



Review article

Wodginite as an indicator mineral of tantalum-bearing pegmatites and granites

Viktor I. ALEKSEEV

Saint Petersburg Mining University, Saint Petersburg, Russia

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Abstract. In the composition of tantalum-niobates the tin-bearing wodginite group minerals (WGM) were found: wodginite, titanowodginite, ferrowodginite, ferrotitanowodginite, lithiowodginite, tantalowodginite, “wolframowodginite”. We reviewed the worldwide research on WGM and created a database of 698 analyses from 55 sources including the author's data. WGM are associated with Li-F pegmatites and Li-F granites. Wodginite is the most prevalent mineral, occurring in 86.6 % of pegmatites and 78.3 % of granites. The occurrence of WGM in granites and pegmatites differs. For instance, titanowodginite and “wolframowodginite” occur three times more frequently in granites than in pegmatites, whereas lithiowodginite and tantalowodginite do not appear in granites at all. The difference between WGM in granites and pegmatites is in finer grain size, higher content of Sn, Nb, Ti, W, and Sc; lower content of Fe³⁺, Ta, Zr, Hf; higher ratio of Mn/(Mn + Fe); and lower ratio of Zr/Hf. The evolutionary series of WGM in pegmatites are as follows: ferrowodginite → ferrotitanowodginite → titanowodginite → “wolframowodginite” → wodginite → tantalowodginite; in granites: ferrowodginite → ferrotitanowodginite → “wolframowodginite” → wodginite → titanowodginite. WGM can serve as indicators of tantalum-bearing pegmatites and granites. In Russia the promising sources of tantalum are deposits of the Far Eastern belt of Li-F granites containing wodginite.

Keywords: wodginite group; titanowodginite; ferrowodginite; “wolframowodginite”; rare-metal lithium-fluoric granite; rare-metal pegmatite; tantalum; rare-metal deposits; typomorphism; isomorphism

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Introduction. The current development of metallurgy and battery industry determines steady growth in consumption of tantalum. The European Commission notes the crucial importance and the shortage of tantalum raw materials, as well as the uneven geographical distribution of its world reserves. Tantalum is on the list of strategic raw materials taken into account by the Decree of the President of the Russian Federation “On the application of special economic measures...” issued on 5 August 2022 under the sanctions regime. The increase in tantalum production is accompanied by changes in the economic geology of rare-metal raw materials. First, deposits of rare-metal Li-F granites in Egypt, China, and other countries are growing in industrial importance along with pegmatite deposits of Australia, Canada, and Brazil [1-3]. Second, economic significance of tin-tantalum ores, composed of cassiterite and wodginite, increases as well.

Wodginite is the least studied industrial mineral of tantalum. We need to systematize empirical information about it. The latest reviews on the mineralogy of wodginite for pegmatite deposits date back to 1989-1992 [4, 5]. The study of wodginite in Russia is particularly relevant, as it has been described only in four regions between 1960 and 1980 [6-8]. The study of accessory minerals provides important information on the origin of igneous rocks, their formation conditions and their correlation features with magmatic complexes of different regions [9, 10]. Therefore, methods of local analysis of substances are the key issues [11, 12]. This article is a modern scientific review of worldwide studies on wodginite group minerals (WGM) since the discovery of wodginite in 1963. The scientific novelty of the work is to generalize the latest results achieved in the 21st century, refine



earlier conclusions and analyze the possibility of using WGM as indicators of tantalum-bearing pegmatites and granites, as well as industrial sources of rare metals. We paid attention to Russian wodginite and used our own data on the Far East deposits.

Current state of research of the wodginite group minerals. Main industrial sources of tantalum are represented by tantalite – columbite minerals, microlite group minerals, Ta-cassiterite, and wodginite. Over the century and a half span of studying tantalum-niobates, a wealth of material was accumulated; a coherent classification of Ta-Nb oxides was created. The Scopus abstract database contains 634 sources on the subject, whereas only 81 of them are related to wodginite. Wodginite ($MnSnTa_2O_8$) was first described as ixiolite in 1909 from a tantalum deposit in Wodgina, Australia [13]. In 1963, E.H.Nickel and coauthors discovered a similar mineral in lithium-caesium pegmatites at the Bernic Lake deposit in Canada and named it after the place of discovery [14].

Currently wodginite is considered a title mineral of relatively rare tin-bearing tantalum-niobate minerals, which are included as accessories in the composition of rare-metal pegmatites (hereafter “pegmatites”) from Australia, Brazil, China, Central Africa, Canada, Europe, and other regions [1, 4, 15] (Table 1). During the development stage of classification, WGM were known from 37 occurrences [5]. After the discovery of wodginite-tantalum ores in the Bernic Lake mine in Canada, wodginite acquired the status of an industrial mineral. This has subsequently increased interest in WGM, and today more than 79 points of their occurrence are known [16]. We observe a gradual increase in the industrial importance of wodginite in the tantalum deposits of provinces such as Borborema in Brazil, Guarda-Belmonte in Portugal, Damara in Namibia, Kibara in DR Congo, Masvingo in Zimbabwe, Superior and Separation Rapids in Canada, Bastar-Malkangiri in India, Cathaysia in China, Balingup and Wodgina in Australia, Kalba-Narym in Kazakhstan, and others.

In 20th century, wodginite was known only from pegmatites, but since 2002, there has been a growing flow of information on accessory WGM in rare-metal lithium-fluoric granites (hereafter granites) of Algeria (Ebelekan, Filfila), Egypt (Abu Dabbab, Nuweibi, Mueilha), Spain (Penouta), China (Yichun, Dajishan), the Czech Republic (Hub) [1, 3, 17] (Fig.1, Table 2). The reasons for the late discovery of WGM in granites are the insignificant size of these minerals and their similarity to tantalite. Tantalum-bearing granites that contain wodginite have been established in the Nubian-Arabian shield in Egypt, the Maghrebian thrust belt in Algeria and Morocco, the Iberian Massif in Spain, and Cathaysia in China.

In Russia, WGM have not been studied enough: they were found only in pegmatites of the Kola Peninsula (Voron'i Tundry, Keivy), Eastern Sayan (Vishnyakovskoye, Malorechenskoye), the Urals (Taiginskoye) and Eastern Transbaikalia [18-20]. In granites from Russia, wodginite has been described only from the Voznesenskoye deposit (Primorye) [21, 22]. We established the presence of wodginite in the granites of the Kester deposit (Yakutia) [23].

Actual material and methods. The review of wodginite studies used published data for the period 1963-2022 and author's materials on rare-metal and tin deposits of the Far East of Russia and Egypt. Information on the composition, physical properties and structure of minerals is organized in the form of a summary database, which includes 470 analyses (44 sources) of WGM from pegmatites and 228 analyses (11 sources) of WGM from granites obtained mainly by the EPMA method. It should be noted that the actual number of analyses underlying the review is significantly larger, as we used representative analyses from arrays with volumes of tens and hundreds of samples from the publications. The article uses original author's data obtained during the study of granites from the Arga-Ynnakh-Khay massif in Yakutia with the Sn-Ta Kester deposit and from the Abu Dabbab and Nuweibi massifs with Sn-Ta deposits in Egypt.

The study of WGM, their occurrence statistics, composition and physical properties was assessed. A comparative analysis of parameters of identical minerals in pegmatites and granites was carried out. The data were statistically processed taking into account parameter distribution [24] using Microsoft Excel 2010 and Statistica 8.0 programs. The study of WGM properties for solving genetic problems was based on principles set out in [25].



