

3 Wolframioxiolite and Niobian Ferberite from Zinnwaldite Granitic Rocks of the Chukchi Peninsula

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3 **Abstract**—The finding of wolframioxiolite with inclusions of niobian ferberite is described from zinnwaldite
2 granite and ongonite of the Severny pluton of the Chukchi Peninsula. The optical, morphological, and chem-
ical properties of minerals are characterized and compared with their analogues from other regions. The pet-
rologic and mineragenic index implications of the minerals are discussed with allowance for our contempo-
rary mineralogical knowledge on W-bearing Ta–Nb minerals.

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INTRODUCTION

The relationships of tungsten mineralization with
granites are still a matter of debate and require a com-
prehensive approach to their consideration (Syrtsko
et al., 2008). The study of accessory tungsten and asso-
ciated Ta–Nb minerals are helpful in this respect. The
1 microcline–albite granitic sills and ongonite dikes
2 with zinnwaldite and topaz were found during special-
3 ized geological mapping of the Severny pluton near
the eastern coast of the Chaun Gulf of the Chukchi
Peninsula (Alekseev, 2005). The study of the accessory
minerals resulted in the first finding of a rare min-
eral—wolframioxiolite—in granites of the Far East.
The specific attributes of this mineral and its genetic
implications are discussed in this paper.

Wolframioxiolite (Fe,Mn,Nb)(Nb,W,Ta)O₄ was
discovered by Ginzburg et al. (1969) in the Fersman
Mineralogical Museum collection. At present, the
mineral is discredited by the IMA (the **IMA/CNMNC
List ...**, 2010) and considered to be an ixiolite variety
containing about 0.3 W atoms per formula unit. The
results of the structural study of wolframioxiolite
allowed Wang et al. (1988) to refer it to the minerals
with medium-size cations in the structure with chains
of octahedrons (Strunz and Nickel, 2001). The min-
eral is close to ferberite; quitianlingite; koragoite;
wodginite; and, above all, to ixiolite.

The Ta–Nb minerals themselves are difficult to
study because of their diverse compounds, structural
motifs, nonstoichiometric composition, and mor-
photropism (Voloshin, 1993). The study of their W-
bearing varieties or niobian wolframite meets addi-
tional difficulties particularly related to the fine crystal
chemical discrepancy in the Nb, Ta, and W deport-
ment and very small mineral grains. All these features
were reflected in the discussion about “wolframioxiolite”

(Amichba and Dubakina, 1976; Borneman–
Starynkevich et al., 1976; Voloshin et al., 1988; 1993;
Černý, 1995; Černý et al., 2007). Most researchers,
except for Kornetova et al. (1982), point out its indi-
viduality, calling attention to its nonstoichiometry and
the constant occurrence of phase microheterogene-
ities, which indicate its metastable character and sus-
ceptibility to exsolution, recrystallization, etc.

The number of wolframioxiolite findings in the
world increases with time. In Russia, the mineral was
described in greisens of North Yakutia (Amichba and
Dubakina, 1976) and Siberian and Ural pegmatites
(Kornetova et al., 1982; Černý, 2001). Worldwide, it is
known in pegmatites from Italy (Aurisicchio et al.,
2002), the Czech Republic (Novák et al., 1999, 2008;
Černý et al., 2001, 2007), Ukraine (Tsareva et al.,
1993), China (Zhang et al., 2003), North America
(Černý et al., 1999), Thailand (Linnen and Williams–
Jones, 1993; Suwimonprecha, 1995), Austria, Slova-
kia, and Madagascar. All the findings are microin-
clusions in beryl, albite, topaz, niobian rutile, columbite,
and polycrase crystals. The exsolution many times
described in wolframioxiolite from pegmatites points
to its early high-temperature crystallization and the
possibility of its identification in the parental granites.
In Russia, wolframioxiolite in such a situation was
found only in the Ary-Bulak ongonite from Trans-
baikalia (Peretyazhko et al., 2007). Beyond Russia, it
was described as inclusions in zinnwaldite, topaz, and
albitic matrixes in rare-metal granites from the Ale-
meda and Tin Amzi plutons in South Algeria (Chalal
and Marignac, 1997; Kesraoui and Nedjari, 2002), the
Zrari pluton in Central Morocco and the Beauvoir
pluton in France (Marignac et al., 2001), and a Toto-
gyz intrusion in North Kazakhstan (Letnikov, 2008).

