J.A., Martin, D.A., and Kjarsgaard, I.M., Geology, geochemistry and mineralogy of indium resources at Mount Pleasant, New Brunswick, Canada, *Ore Geol. Rev.*, 2006, vol. 28, no. 1, pp. 123–145.
- Singh, Y., Pandit, P.S.C., Bagora, S., and Jain, P.K., Mineralogy, geochemistry, and genesis of co-genetic granite-pegmatite-hosted rare metal and rare earth deposits of the Kawadgaon area, Bastar Craton, Central India, *J. Geol. Soc. India*, 2017, vol. 89, no. 2, pp. 115–130.
- Sokolov, S.V. and Nechelyustov, G.N., Cassiterite from rare metal pegmatites of the Otboinoe field (East Sayan). In: *Osnovnye problem v uchenii of endogennykh rudnykh mestorozhdeniyakh: novye gorizonty* (The Main Problems in the Theory of Endogenous Ore Deposits: New Horizons), Moscow: IGEM RAS, 2017, pp. 331–334.
- Solodov, N.A., Semenov, E.I., and Burkov, V.V., *Geologicheskii spravochnik po tyazhelym litofil'nykh redkim metallam* (Geological Handbook on Heavy Lithophile Rare Metals), Moscow: Nedra, 1987.
- Soloviev, S.G., Kryazhev, S., and Dvurechenskaya, S., Geology, igneous geochemistry, mineralization, and fluid inclusion characteristics of the Kougarek tin-tantalum-lithium prospect, Seward Peninsula, Alaska, USA, *Mineral. Deposita*, 2020, vol. 55, pp. 79–106.
- Sosa, G.M., Augsburger, M.S., and Pedregosa, J., Columbite-group minerals from rare metal granitic pegmatites of the Sierra de San Luis, Argentina, *Eur. J. Mineral.*, 2002, vol. 14, pp. 627–636.
- Souza, V.S. and Botelho, N.F., Composição química e isótopos de oxigênio em cassiterita e wolframita nos greisens do albita granito Palanqueta, depósito de estanho de Bom Futuro (RO), *Revista Brasileira de Geociências*, 2009, vol. 39, no. 4, pp. 695–704.
- Spilde, M.N. and Shearer, C.K., A comparison of tantalum-niobium oxide assemblages in two mineralogically distinct rare-element granitic pegmatites, Black Hills, South Dakota, *Can. Mineral.*, 1992, vol. 30, no. 3, pp. 719–737.
- Štemprok, M., Solubility of tin, tungsten and molybdenum oxides in felsic magmas, *Mineral. Deposita*, 1990, vol. 25, pp. 205–212.
- Suwimonprecha, P., Černý, P., and Friedrich, G., Rare metal mineralization related to granites and pegmatites, Phuket, Thailand, *Econ. Geol.*, 1995, vol. 90, no. 3, pp. 603–615.
- Taylor, I.R. and Wall, V.J., The behaviour of tin in granitic magmas, *Econ. Geol.*, 1992, vol. 87, pp. 403–420.
- Tindle, A.G. and Breaks, F.W., Oxide minerals of the separation rapids rare-element granitic pegmatite group, north-western Ontario, *Can. Mineral.*, 1998, vol. 36, pp. 609–635.
- Trumbull, R.B., Tin mineralization in the Archaean Since-ni rare element pegmatite field, Kaapvaal craton, Swaziland, *Econ. Geol.*, 1995, vol. 90, pp. 648–657.
- Tsareva, G.M., Naumov, V.B., Kovalenko, V.I., Tsepin, A.I., and Andreeva, I.A., Magmatic cassiterite, wolframite, columbite and wolframioxiolite in Volyn chamber pegmatites (data from the study of inclusions in topazes), *Dokl. Earth Sci.*, 1993, vol. 330, no. 3, pp. 366–368.
- Vdovina, I.A., Crystal morphology of cassiterite as one of the criteria for the economic assessment of the tin ore deposit, *Zap. Ross. Mineral. O-va*, 1987, no. 1, pp. 60–65.

- Wang, R.C., Fontan, F., and Monchoux, P., Interrelations et évolution comparée de la cassitérite et des niobotantalates dans les différents faciès du granite de Beauvoir (Massif d'Échassières): données analytiques, *Géologie de la France*, 1987, nos. 2–3, pp. 237–245.
- Weibel, M., Amblygonite, cassite rite, and associated minerals from Caceres, western Spain, *Am. Mineral.*, 1956, vol. 41, pp. 41–48.
- Wight, S.A., Vicenzi, E.P., Meier, D.C., and Benkstein, K.D., An X-ray and cathodoluminescence study of cassiterite (SnO₂), *Microscop. Microanal.*, 2010, vol. 16, pp. 804–805.