Table 1

Chemical composition (wt.%) of wodginite group minerals in rare-metal pegmatites of the world

Deposit	N	MnO	FeO	SnO ₂	TiO ₂	Fe ₂ O ₃	Ta ₂ O ₅	Nb ₂ O ₅	Li ₂ O	WO ₃	ZrO ₂	HfO ₂	CaO	Sc ₂ O ₃	Source
Wodginite															
Keivy, Russia	1	10.88	0.54	17.50	1.45	0.33*	62.94	4.92	–	1.07	–	–	–	–	[18]
Kalba, Kazakhstan	1	10.91	3.06	10.26	0.81	3.23*	67.50	7.09	–	–	–	–	–	–	[6]
Eastern Sayan, Russia	2	7.96	–	6.66	1.58	4.37	73.20	4.56	–	–	–	–	0.81	–	[7]
Vishnyakovskoe, Russia	36	9.76	0.81	12.30	0.32	0.10*	71.03	3.06	–	0.00	–	–	0.07	–	[19]
Challanpara, India	1	9.74	1.73	11.79	1.45	0.89*	67.96	3.06	–	0.68	1.31	0.00	–	–	[26]
Seridózinho, Brazil	1	7.20	4.80	13.10	0.10	1.31*	68.40	3.50	–	–	1.50	–	–	–	[27]
Peerless, USA	4	10.30	0.28	17.10	0.10	0.45	66.50	4.30	–	–	–	–	–	–	[28]
Varuträsk, Sweden	2	10.14	0.26	10.70	0.02	–	65.34	9.70	–	0.01	2.05	0.82	0.01	–	[29]
Red Cross Lake, Canada	3	11.01	0.03	16.13	0.03	–	64.02	6.27	–	0.00	1.21	0.24	0.03	–	[30]
Wodgina, Australia	1	10.70	–	13.00	1.40	0.80	68.60	4.00	–	–	–	–	–	–	[31]
Muhembe, Rwanda	1	4.30	6.30	14.50	0.90	1.70	61.10	10.90	0.20	–	0.00	–	–	0.00	[15]
Nanping, China	1	9.00	1.30	14.00	0.10	2.00	67.00	5.90	0.17	–	0.00	–	–	0.00	[15]
Kariblb, Namibia	1	11.00	–	14.50	–	–	68.90	4.40	–	–	–	–	–	0.00	[15]
Tahara, Japan	1	9.60	1.60	7.40	4.70	0.10	71.00	0.80	–	0.60	0.20	–	–	1.70	[15]
Tanco, Canada	1	8.90	2.30	8.80	5.50	1.20	60.40	11.10	0.14	–	0.00	–	–	–	[15]
Guarda-Belmonte, Portugal	3	6.88	7.70	10.73	4.01	2.96*	59.10	11.58	–	–	–	–	–	–	[32]
La Viquita, Argentina	8	5.43	2.32	10.03	1.39	1.60	71.28	3.23	0.19	0.05	0.99	–	0.02	0.00	[33]
Leggia valley, Switzerland	2	8.40	3.79	14.53	0.54	1.43*	68.50	3.04	–	0.84	–	–	0.00	0.00	[34]
Emmons, USA	3	9.63	1.64	16.44	0.32	0.54*	69.23	3.55	0.05	–	–	–	–	–	[35]
Aclare, Ireland	1	7.73	4.89	12.78	1.18	1.53	64.35	8.65	–	–	–	–	0.09	–	[36]
Viitaniemi, Finland	1	8.80	1.20	11.80	0.30	–	70.60	5.50	–	–	–	–	1.20	–	[37]
Numbi, DR Congo	1	6.42	4.67	14.12	0.49	1.60	61.14	7.46	–	0.70	1.11	–	–	–	[38]
Pusterwald, Austria	1	8.17	5.10	15.96	0.44	2.07*	59.75	9.81	–	–	–	–	0.82	–	[39]
Annie Claim, Canada	2	10.84	1.01	14.83	0.07	0.00	62.62	7.25	–	0.11	1.85	0.45	0.01	0.00	[40]
Bernic Lake, Canada	1	9.04	1.87	13.20	2.39	0.27*	70.05	1.35	–	–	–	–	–	–	[14]
Govindpal, India	6	10.04	0.95	15.78	0.68	0.07*	65.60	4.95	–	0.17	0.35	–	0.05	–	[41]
Nanping, China	2	9.64	0.84	15.83	0.25	1.36*	67.72	4.18	0.11	0.04	–	–	–	0.17	[42]
Pendalras, India	12	8.87	2.67	12.99	0.93	0.92*	60.70	5.07	–	2.70	1.08	0.32	0.12	–	[26]
Wodgina, Australia	1	10.47	1.34	8.92	0.00	0.96*	70.49	7.63	–	–	–	–	0.42	–	[13]
Tin Mountain, USA	7	7.85	2.60	15.33	0.31	1.44	65.40	4.80	–	–	–	–	–	–	[43]
Musselwhite, Canada	5	11.05	0.29	14.36	0.55	0.48*	68.08	3.84	–	0.30	0.99	–	0.07	0.15	[44]
Rubellite Dyke, Canada	3	10.56	0.69	15.54	0.85	0.51*	68.03	3.31	–	0.14	–	–	0.02	0.18	[45]
Separation Rapids, Canada	5	9.66	1.69	15.32	0.89	1.78	62.29	6.87	0.04	1.31	–	–	–	0.02	[46]
Tanco Lower, Canada	164	8.89	2.05	13.10	2.50	1.12	64.60	6.18	0.07	0.06	–	–	–	0.15	[47]
Herbb N 2, USA	4	8.13	3.30	12.30	3.65	0.45	67.18	5.25	–	–	–	–	–	–	[48]
Titanowodginite															
Fonte del Plete, Italy	3	11.06	–	6.76	9.63	–	64.08	5.64	–	0.31	–	–	–	–	[49]
Feio, Brazil	1	0.20	12.96	2.79	10.59	0.93*	68.07	5.71	–	–	0.26	–	0.00	0.29	[50]
Nancy, Argentina	5	7.52	4.94	0.03	11.88	1.44	66.56	6.94	–	0.22	–	–	0.10	–	[51]
Separation Rapids, Canada	2	8.59	4.30	7.75	8.68	1.00	54.95	14.29	0.00	0.07	–	–	–	0.05	[46]
Ferrowodginite															
Keivy, Russia	1	0.87	17.81	10.88	0.39	7.23*	51.18	18.96	–	–	–	–	0.00	–	[18]
Eastern Transbaikal, Russia	1	6.94	5.26	9.44	0.93	7.89	63.16	7.21	–	–	–	–	–	–	[8]
Cap de Creus, Spain	1	5.25	6.29	11.82	0.53	1.92	64.90	6.63	–	–	–	–	–	–	[52]
Borborema, Brazil	3	3.16	11.07	12.40	0.82	3.01*	60.53	11.21	–	–	0.73	–	0.00	0.16	[53]
Seridózinho, Brazil	1	3.50	9.10	13.10	0.10	1.13*	59.40	12.80	–	–	1.50	–	–	–	[27]
La Viquita, Argentina	3	5.43	2.32	10.03	1.39	1.60	71.28	3.23	0.19	0.05	0.99	–	0.02	0.00	[33]
Numbi, Congo	1	5.23	6.33	12.33	2.10	2.06	56.37	10.91	–	1.69	0.69	–	–	–	[38]
Annie Claim, Canada	2	5.05	6.73	11.63	0.02	0.50	59.58	8.71	–	0.67	4.95	1.18	0.03	0.00	[40]
Pilawa Gorna, Poland	4	3.13	9.05	12.50	1.63	2.13	55.21	13.86	–	2.06	0.51	–	–	0.12	[54]
Nanping, China	6	5.36	5.94	14.54	1.16	1.72	62.13	8.08	0.01	0.02	–	–	–	0.16	[42]
Separation Rapids, Canada	4	3.00	9.13	13.02	2.44	2.32	54.85	13.53	0.01	1.58	–	–	–	0.03	[46]
Nyanga 2, Uganda	1	6.00	6.70	8.60	2.30	1.63*	68.00	7.70	–	–	–	–	–	–	[55]
Sukula, Finland	3	3.00	7.00	10.00	3.00	0.23*	62.00	12.67	–	–	–	–	–	–	[56]
Ferrotitanowodginite															
San Elias, Argentina	9	2.48	8.96	3.04	7.31	1.76	67.97	7.32	–	0.03	0.09	–	0.01	0.00	[57]
La Calandria, Argentina	7	4.58	7.29	4.57	7.90	4.31	44.04	23.62	–	1.24	0.62	–	0.02	–	[58]
Nancy, Argentina	3	3.95	8.07	0.05	9.20	2.70	71.00	4.12	–	0.07	–	–	0.18	–	[51]
Separation Rapids, Canada	2	2.57	10.39	8.23	8.37	1.05	62.99	11.97	0.00	0.03	–	–	–	0.05	[46]
“Wolframowodginite”															
Separation Rapids, Canada	5	11.57	1.23	9.37	0.70	3.75	46.27	10.39	0.06	16.01	–	–	–	0.05	[46]

Notes. The average contents are given according to sources (N – number of analyses). For samples of more than 10 tests, median contents are given [24]. Dash – no data. Fe₂O₃* – calculated value.