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DESCRIPTION OF WOLFRAMOIXIOLITE

Taking advantage of the instrumentation of the Center for Collective Use at St. Petersburg State Mining University, we managed to identify wolframoixiolite in zinnwaldite-bearing granite and ongonite of the Chukchi Peninsula. Wolframoixiolite was detected at more than ten observation points in the northern part of the main cupola of the Severny pluton about 30 km² in area. All the findings were exclusively related to the fine-grained zinnwaldite granite and ongonite containing topaz and fluorite, which are the main ore-bearing rocks in the area (Alekseev, 2005). Under a microscope, wolframoixiolite is observable much more often than zircon (up to 5–20 grains per thin section) and is one of the main accessory minerals in zinnwaldite-bearing granites.

The mineral is distinguished by its stable morphology forming euhedral long-prismatic crystals with sharp or obtuse apices and rhombic, equant, or slightly oblong cross sections (Figs. 1a–1d). The crystals are 5–50 μm long occasionally up to 100–150 μm and 1–8 μm across, while, in some cases, up to 25–35 μm. The mineral tends to form parallel and telescoping intergrowths or complex pockets (Fig. 1e). Its largest crystals are incorporated into zinnwaldite and often are partly ingrown in adjoining quartz, topaz, or fluorite grains. The smaller (3–30 × 30–60 μm in size) inclusions are found in topaz and less frequently in microcline, albite, and at interfaces between feldspar grains. Occasionally, colonies of skeletal wolframoixiolite ingrowths several μm across are observed in zinnwaldite (Fig. 1f). The pleochroic halos surrounding wolframoixiolite grains in mica provide evidence for radioactive inclusions in the mineral (Figs. 1c, 1d). Wolframoixiolite in ongonite is small in size (2–10 × 20–50 μm), nonuniformly distributed in albite, or forms ingrowths in mica and topaz phenocrysts (Figs. 1g, 1h). In transmitted light, the mineral is opaque, but crystals less than 10 μm thick are reddish brown, translucent, and reveal slight pleochroism according to the biotite scheme. In crossed polars, the mineral often has a parallel extinction, but crystals cut close to (010) are characterized by inclined extinction with an angle of 15°. The elongation is optically positive, while the birefringence is 0.009–0.010.

The study of wolframoixiolite using a JSM-6460 LV SEM equipped with an Oxford EDS (the beam diameter is 3 μm) allowed us to elucidate its anatomy and estimate its composition. The large prismatic grains are parallel, en echelon arranged, or telescoping intergrowths of nearly parallel individual crystals; the major largest crystal commonly stands out (Fig. 2). The BSE images and X-ray spectroscopy showed variation in the composition of the crystals, first of all, in the Nb/W ratio. The variations are nonuniform and controlled by vague growth zones, which are parallel to the crystal extinction. Generally, the mineral corresponds in composition to its analogues from other

regions and is close to wolframoixiolite from rare-metal granites (Table 1; Fig. 3). The elevated Ta₂O₅/Nb₂O₅ and FeO/MnO ratios and the absence of Sn are specific attributes of the wolframoixiolite from the Chukchi Peninsula.

The compositional variability of wolframoixiolite is determined by the isomorphism of the heterovalent cations (Sc³⁺, Ti⁴⁺, Fe³⁺, Sn⁴⁺, Ta⁵⁺) at the constitutional role of Mn²⁺, Fe²⁺, Nb⁵⁺, and W⁶⁺, as well as by the mutual isomorphism of Nb⁵⁺ and W⁶⁺. The triangle diagram shows the two-phase composition of the studied grains (Fig. 4), and both phases are related to the same columbite → wolframite crystal chemical trend earlier described for wolframoixiolite (Černý et al., 2007).