- Wille, G., Lerouge, C., and Schmidt, U., A multimodal microcharacterisation of trace-element zonation and crystallographic orientation in natural cassiterite by combining cathodoluminescence, EBSD, EPMA and contribution of confocal Raman-in-SEM imaging, *J. Microscopy*, 2018, vol. 270, no. 3, pp. 309–317.
- Williams, F.A., Meehan, J.A., Paulo, K.L., John, T.U., and Rushtan, H.G., Economic geology of the decomposed columbite-bearing granites, Jos plateau, Nigeria, *Econ. Geol.*, 1956, vol. 51, no. 4, pp. 303–332.
- Wise, M.A. and Brown, C.D., Chemical composition of coexisting columbite-group minerals and cassiterite from the Black Mountain pegmatite, Maine, *Eur. J. Mineral.*, 2011, vol. 23, pp. 817–828.
- Xie, L., Wang, R.-C., Groat, L.A., Zhu, J.-C., Huang, F.-F., and Cempirek, J., A combined EMPA and LA-ICP-MS study of Li-bearing mica and Sn-Ti oxide minerals from the Qiguling topaz rhyolite (Qitianling District, China): The role of fluorine in origin of tin mineralization, *Ore Geol. Rev.*, 2015, vol. 65, no. 4, pp. 779–792.
- Xie, L., Wang, Z.J., Wang, R.C., Zhu, J.C., Che, X.D., Gao, J.F., and Zhao, X., Mineralogical constraints on the genesis of W–Nb–Ta mineralization in the Laiziling granite (Xianghualing district, south China), *Ore Geol. Rev.*, 2018, vol. 95, pp. 695–712.
- Xie, L., Liu, Y., Wang, R., Hu, H., Che, X., and Xiang, L., Li–Nb–Ta mineralization in the Jurassic Yifeng granite-aplite intrusion within the Neoproterozoic Jiuling batholith, south China: A fluid-rich and quenching ore-forming process, *J. Asian Earth Sci.*, 2019, vol. 185, p. 104047.
- Yan, Q.-H., Qiu, Z.-W., Wang, H., Wang, M., Wei, X.-P., Li, P., Zhang, R.-Q., Li, C.-Y., and Liu, J.-P., Age of the Dahongliutan rare metal pegmatite deposit, West Kunlun, Xinjiang (NW China): Constraints from LA-ICP-MS U–Pb dating of columbite-(Fe) and cassiterite. *Ore Geol. Rev.*, 2016, vol. 100, pp. 561–573.
- Yang, Y., Zhang, Y., Simon, A., and Ni, P., Cassiterite dissolution and Sn diffusion in silicate melts of variable water content, *Chem. Geol.*, 2016, vol. 441, pp. 162–176.
- Yao, J., Mathur, R., Powell, W., Lehmann, B., Tornos, F., Wilson, M., and Ruiz, J., Sn-isotope fractionation as a record of hydrothermal redox reaction, *Am. Mineral.*, 2018, vol. 103, pp. 1591–1598.
- Zhang, R., Lehmann, B., Seltmann, R., and Li, C., Cassiterite U–Pb geochronology constrains magmatic-hydrothermal evolution in complex evolved granite systems: The classic Erzgebirge tin province (Saxony and Bohemia), *Geology*, 2017, vol. 45, no. 12, pp. 1095–1098.
- Zhang, Y.H., Zhou, J.X., Tan, S.C., Li, H.M., Hao, S., Jiang, Y.G., and He, X.H., Genesis of the oxidized Sn ores in the Gejiu district, Yunnan Province, SW China, *Ore Geol. Rev.*, 2020, vol. 121, p. 103474.
- Zhang, L. and Jiang, S.-Y., Two episodic Nb–Ta mineralization events and genesis of the Zhaojinggou rare-metal deposit, north margin of the North China Craton, *Ore Geol. Rev.*, 2021, vol. 131, p. 103994.
- Zhilinsky, G.B., Kislitsyna, V.P., Kopyatkevich, I.R., Lavrinenko, L.I., and Novitsky, Yu.V., *Iskusstvennye monokristally kassiterita* (Synthetic Monocrystals of Cassiterite), Moscow: Nauka, 1981.
- Zhu, Z.-Y., Wang, R.-C., Che, X.-D., Zhu, J.-C., Wei, X.-L., and Huang, X., Magmatic-hydrothermal rare element mineralization in the Songshugang granite (northeastern Jiangxi, China): Insights from an electron-microprobe study of Nb–Ta–Zr minerals, *Ore Geol. Rev.*, 2015, vol. 65, pp. 749–760.
- Zubkov L.B. Speciation of trace elements in cassiterites, Nauchn. Tr. Nauchn-Issled. *Proekt. Inst. Redkometal. Promyshlen.*, 1971, vol. 35, pp. 41–69.

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