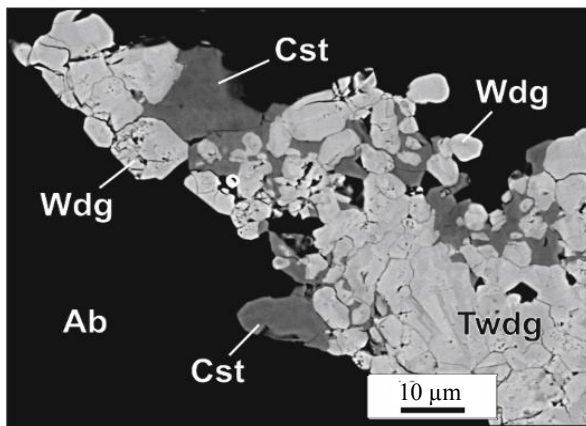


Fig. 1. Wodginite (Wdg), titanowodginite (Twdg) and cassiterite (Cst) in albitic (Ab) rare-metal granite from the Nuweibi deposit in Eastern Egypt. Image in backscattered electrons

Classification, structure and properties of minerals of the wodginite group. According to the current classification of the International Mineralogical Association (IMA) [16], the following minerals of the wodginite group are distinguished: wodginite ($MnSnTa_2O_8$) [14]; titanowodginite ($MnTiTa_2O_8$) [5]; ferrowodginite ($FeSnTa_2O_8$) [5]; ferrotitanowodginite ($FeTiTa_2O_8$) [57]; lithiowodginite ($LiTaTa_2O_8$) [59]; tantalowodginite ($(Mn_{0.5}\square_{0.5})TaTa_2O_8$) [35]; and “wolframowodginite” (unapproved mineral species) ($MnTi(Ta,W)_2O_8$) [46] (Tables 1, 2). Varieties of WGM differ in the ratio of major and minor elements ($> 0.01\%$): W, Fe^{3+} , Ca, Sc, Zr, Hf.

The history of decoding the structure of wodginite is presented in article [31]. Three positions of cations in hexagonal coordination are distinguished: *A* (Mn), *B* (Sn), and *C* (Ta). Oxygen octahedra form zigzag chains with edge joints, connected in rhythmically repeating layers of three types: *ABA* – *CCC* – *BAB* – *CCC*. General distribution of cations: ABC_2O_8 ($Z = 4$). Thus, the crystal lattice of wodginite is a derivative of a disordered lattice of ixiolite and more ordered than the columbite-tantalite lattice AB_2O_6 , consisting of layers of octahedra *ABB*. Wodginite can be considered as a maximally ordered ixiolite with an enlarged fourfold elementary cell [60-62]. This is confirmed experimentally: ixiolite containing SnO_2 (up to 19.5 %) and TiO_2 (up to 15.8 %) when heated turns into wodginite. The type of wodginite structure is intermediate between layered and framework depending on the ratio of cations in the formula ABC_2O_8 , which is reflected in the structure of lithiowodginite, where $B = C$ and the composition of the mineral is described by the formula AB_3O_8 [59].

Table 2

Chemical composition (wt.%) of wodginite group minerals in rare-metal granites of the world

Deposit	N	MnO	FeO	SnO ₂	TiO ₂	Fe ₂ O ₃	Ta ₂ O ₅	Nb ₂ O ₅	Li ₂ O	WO ₃	ZrO ₂	HfO ₂	CaO	Sc ₂ O ₃	Source
Wodginite															
Kester, Yakutia	12	9.95	3.36	11.46	1.23	1.95*	58.93	12.72	–	1.76	–	–	–	–	Author's data
Abu Dabbab, Egypt	128	10.63	1.80	13.60	2.27	1.21*	62.63	7.97	–	–	–	–	–	–	Author's data
Penouta, Spain	6	6.51	4.59	15.18	0.10	1.48	62.62	6.92	–	0.33	0.46	0.67	0.05	0.13	[63]
Greer Lake, Canada	2	10.95	0.00	15.10	0.10	0.65	67.75	3.90	–	–	–	–	–	–	[64]
Nuweibi, Egypt	3	7.38	5.14	13.23	0.38	1.45*	62.50	8.93	–	–	0.65	0.72	–	–	[65]
Ebelekan, Algeria	4	10.60	1.07	11.98	3.02	1.15	59.86	10.36	0.01	0.81	–	–	0.06	0.30	[66]
Yichun, China	5	10.16	0.82	15.46	0.76	1.18	65.47	4.87	–	0.27	–	–	–	0.45	[17]
Nuweibi, Egypt	43	10.25	1.43	13.56	0.42	1.19*	65.95	4.96	–	–	–	–	–	–	[3]
Gedongping, China	2	10.45	3.61	10.36	1.73	3.25*	64.57	6.91	–	1.16	–	–	–	0.00	[67]
Dajishan, China	2	11.54	1.27	9.52	1.05	1.66*	57.95	14.08	–	2.12	–	–	–	–	[68]
Songshugang, China	3	4.12	9.90	6.38	7.31	1.77*	53.89	15.22	0.03	1.93	–	–	–	0.21	[69]
Titanowodginite															
Voznesenskoye, Russia	1	7.90	3.70	6.90	10.90	–	51.20	16.80	–	1.90	–	–	–	–	[21]
Ebelekan, Algeria	1	9.97	2.11	7.90	8.13	0.26	57.13	11.76	0.03	1.48	0.00	0.00	0.00	0.36	[66]
Yichun, China	5	11.07	0.54	4.52	7.66	0.61	65.39	9.58	–	0.19	–	–	–	0.47	[17]
Ferrowodginite															
Hub, Czech Republic	3	5.62	6.66	9.33	2.58	1.83	57.36	10.91	–	3.36	0.29	–	–	0.16	[70]
Songshugang, China	3	4.98	11.37	5.90	4.59	3.75*	41.22	28.03	0.02	2.30	–	–	–	0.26	[69]
Ferrotitanowodginite															
Gedongping, China	2	4.43	9.29	8.19	5.01	2.18*	54.91	12.75	–	2.10	–	–	–	0.00	[67]
Nuweibi, Egypt	2	6.30	6.20	11.73	3.48	0.73*	58.75	13.00	–	–	–	–	–	–	Author's data
“Wolframowodginite”															
Songshugang, China	3	8.33	8.85	4.35	1.68	0.43*	38.97	17.98	0.21	18.39	–	–	–	0.79	[69]

* See notes to Table 1.