The factor analysis of the chemical components in wolframoixiolite revealed three tendencies. The elements of wolframite (Fe, W, and Mn) and wolframoixiolite (Nb, Ti, and Ta) are neatly divided by the main factor (Fig. 5a). The coordinates of the constitutional elements almost lie on the main factor axis: Fe and W strictly linked to each other tend to the pole of the hemisphere with positive values and ferberite data points, whereas Nb is close to the pole of the negative ixiolitic semisphere. The main components are accompanied by admixtures: Mn is related to wolframite and Na and Ti, to wolframoixiolite. The second statistical factor has a structural nature: the substitution of Nb with Ta in site *B* is attended by an increase in Ti, which replaces W and with the appearance of Mn and Sc in site *A* (Fig. 5a). According to the third factor distribution, Sc is negatively correlated with Ti and Mn, which is likely owing to the heterovalent isomorphism of both sites (Fig. 5b).

The monomineralic selection of wolframoixiolite is characterized by other crystal chemical relations between W and Nb. All the constitutional components of wolframoixiolite, except for Ta, group in the region of positive loadings on the first factor (Fig. 6a). This testifies to the homogeneous selection and affiliation of all the samples to the same mineral undergoing the conjugate compositional variations in line with the fluctuating crystallization conditions. The antagonism of Ta with respect to all the components (especially to Fe and W) is related to the deviation of the stoichiometry of the Ta-bearing varieties and, probably, to the specific structural domains formed due to the morphotropic deportment of Ta in a system with Nb (Voloshin, 1993).

The second factor resembles the complex (Fe₃²⁺W₃⁶⁺Ta⁵⁺)₊₁ · (Mn₃²⁺Nb₅⁵⁺)_{–1} isomorphism. The third factor comparable to the second one in the contribution to the dispersion sum (26.6 and 19.1%, respectively) shows the same isomorphous scheme with an inverted role of W and Nb (Figs. 6a, 6b). Thus, factors 2 and 3 show W and Nb interchangeability in the ixiolitic coordination structure and, probably, varia-