Isomorphism of the WGM. Polyelemental isomorphism in three positions of the crystalline structure *A*, *B* and *C* determines the difference between mineral species of WGM: $A = (\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Li}, \text{Ca}, \square)$, $B = (\text{Sn}^{4+}, \text{Ti}, \text{Fe}^{3+}, \text{Ta}, \text{Sc}, \text{Zr})$, $C = (\text{Ta}, \text{Nb}, \text{W}^{6+})$ [4, 15, 60]. Position *A* is occupied in wodginite and titanowodginite (> 50 %) by Mn cations which are replaced by Fe^{2+} cations in appropriate conditions to form ferrowodginite and ferrotitanowodginite [15]. The characteristic feature of the low-valent position *A* is the presence of a significant number of vacancies that compensate for the excess charges of high-valent cations (Ta^{5+} , W^{6+}) populating positions *B* and *C* in tantalowodginite, lithiowodginite and “wolframowodginite” [15, 29, 63] (Tables 1, 2). Position *B* in WGM is crystallographically unstable due to competition between heterovalent cations Sn^{4+} , Ti^{4+} , Fe^{3+} , Ta^{5+} , Sc^{3+} , Zr^{4+} . The composition of the octahedral layer *B* is of great importance for the classification of WGM and genetic studies [59, 46, 60]. Tin plays a major crystallographic role – an activator of the polymorphic transformation of the disordered ixiolite structure into an ordered wodginite structure. Upon heating ixiolite with SnO_2 content < 0.2 %, rhombic columbite-tantalite is formed, and with $\text{SnO}_2 \geq 9\text{-}10\%$ – monoclinic wodginite [59]. Tin substitutes in the wodginite structure are Ti, Fe^{3+} , Ta, Sc, Zr [8, 71] (Tables 1, 2).

In tantalum-niobates, titanium usually plays a large role but in WGM the isomorphism $\text{Ti} \leftrightarrow \text{Ta}$ is limited. The most effective way to incorporate Ti into the structure is $\text{Ti}^{4+} \leftrightarrow \text{Sn}^{4+}$ with the formation of titanowodginite [15, 60] (Tables 1, 2, Fig.1). The main scheme of isomorphism in the series tantalite \rightarrow wodginite, titanowodginite \rightarrow microlite: ${}^A[\text{Fe}, \text{Mn}]^{2+} + 2{}^C[\text{Nb}, \text{Ta}]^{5+} \leftrightarrow 3{}^B[\text{Sn}, \text{Ti}]^{4+}$ [27, 28]. Wodginite and titanowodginite differ sharply in concentration of SnO_2 and TiO_2 , indicating possibly a miscibility gap between WGM with compositions $(\text{Fe}, \text{Mn})\text{SnTa}_2\text{O}_8$ and $(\text{Fe}, \text{Mn})\text{TiTa}_2\text{O}_8$ but requiring further study [17].

Since wodginite is formed under oxidizing conditions, a small part of iron in it is in the form of Fe^{3+} cations [4, 70, 71] (Tables 1, 2). The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in wodginite has a higher value than in tantalite [41]. Sn^{4+} and Fe^{3+} cations are interchangeable in the structure of wodginite and in the absence of tin, its role is played by Fe^{3+} [8, 61, 62]. In iron-bearing varieties of WGM – ferrowodginite, ferrotitanowodginite, “wolframowodginite” – electron neutrality is achieved by occupying position *B* of a part of tantalum cations: $2{}^B[\text{Sn}^{4+}] \leftrightarrow {}^B[\text{Fe}^{3+}] + {}^B[\text{Ta}^{5+}]$ [15, 59].

In all types of pegmatites, especially tantalum wodginite and lithiowodginite, there is an excess of cations (Ta + Nb) in position *C*, reaching up to 3.7 cations per formula unit [15, 60]. Ta is introduced into position *B* (Table 3) according to the scheme: $2{}^B\text{Ta}^{5+} + {}^A\square \leftrightarrow {}^A\text{Mn}^{2+} + 2{}^B\text{Sn}^{4+}$ [41]. In lithiowodginite, the excess of positive charge of Ta^{5+} cations in position *B* is regulated by the mechanism: ${}^A[\text{Mn}^{2+}] + {}^B[\text{Sn}^{4+}] \leftrightarrow {}^A[\text{Li}^+] + {}^B[\text{Ta}^{5+}]$ [15].

In position *C*, Ta and Nb dominate, forming layers of NbO_6 and TaO_6 octahedra, the most stable element of the layered structure of pegmatites. The predominance of undistorted Ta-O octahedra is the key to the highly ordered structure of wodginite [59]. Isomorphism $\text{Ta} \leftrightarrow \text{Nb}$ is limited by a value of 8 cations per formula unit [15, 60]. Tungsten can settle in position *C* [59]. The structural similarity between wodginite and wolframite has been experimentally confirmed [72]. The presence of a significant impurity WO_3 in wolframite and its correlation with $(\text{FeO} + \text{Fe}_2\text{O}_3)$ content has been noted in granites [63, 68] and pegmatites [26, 46]. The hypothesis has been put forward about the existence of “wolframowodginite”, described in pegmatites of the Separation Rapids deposit in Canada [46] and in granites of Songshugang deposit in China [69]. For iron-bearing varieties of WGM, a mechanism for settling tungsten has been proposed: ${}^B[\text{Sn}^{4+}] + {}^C[\text{Ta}^{5+}] \leftrightarrow {}^B[\text{Fe}^{3+}] + {}^C[\text{W}^{6+}]$; for manganese-bearing varieties: ${}^B[\text{Sn}^{4+}] + 2{}^C[\text{Ta}^{5+}] \leftrightarrow {}^B[\text{Mn}^{2+}] + 2{}^C[\text{W}^{6+}]$; for lithium-bearing wodginite: $2{}^A[\text{Li}^+] + 2{}^A[\text{Mn}^{2+}] \leftrightarrow {}^C[\text{W}^{6+}]$ [46] (see Tables 1, 2).

Physical properties of WGM. The properties of WGM have been studied mainly on the example of wodginite from pegmatites. It is represented by hypidiomorphic prismatic and wedge-shaped crystals of dark reddish-brown or black color; its lustre is greasy and semi-metallic. Often the mineral forms irregular segregations in the interstices of feldspar, albite and mica or microinclusions in columbite-tantalite, cassiterite, microlite. The sizes of WGM crystals in pegmatites vary from 2-10 microns in microinclusions to 13 cm in albite aggregates, averaging ≈ 1 cm. In granites, the grain sizes are significantly smaller: 1-100 microns, on average 27 microns.



Table 3

Distribution of main cations in the structure of wodginite group minerals in rare-metal pegmatites and granites of the world

Cation in position	Wodginite				Titanowodginite				Ferrowodginite				Ferrotitanowodginite			
	Me (612)	Min	Max	IQR	Me (18)	Min	Max	IQR	Me (36)	Min	Max	IQR	Me (17)	Min	Max	IQR
Pegmatites																
A: Mn	0.86	0.38	1.03	0.20	0.66	0.02	0.94	0.29	0.35	0.07	0.67	0.22	0.28	0.20	0.37	0.14
Fe ²⁺	–	–	0.42	0.11	–	–	1.05	0.35	–	–	0.93	0.61	–	–	–	0.00
Li	–	–	0.04	0.00	–	–	–	0.00	–	–	0.01	0.00	–	–	–	0.00
B: Sn	0.58	0.30	0.75	0.15	0.19	–	0.30	0.20	0.51	0.36	0.62	0.10	0.15	–	0.30	0.11
Ti	0.06	–	0.42	0.10	0.75	0.62	0.87	0.09	0.09	–	0.23	0.14	0.58	0.57	0.72	0.05
Fe ³⁺	0.07	–	0.37	0.10	0.07	–	0.11	0.03	0.16	–	0.68	0.08	0.17	0.07	0.31	0.12
Ta	0.20	0.09	0.50	0.09	0.05	0.02	0.08	0.02	0.22	0.15	0.34	0.11	0.20	0.09	0.25	0.04
C: Ta	1.79	1.51	1.77	0.21	1.71	1.41	1.71	0.10	1.49	1.22	1.63	0.29	1.55	1.05	1.75	0.45
Nb	0.24	0.04	0.52	0.16	0.28	0.25	0.62	0.13	0.52	0.24	0.85	0.23	0.42	0.19	1.02	0.33
W	–	–	0.08	0.00	–	–	0.01	0.00	–	–	0.05	0.02	–	–	0.03	0.01
Granites																
A: Mn	0.93	0.33	1.03	0.17	0.82	0.62	0.93	0.16	0.44	0.39	0.50	0.06	0.46	0.38	0.54	0.08
Fe ²⁺	0.06	–	0.66	0.12	–	–	0.28	0.14	0.30	–	0.61	0.30	0.54	0.46	0.62	0.08
Li	–	–	0.01	0.00	–	–	0.01	0.00	–	–	–	0.00	–	–	–	0.00
B: Sn	0.56	0.24	0.67	0.16	0.25	0.18	0.31	0.06	0.30	0.22	0.39	0.09	0.40	0.33	0.47	0.07
Ti	0.08	0.01	0.53	0.11	0.59	0.57	0.75	0.09	0.26	0.20	0.32	0.06	0.32	0.26	0.38	0.06
Fe ³⁺	0.12	0.05	0.26	0.03	0.02	–	0.05	0.02	0.20	0.14	0.26	0.06	0.11	0.06	0.17	0.06
Ta	0.23	0.11	0.36	0.07	0.06	0.02	0.19	0.08	0.25	0.25	0.25	0.00	0.17	0.15	0.19	0.02
C: Ta	1.58	1.29	1.69	0.07	1.46	1.26	1.57	0.24	1.08	0.78	1.39	0.31	1.39	1.36	1.41	0.04
Nb	0.40	0.20	0.66	0.22	0.52	0.43	0.70	0.14	0.84	0.52	1.16	0.32	0.59	0.58	0.59	0.00
W	0.01	–	0.06	0.04	0.04	–	0.05	0.02	0.07	0.05	0.09	0.02	0.03	–	0.06	0.03

Notes. The formula coefficients of cations (f.c.) in positions A, B, C, calculated for the formula ABC_2O_8 are given. Dash – f.c. < 0.005. Me – median value of f.c. (in parentheses – number of samples). Min and Max – minimum and maximum values of f.c. IQR – interquartile range of f.c. [24].

The syngony of WGM is monoclinic ($C2/c$). Simple and polysynthetic twins are characteristic. Cleavage is imperfect. Density ranges from 7.03 to 7.81 g/cm³; hardness is between 5.5 and 6. Optical properties: $N_p = 2.14-2.20$, $N_g = 2.23-2.27$, $\Delta = 0.07-0.09$, (+), $c:N_g = 26^\circ$. Under the microscope, it shows pleochroism from light yellow to reddish-brown; has a concentric-zonal and sectoral coloration [4, 7, 16].

Minerals of the wodginite group – indicators of tantalum-bearing pegmatites and granites.

Parent rocks and paragenesis of WGM. In the past two decades, researchers have identified two types WGM with industrial application in tantalum-bearing pegmatites and granites. This has prompted the investigation of the typomorphic features of these WGM in relation to their host rocks. Wodginite and other WGM occur as accessory minerals in rare-metal lithium-mica pegmatites of the Li-Cs-Ta geochemical type (LCT pegmatites) [29, 73]. Given the important role of fluorine in rare-metal pegmatite mineralization [29, 30, 69], parent rocks with WGM can be called lithium-fluoric pegmatites. Intrusive and exocontact bodies of pegmatites at deposits such as Wodgina (Australia), Bernic Lake (Canada), Koktogai (China), Bikita (Zimbabwe), Varuträsk (Sweden), Vishnyakovskoe (Russia) and others are located on crystalline shields, in Caledonian and Hercynian folded structures and have Precambrian or Paleozoic age [1, 4, 7]. Mesozoic and Cenozoic pegmatites containing wodginite are also found [34, 35].

Minerals of the wodginite group are concentrated in lepidolite- and muscovite-albite aggregates of intermediate zones, less often in quartz cores and miarolitic cavities of pegmatites. The following accessory and industrial minerals are observed in the composition of pegmatites: ambligonite-mon-tebrasite, pollucite, spodumene, petalite, garnet (spessartine-almandine), tourmaline (schorl-elbaite), beryl, topaz, lithiophilite, triphylite, triplite, eosphorite, eucryptite, chrysoberyl, ilmenite, zircon, thorianite, uraninite, monazite, xenotime, Be-silicates (bertrandite, bavenite, milarite, helvine), sulfides



(arsenopyrite, lollingite, herzenbergite, stannite, kesterite, molybdenite). Ta-cassiterite, apatite-(CaF), Hf-zircon and tantalum-niobates: tantalite-(Mn), columbite-(Mn), ixolite, minerals of the microlite group, tapiolite are constant companions of WGM. Other Ta-Nb oxides such as Ta-rutile, ilmenorutile, rynersonite, fersmite, euxenite-(Y), polycrase-(Y), tantite, simpsonite, uranmicrolite, stibiomicrolite, pyrochlore, samarskite, fergusonite are occasionally encountered. Some companion minerals (cassiterite, tapiolite, minerals of the microlite group, minerals of the tantalite – columbite series, and others) accompany WGM by replacing them [1, 43, 47]. Parallel and irregular intergrowths of WGM with tapiolite [27, 47, 51], rhythmically-zonal intergrowths with tantalite-(Mn) [32, 37, 45] are described; rims and inclusions of wodginite in Ta-rutile [51, 53, 58] are common. The co-occurrence of wodginite and other WGM – titanowodginite, ferrowodginite, tantalowodginite, ferrotitanowodginite – is not uncommon. It has been described in pegmatites of Argentina (San Elías, La Calandria, Nancy), Brazil (Roncadeira, Seridózinho), India (Govindpal), Canada (Bernic Lake, Separation Rapids, Peerless, Annie Claim), China (Nanping), DR Congo (Numbi), Poland (Pilawa Gorna) and USA (Emmons) [1, 40, 46]. The relationship between WGM species is poorly studied.

Wodginite occurs as inclusions in cassiterite pegmatites that reflect the composition of impurities in the host mineral. This suggests that wodginite-cassiterite solid solution is breaking down [2, 32, 54]. Wodginite in cassiterite is xenomorphic, predominantly homogeneous; inclusions are found along networks of tantalum-enriched zones separated by depleted cassiterite zones [40]. Submicroscopic (< 0.1 µm) segregations of tantalates (ferrowodginite, tapiolite-(Fe), columbite-(Mn) – products of the breakdown of the discredited “staringite” solid solution) are described in cassiterite [53]. The growth zonality from the core to the periphery of Ta, Mn, Sn, Nb, Fe and Ti content serves as an indicator of primary accessory wodginite [32, 59, 66].

In recent years, WGM has been found in tantalum-bearing granites of Li-F geochemical type at deposits in Nuweibi (Egypt), Yichun (China), Penouta (Spain), Voznesenskoye (Russia), etc. (Fig. 1). The granites form small Phanerozoic intrusions in Hercynian and Mesozoic folded formations [65, 69, 74]. Minerals of the wodginite group are part of light-colored quartz-microcline-albite aggregates with a “snowball” structure including topaz, fluorite, spessartine, tourmaline, beryl, amblygonite-montebrasite, and others. Accessory minerals are constant companions of wodginite in granites: columbite-(Mn), tantalite-(Mn), Ta-cassiterite, microlite, apatite-(CaF), Hf-zircon. This association sometimes includes tapiolite-(Fe), stibiotantalite, wolframite, monazite, xenotime, pyrophanite, U-thorite, uraninite, euxenite, polycrase-(Y), Fe and Mn oxides, sulfides (pyrite, galena, sphalerite, bismuthinite). The combination of wodginite and titanowodginite in granites is quite rare [17, 66, 67] (Fig. 1). The same situation applies to wodginite, ferrowodginite and “wolframowodginite” [69]. Crystal aggregates (inclusions, overgrowth, etc.) of WGM with cassiterite and tantalite-(Mn) are typical of granites [3, 75, 76]. Minerals of the wodginite group form rims in tantalite-(Mn) [65] and Ta-rutile [21]; development of wodginite along the growth surfaces of Ta-rutile has been described, which emphasizes a sectoral structure of the latter [74].