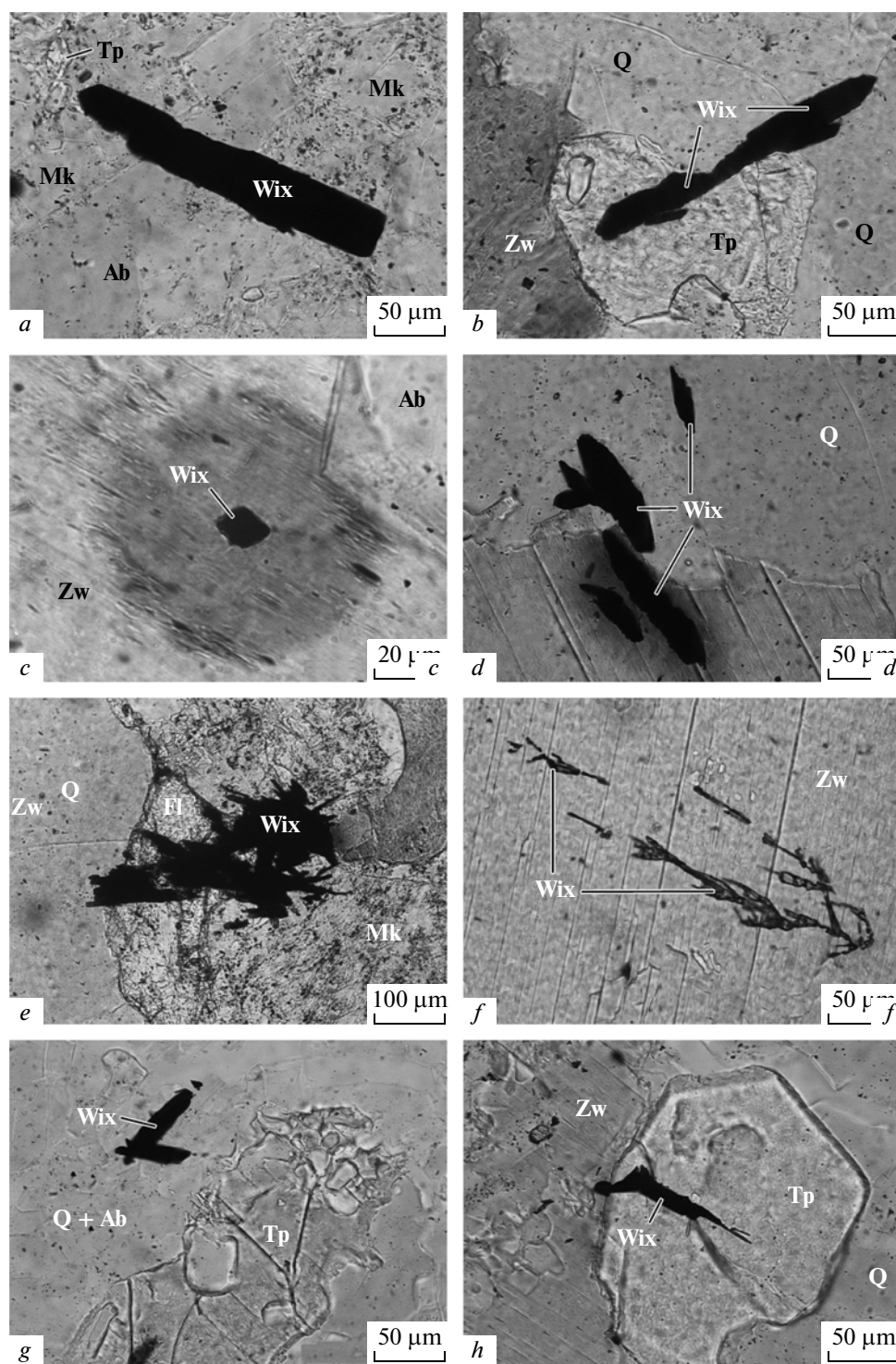
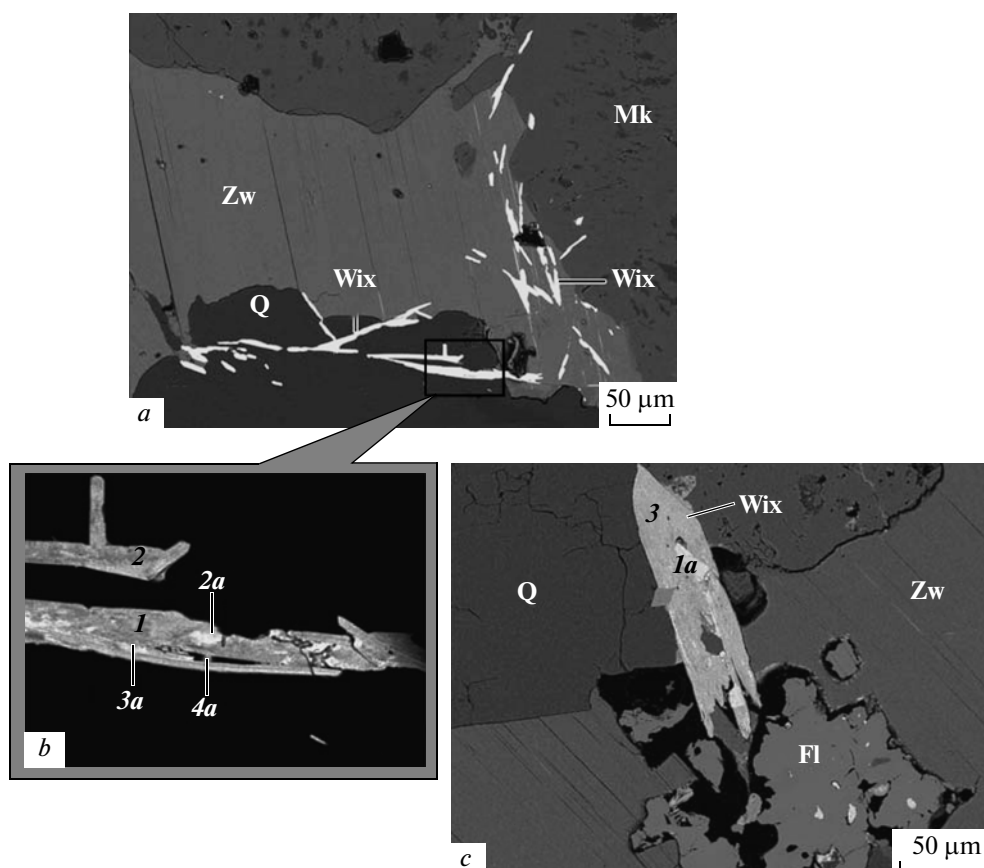