Thus, WGM are associated with Li-F pegmatites and Li-F granites that are part of similar parageneses: Ta-cassiterite, apatite-(CaF), Hf-zircon, tantalite-(Mn), columbite-(Mn), ixolite, minerals of microlite group, tapiolite, and WGM. An assessment of the relative occurrence of WGM based on literature data showed that wodginite predominates significantly in pegmatites: wodginite – 86.6 %; ferrowodginite – 6.4 %; titanowodginite – 2.4 %; ferrotitanowodginite – 2.8 %; “wolframowodginite” – 0.9 %; tantalowodginite – 0.9 %; lithiowodginite – 0.2 %. The occurrence of WGM in granites is noticeably different. With a leading role of wodginite in granites, titanowodginite and “wolframowodginite” are three times more common in granites, and lithiowodginite and tantalowodginite are not found at all: wodginite – 78.3 %; titanowodginite – 7.6 %; ferrowodginite – 6.5 %; ferrotitanowodginite – 4.4 %; “wolframowodginite” – 3.3 % (Fig. 2). In general, among WGM, wodginite is the most common: 86.6 % in pegmatites and 78.3 % in granites.

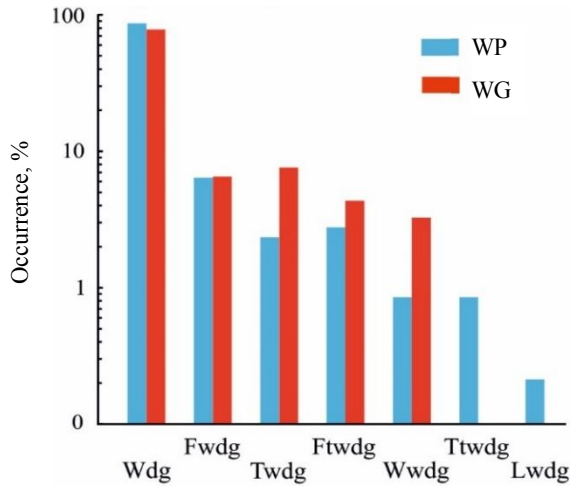


Fig.2. Relative occurrence of minerals of the wodginite group in rare-metal pegmatites (WP) and granites (WG) of the world: Fwdg – ferrowodginite, Ftwdg – ferrotitanowodginite, Wwdg – “wolframowodginite”, Ttwdg – tantalowodginite, Lwdg – lithiowodginite

Chemical composition of minerals of the wodginite group in pegmatites and granites. When comparing wodginite minerals in pegmatites and granites, their chemical composition is the most informative. The main components of wodginite are Ta, Sn, Nb, Mn, Fe²⁺, Ti, Li, W. The most important impurity elements (> 0.01 %) are Ca, Sc, Zr, Hf (see Tables 1, 2). Based on a database, the composition of mineral species of the wodginite was calculated (Tables 3, 4). Data on small concentrations of non-formulaic elements – F, Na, Mg, Al, Si, Zn, As, Sr, Y, Sb, REE, Pb, Bi, Th, U [16], that could be the result of microlite substitution [46, 51, 58], capture of mineral inclusions by microprobe and other analytical errors [3, 26, 65], were not taken into account in the calculations. Our review shows a satisfactory correspondence of published compositions of wodginite minerals (see Tables 1 and 2) to the

classification of MMA minerals [16] (Fig.3). Three trends in the symbate changes in atomic quantities of Ta and Mn cations of wodginite during differentiation of pegmatites and granites have been established. A series of wodginite evolution in pegmatites is as follows: ferrowodginite → ferrotitanowodginite → titanowodginite → “wolframowodginite” → wodginite → tantalowodginite. In granites it is as follows: ferrowodginite → ferrotitanowodginite → “wolframowodginite” → wodginite → titanowodginite. It is characteristic that the composition points of the iron-bearing wodginite species occupy the field of mixing gap between tapiolite-(Fe) and tantalite-(Fe) (Fig.4), which is noted in article [53].

Table 4

Variations of main components in minerals of the wodginite group in rare-metal pegmatites and granites of the world

Component	Wodginite			Titanowodginite			Ferrowodginite			Ferrotitanowodginite			“Wolframowodginite”		
	Me (612)	Min	Max	Me (18)	Min	Max	Me (36)	Min	Max	Me (17)	Min	Max	Me (7)	Min	Max
Pegmatites															
MnO	9.19	4.30	12.40	7.73	0.20	11.29	4.22	0.67	6.94	3.73	0.67	7.10	10.74	8.55	16.54
FeO	1.39	0.00	10.86	4.86	0.00	12.96	7.40	0.54	17.81	7.34	5.43	10.91	0.00	0.00	3.10
SnO ₂	13.58	6.22	19.20	2.79	0.00	8.65	12.54	8.13	18.80	5.89	0.00	8.94	8.10	4.85	17.50
TiO ₂	0.49	0.00	5.50	10.62	7.52	12.95	1.29	0.01	6.48	7.00	5.77	12.99	0.08	0.05	1.80
Fe ₂ O ₃	0.00	0.00	4.72	1.02	0.00	2.19	1.62	0.00	7.89	2.61	0.44	7.83	2.58	0.33	7.05
Ta ₂ O ₅	67.17	55.55	85.04	65.18	53.68	68.95	60.13	48.78	68.00	49.38	38.90	75.02	44.55	34.67	62.94
Nb ₂ O ₅	4.62	0.00	14.47	6.64	4.08	15.66	10.33	3.83	18.96	19.77	2.78	26.72	7.27	4.00	17.97
Li ₂ O	0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.00	0.11	0.00	0.00	0.11	0.00	0.00	0.16
WO ₃	0.00	0.00	3.82	0.14	0.00	0.58	0.00	0.00	3.25	0.62	0.00	2.42	12.54	1.07	34.63
Granites															
MnO	10.28	3.95	12.55	11.04	7.90	11.30	5.36	4.27	6.15	5.32	4.34	6.49	7.77	5.93	11.29
FeO	1.59	0.00	10.46	0.57	0.36	3.70	9.11	5.46	11.91	7.85	5.92	9.36	8.76	7.19	10.61
SnO ₂	13.58	4.50	17.31	5.05	3.73	7.90	7.47	3.23	11.48	9.53	6.97	13.80	3.77	0.86	8.42
TiO ₂	1.55	0.00	7.55	7.92	7.12	10.90	3.14	1.83	6.20	4.30	2.41	5.97	0.79	0.79	3.45
Fe ₂ O ₃	0.00	0.00	3.52	0.68	0.00	0.72	0.82	0.00	1.97	0.00	0.00	0.00	0.00	0.00	0.00
Ta ₂ O ₅	63.21	47.32	71.00	67.86	51.20	66.04	53.95	31.10	58.47	57.36	53.50	59.09	35.33	34.69	46.89
Nb ₂ O ₅	7.63	1.20	20.94	10.14	8.07	16.80	14.75	9.97	38.59	13.00	11.77	13.72	19.89	13.49	20.57
Li ₂ O	0.00	0.00	0.09	0.00	0.00	0.03	0.00	0.00	0.06	0.00	0.00	0.00	0.18	0.15	0.29
WO ₃	0.00	0.00	3.33	0.22	0.02	1.90	2.84	1.30	4.42	0.77	0.00	2.65	18.03	13.22	23.93

Notes. Me – median value (in parentheses – number of samples); Min and Max – minimum and maximum content values, wt.%.