Fig. 1. Wolframioxiolite in zinnwaldite granites of the Severny pluton of the Chukchi Peninsula: photomicrographs of thin sections (plane light) of (a–f) microcline–albite granite and (a–f) ongonite; (a) prismatic crystals in albite and microcline and (b) in topaz and quartz; (c) cross and (d) oblique sections of crystals in zinnwaldite with pleochroic halos; (e) crystal intergrowth in microcline at the boundary with zinnwaldite, quartz, and fluorite; (f) colony of ingrowths of skeletal crystals in zinnwaldite; (g) crystal intergrowth in the quartz–albite groundmass of ongonite near a topaz phenocryst; (h) crystal intergrowth in a topaz phenocryst in ongonite. Minerals: Ab, albite; Fl, fluorite; Mc, microcline; Q, quartz; Tp, topaz; Wix, wolframioxiolite; Zn, zinnwaldite.



3 **Fig. 2.** Wolframoixiolite in zinnwaldite granite of the Severny pluton of the Chukchi Peninsula. BSE images. The areas of the microprobe analyses of wolframoixiolite (1–3), wolframite (1a–3a), and an unknown uranium mineral (4a) are marked by numerals corresponding to the numbers in Tables 1 and 2. The symbols are the same as in Fig. 1.

tion in the numbers of Nb and W octahedral layers. Judging from the loadings of the additional components on these factors, Ti is able to substitute for W. The high-Nb wolframoixiolite varieties are characterized by elevated contents of Sc possibly substituting for Fe^{3+} . In accordance with the aforesaid, the empiric formula of the wolframoixiolite from the Chukchi Peninsula

is $(\text{Fe}_{0.46}\text{Nb}_{0.31}\text{Mn}_{0.14}\text{Sc}_{0.05})_{0.96}(\text{Nb}_{0.40}\text{W}_{0.30}\text{Ta}_{0.15}\text{Ti}_{0.15})_{1.00}\text{O}_{4.00}$. It is noteworthy that the bulk composition of the mineral is similar to that of the Chinese quitianlingite (Yang et al., 1985) with the formula $(\text{Fe}_{0.54}\text{Nb}_{0.23}\text{Mn}_{0.22}\text{Sc}_{0.00})_{0.99}(\text{Nb}_{0.45}\text{W}_{0.37}\text{Ta}_{0.14}\text{Ti}_{0.04})_{1.00}\text{O}_{4.00}$ based on 4 atoms of oxygen.