The concentrations of the elements of WGM in earlier published reviews [4, 15] are narrower than the newest data (see Tables 1-4), and there is no information about most types of WGM. In composition WGM are primarily tantalum and tin oxides. In the observed evolutionary series of WGM, the amounts of Ta and Sn increase and reach the following values in the wodginite of pegmatites: 67.74 (85.04) %* Ta_2O_5 and 13.12 (19.20) % SnO_2 ; in granites, they are 63.13 (71.00) % and 13.33 (17.31) % respectively (Table 4, Fig. 3, 4). The ratio of Ta/(Ta + Nb) in these series increases, correlating with Mn/(Mn + Fe), and in the wodginite it is 0.90 and 0.82 respectively (Fig.4). The content of niobium in the wodginite is minimal: 4.68 (14.47) % Nb_2O_5 in pegmatites, and 8.11 (20.94) % in granites; the ratio of Ta/(Ta + Nb) is 0.90 and 0.82 respectively. The maximum content of Ta_2O_5 is seen in pegmatites: 80.71 (81.02) % in tantalum wodginite and 97.80 % in lithiowodginite [16, 35]. The minimum content of Ta_2O_5 is typical for “wolframowodginite”: 46.27 % in pegmatites and 38.97 % in granites.

The highest content of MnO is observed in the wodginite of pegmatites and granites: 9.16 (12.40) % and 9.85 (12.55) %. By this parameter, “wolframowodginite” stands out: 11.57 (16.54) % and 8.33 (11.29) % respectively (Table 4). The manganese content Mn/(Mn + Fe) is often increased in WGM of granites, compared to WGM of pegmatites (Fig.4). In 1992 WGM with high contents of FeO and TiO_2 were distinguished, they were found in the pegmatite deposits of Sukula (Finland), Bernic Lake (Canada), San Elias (Argentina) (see Table 1) and named ferrowodginite, ferrotitanowodginite and titanowodginite [15, 57] (see Fig.3). In 2002-2022 these minerals were found in the granites of China (Songshugang, Yichun, and the others), Algeria (Ebelekan), Egypt (Nuweibi), Czech Republic (Hub), Russia (Voznesenskoye) (see Table 2, Fig.1).

In Fe- and Ti-bearing WGM such elements as Mn, Sn, Ta are isomorphously replaced. In ferrowodginite and ferrotitanowodginite of pegmatites and granites, the concentrations of FeO are 7.80-8.08 (10.91-17.81) % and 7.75-9.02 (9.36-11.91) %. In titanowodginite the content of TiO_2 is respectively 10.57 (12.95) % and 8.19 (10.90) % (see Tables 1, 2, 4). The iron-rich and titanium-rich types tend to geochemically primitive pegmatites, and on the differentiated pegmatite deposits they are found in the early intrusive phases [64]. With magmatic differentiation, the chemical

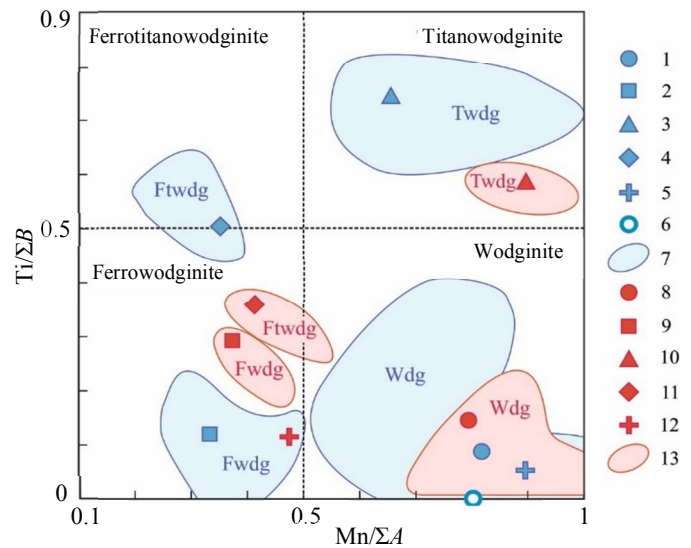


Fig.3. Variations in composition of the wodginite group minerals in rare-metal pegmatites (1-7) and granites (8-13) of the world
1-6 – average fractions of Ti and Mn cations in minerals of pegmatites: wodginite (1), ferrowodginite (2), titanowodginite (3), ferrotitanowodginite (4), “wolframowodginite” (5), tantalowodginite (6); 7 – fields of cationic relations in minerals of pegmatites; 8-12 – average fractions of Ti and Mn cations in minerals of granites: wodginite (8), ferrowodginite (9), titanowodginite (10), ferrotitanowodginite (11), “wolframowodginite” (12); 13 – fields of cationic relations in minerals of granites; ΣA , ΣB – sums of cations in position A (Mn^{2+} , Fe^{2+} , Li, Ca), B (Sn^{4+} , Ti, Fe^{3+} , ^{B}Ta , Sc, Zr)

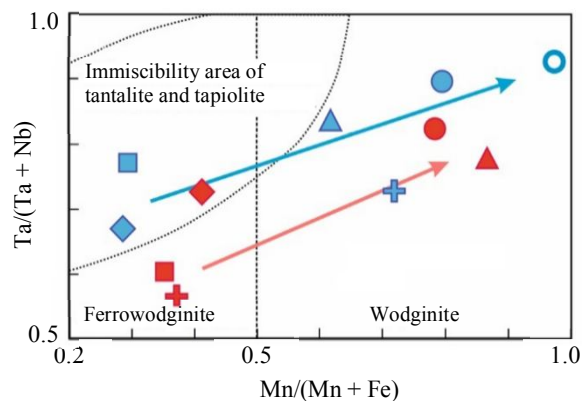


Fig.4. Variations in composition of the wodginite group minerals in rare-metal pegmatites and granites of the world in the diagram “columbite quadrilateral”
The ratio of the atomic number of the main cations in minerals is shown (see symbols in Fig.3).
Arrows indicate trends of composition evolution of minerals in pegmatites (blue) and granites (red)

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



potentials of Ta and Sn increase and the accessory ferrowodginite of pegmatites is sequentially replaced by titanowodginite, “wolframowodginite” and wodginite [15]. A different pattern is noted in the granites of Egypt and China: ferrowodginite of granites is replaced by “wolframowodginite”, wodginite and titanowodginite [17] (see Fig. 1, 4).

The finding of a tungsten variety of wodginite in the pegmatites of Separation Rapids in Canada is important [46]. The detection of wodginite with increased content of WO_3 in pegmatites [26, 59] and granites [68, 69] suggests the possibility of isolating a new mineral “wolframowodginite”. The concentration of WO_3 in “wolframowodginite” of pegmatites reaches 16.01 (34.63) %, in granites it is 18.39 (23.93) % (Table 4). Tungsten, along with tin, is a typical element of residual rare-metal melts, saturated with fluorine, and isomorphously replaces niobium in wodginite (see Table 3) [46, 59, 69]. “Wolframowodginite” is enriched with lithium and is surpassed in its content only by lithio-wodginite: Li_2O 0.06 (0.16) % in pegmatites and 0.21 (0.29) % in granites.

The leading crystal-chemical role of Sn in WGM, considered to be the only determining in the transformation of disordered ixiolite structure into ordered wodginite structure [14, 60], was refuted by experimental data. In the oxidative environment of differentiating rare-metal magma, in the absence of tin its role in the structure of wodginite is played by Fe^{3+} [8, 62, 71]. In pegmatites, the highest content of Fe_2O_3 is observed in ferrotitanowodginite 3.14 (7.83) % and “wolframowodginite” 3.75 (7.05) % [46, 58]; in granites: in ferrowodginite 0.91 (1.97) % [69]. The role of Fe^{3+} cations is minimal in wodginite of granites and pegmatites: Fe_2O_3 0.20 and 0.56 % respectively (see Tables 3, 4).

Among the impurity elements of WGM, the increased role of Ca in pegmatite wodginite (up to 0.14) [7, 37, 39] and Sc – in “wolframowodginite” of granites (f.c. 0.01-0.16) [69] (see Table 3) is noticeable. Like the accompanying tantalum-niobates, WGM contain impurities of Zr and Hf, that due to the reduction of volumes of crystallizing zircon in rare-metal magma, saturated by F, B, P, H_2O , enter into isomorphic relations with Sn, Ta, Ti, Fe^{3+} . At the late-magmatic stage of crystallization, wodginite of pegmatites becomes the main carrier of Zr and Hf: ZrO_2 0.35 (2.28) %, HfO_2 0.05 (0.92) % [26, 29, 30]; and even more so ferrowodginite of pegmatites: ZrO_2 0.61 (5.98) %, HfO_2 0.08 (1.59) % [33, 40] (see Table 1). The formula coefficient of zirconium in position B is 0.02-0.03 (see Table 3). Wodginite of granites also contains ZrO_2 0.02 (0.85) %, HfO_2 0.03 (1.00) % [63, 65]. The ratio of Zr/Hf in wodginite of granites is low: 1.18-1.54, and in pegmatites: 4.29-8.73 (see Table 2). Researchers note that WGM carry higher concentrations of Zr and Hf than columbite, tantalite and tapiolite [1, 30].

Thus, WGM from granites are enriched with Sn, Nb, W and depleted in Fe^{3+} , Ta, Zr, Hf compared with those from pegmatites. For WGM from granites, the impurity of Sc is characteristic, and Zr is typical for those from pegmatites (see Tables 3, 4). The Mn/(Mn + Fe) ratio in WGM of granites is relatively increased, and the ratio of Zr/Hf is relatively decreased (see Fig. 3, 4). Averaged crystal-chemical formulas of wodginite in pegmatites and granites are: $(\text{Mn}_{0.84}\text{Fe}_{0.17}\text{Ca}_{0.01})_{1.02}(\text{Sn}_{0.57}\text{Ti}_{0.09}\text{Ta}_{0.24}\text{Fe}^{3+}_{0.05}\text{Zr}_{0.02})_{1.01}(\text{Ta}_{1.76}\text{Nb}_{0.23}\text{W}_{0.01})_{2.00}\text{O}_8$; $(\text{Mn}_{0.88}\text{Fe}_{0.23})_{1.11}(\text{Sn}_{0.56}\text{Ti}_{0.14}\text{Ta}_{0.20}\text{Fe}^{3+}_{0.02})_{0.92}(\text{Ta}_{1.61}\text{Nb}_{0.39})_{2.00}\text{O}_8$.

Based on the average composition of minerals, we can identify the deposits where typical types of WGM are described. The deposits in pegmatites are: wodginite from Bernic Lake in Canada, Wodgina in Australia, Nanping in China; titanowodginite from Nancy in Argentina; ferrowodginite from Numbi in DR Congo, Pilawa Gorna in Poland; ferrotitanowodginite from La Calandria in Argentina; “wolframowodginite” from Separation Rapids in Canada (see Tables 1 and 4); the deposits in granites are: wodginite from Abu Dabbab in Egypt; titanowodginite from Ebelekan in Algeria, Yichun in China; ferrowodginite from Songshugang in China; ferrotitanowodginite from Gedongping in China; “wolframowodginite” from Songshugang in China (see Tables 2 and 4).

Typomorphism of wodginite group minerals. This review shows that WGM reflect the formation conditions of Li-F pegmatites and granites, and are recognized as markers of the late-magmatic stage of crystallization of rare-metal granitic melt [4, 49, 66]. Experiments have shown that wodginite and titanowodginite crystallize from granitic magma at a temperature of 700-800 °C [77], or from salt (hydrosilicate) liquids, enriched with Ta and Sn [68]. Wodginite forms in oxidative conditions by transforming ixiolite and columbite [59, 64, 71].



The evolving composition and acid-base properties of the parent medium determine the formation of a standard sequence of tantalum-niobates: columbite-(Fe) → columbite-(Mn) → tantalite-(Mn) → wodginite → microlite → cassiterite [28, 46, 59]. In parageneses with several WGM, the sequence of their crystallization is poorly studied. Based on the available ontogenetic observations, one can assume that the minerals form in a sequence that follows the evolution of the parent magma and corresponds to the outlined series of evolution of WGM in pegmatites [ferrowodginite → ferrotitanowodginite → titanowodginite → “wolframowodginite” → wodginite → tantalowodginite] and evolution of WGM in granites [ferrowodginite → ferrotitanowodginite → “wolframowodginite” → wodginite → titanowodginite] [45, 46, 66] (see Fig.3, 4). From the early to the late minerals, the size of crystals increases: in pegmatites, from 350-4400 microns for iron-rich types to 6-9.6 mm for wodginite, tantalowodginite; in granites from 5-26 microns for ferrowodginite to 18-58 microns for titanowodginite and wodginite (see Fig.1).

The presence of WGM fixes the ultimate differentiation of magma (fluid) to extreme values of Ta/(Ta + Nb) and Mn/(Mn + Fe) in the apical parts of pegmatitic and granitic bodies [3, 47, 77]. Such features of WGM as high content of Ta, Sn, Mn, Li, W, Zr, Hf; increased value of Ta/(Ta + Nb) and Mn/(Mn + Fe) ratios, and decreased ratio of Zr/Hf are signs of high rare-metallicity of the parent melt.

WGM are characteristic of large rare-metal deposits and serve as indicators of tantalum-bearing pegmatites and granites. Wodginite is found in Ta, Sn, Li, W ores (deposits of the Superior province in Canada, Jiangxi province in China, and others). In contrast, in Russia, wodginite was found only in four of the 22 tantalum deposits accounted by the State Register of Mineral Reserves. Since wodginite is typical of rare-metal granites, the prospective sources of tantalum are the deposits of the Far Eastern belt of Li-F granites, containing wodginite [21, 23]. Examples include the large Voznesenskoye and Kester deposits [22, 23].

Conclusions

- Minerals of the wodginite group stand out among tantalum-niobates by a highly ordered structure, determined by the isomorphous incorporation of tin cations: ${}^4[\text{Fe}, \text{Mn}]^{2+} + 2{}^{\text{C}}[\text{Nb}, \text{Ta}]^{5+} \leftrightarrow \leftrightarrow 3{}^{\text{B}}[\text{Sn}, \text{Ti}]^{4+}$. Polyelemental isomorphism in three crystal-chemical positions allows distinguishing the wodginite group, which includes seven minerals: wodginite, titanowodginite, ferrowodginite, ferrotitanowodginite, lithiumwodginite, tantalowodginite, “wolframowodginite”.

- Minerals of the wodginite group occur in Li-F pegmatites and Li-F granites with similar parageneses: Ta-cassiterite, fluorapatite, Hf-zircon, tantalite-(Mn), columbite-(Mn), ixiolite, microlite, tapiolite and WGM. Among WGM, wodginite is the most common: 86.6 % in pegmatites and 78.3 % in granites.

- WGM differ in their occurrence in granites and pegmatites: with wodginite being dominant in granites, titanowodginite and “wolframowodginite” are encountered three times more often; lithioowodginite and tantalowodginite are not encountered at all.

- WGM differ between granites and pegmatites in terms of smaller grain size, higher content of Sn, Nb, Ti, W, Sc, lower content of Fe^{3+} , Ta, Zr, Hf, higher value of Mn/(Mn + Fe) and lower value of Zr/Hf.

- The differentiation of rare-metal-granitic magma determines the evolution of WGM composition. The evolutionary series of WGM in pegmatites are ferrowodginite → ferrotitanowodginite → titanowodginite → “wolframowodginite” → wodginite → tantalowodginite. The evolutionary series of WGM in granites are ferrowodginite → ferrotitanowodginite → “wolframowodginite” → wodginite → titanowodginite.

- Minerals of the wodginite group serve as indicators of tantalum-bearing pegmatites and granites. In Russia the prospective sources of tantalum are the deposits of the Far Eastern belt of Li-F granites containing wodginite.



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Author Viktor I. Alekseev, Doctor of Geological and Mineralogical Sciences, Professor, alekseev_vi@pers.spmi.ru, <https://orcid.org/0000-0002-1512-9347> (Saint Petersburg Mining University, Saint Petersburg, Russia).