DESCRIPTION OF FERBERITE

Ferberite occurs as numerous irregular inclusions with keen boundaries in wolframoixiolite crystals, being localized in their axial parts or at sharp apices. The ferberite inclusions were noted repeatedly, and

their occurrence is more likely a rule than an exclusion. The ferberite inclusions have a relatively constant size with their total area not exceeding 5–10% of the area of the host mineral. Its composition corresponds to niobian ferberite similar to that described in other regions (Table 2; Fig. 3). Nb-wolframite from pegmatites of Ukraine (Tsareva et al., 1993) and the Czech Republic (Černý et al., 2007) are the closest analogues. The relatively low Nb content and absence of Sn and Ta are typical of ferberite from the Chukchi Peninsula. This is especially interesting because of the high Ta content in the host wolframoixiolite. The composition of the studied ferberite is intermediate between wolframoixiolite and common wolframite (Fig. 4). The empiric formula is $(\text{Fe}_{0.62}\text{Mn}_{0.20}\text{Nb}_{0.12}\text{Sc}_{0.04})_{0.98}(\text{Nb}_{0.23}\text{W}_{0.71}\text{Ti}_{0.06})_{1.00}\text{O}_{4.00}$.

Along with ferberite, wolframoixiolite usually contains one or several uranium minerals responsible for the pleochroic halos in the host zinnwaldite. The direct study of these inclusions is hampered by their small size (<1 μm) (Fig. 2c); however, U (up to 10.54%), Bi (up to 31.69%), and As (up to 3.47%) have been detected in their composition. It is noteworthy that the first researchers of wolframoixiolite also

² The positive correlation of Nb with Mn and Fe allowed us to place some excess of Nb in site B into site A.

Table 1. Chemical composition (wt %) and crystal chemical formulas of wolframoixiolite

Component	Wolframoixiolite, Chukchi Pen.				Wolframoixiolite from granites			
	1	2	3	4	5	6	7	8
Sc ₂ O ₃	—	4.35	—	1.49	—	—	0.51	—
TiO ₂	5.25	3.31	6.23	4.77	0.52	1.27	2.67	2.55
MnO	4.90	4.30	3.42	3.83	7.49	8.64	6.21	6.93
FeO*	13.96	13.65	12.12	13.06	14.31	12.22	14.37	13.70
Nb ₂ O ₅	34.66	29.69	39.19	36.56	34.39	42.56	45.76	36.84
Ta ₂ O ₅	—	15.95	18.27	12.76	10.40	16.93	6.72	2.63
WO ₃	41.23	28.75	20.77	27.53	30.42	26.53	23.20	34.69
SnO ₂	—	—	—	—	0.93	—	0.10	0.84
Total	100.00	100.00	100.00	100.00	98.46	98.15	99.54	98.17
Formula coefficients								
Sc	—	0.16	—	0.05	—	—	0.02	—
Ti	0.17	0.11	0.20	0.14	0.02	0.04	0.09	0.08
Mn	0.17	0.16	0.12	0.14	0.29	0.29	0.22	0.26
Fe	0.49	0.49	0.43	0.47	0.54	0.41	0.50	0.50
Nb	0.66	0.58	0.74	0.70	0.70	0.77	0.86	0.72
Ta	—	0.19	0.21	0.15	0.13	0.18	0.08	0.03
W	0.45	0.32	0.23	0.31	0.36	0.28	0.25	0.39
Sn	—	—	—	—	0.02	—	0.00	0.02

Note: (1–3) Representative microprobe analyses of wolframoixiolite from granites of the Chukchi Peninsula, see Figs. 2a–2c; (4) the average composition of wolframoixiolite from the Chukchi Peninsula (25 analyses); (5–8) compositions of wolframoixiolite from topaz granites: (5) Alameda, Algeria (Chalal et al., 1997), (6) Totogyz, Kazakhstan (Letnikov, 2008), (7, 8) Zrari, Morocco and Beauvoir, France (Marignac et al., 2001). FeO* is FeO + Fe₂O₃. The empiric formulas are recalculated to 4 atoms of oxygen.

identified inclusions of an unknown uranium mineral (Ginzburg et al., 1969; Kornetova et al., 1982).

DISCUSSION

Ixiolite is an accessory mineral of the evolved granitic pegmatites. The heterogeneity at the micrometric level reflecting the lowest organization of Ta–Nb minerals of the ixiolitic structural type (ixiolite → tantalite → wodginite) is the most important feature. Its crystal lattice is formed by zigzagging chains of edge-shared octahedrons, which lie in the planes and are joined by apices into the framework. This structure opens up possibilities for the formation of layered superstructures, complex heterovalent W–Nb–Ta–Sn–Ti and Fe–Mn–Sc isomorphism, and causes the appearance of wolframoixiolite or wolframowodginite. Voloshin (1993) developed an idea about the incorporation of W into the structure of Ta–Nb minerals and

suggested the possibility to form a mineral intermediate between wolframite and ixiolite by means of cation ordering by the layers. This idea is confirmed by the discovery of quitianlingite (Fe,Mn)₂(Nb,Ta)₂WO₁₀—a mineral with an ixiolitic superstructure including layers of octahedrons with various cation infillings (Yang et al., 1985).

Without entering into a discussion concerning the appropriateness of wolframoixiolite as an individual mineral species, note that the results of the study of this mineral from the Chukchi Peninsula support the idea offered by Voloshin. The studied mineral has a stable morphology, certain dimensions, and a structural position in the aggregates. The fluctuation of its composition within certain limits shows that it is a metastable nonstoichiometric mineral stable at the high temperature of the magmatic stage of the mineral formation. Its morphological and compositional fea-

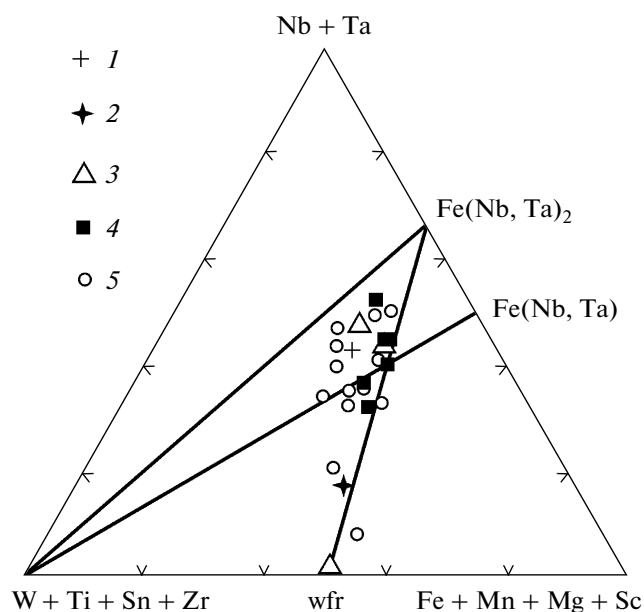


Fig. 3. Chemical compositions of wolframioxiolite and niobian wolframite from the Chukchi Peninsula and other regions. (1) Wolframioxiolite and (2) niobian wolframite from the Chukchi Peninsula; (3–5) wolframioxiolite and niobian wolframite from the (3) greisen (Amichba and Dubakina, 1976; Voloshin, 1988; Marignac et al., 2001), (4) pegmatite (Ginzburg et al., 1969; Knorring and Fadipe, 1981; Kornetova et al., 1982; Yang et al., 1985; Voloshin, 1988; Tsareva et al., 1993; Černý et al., 2001, 2007; Aurisicchio et al., 2002); (5) rare-metal granite (Chalal and Marignac, 1997; Marignac et al., 2001; Letnikov, 2008).

tures are close to the analogues described in Pamirs (Konovalenko et al., 1982), Algeria (Chalal and Marignac, 1997), the Island of Elba (Aurisicchio et al., 2002), and Kazakhstan (Letnikov, 2008). The susceptibility to parallel intergrowths and inclusions of Nb-ferberite and an unknown Bi–U mineral are typical of wolframioxiolite from the Chukchi Peninsula. It is characterized by elevated Ta_2O_5/Nb_2O_5 and FeO/MnO ratios and the absence of Sn. It should be noted that this is the main accessory mineral in zinnwaldite granite readily identified even under a polarization microscope.

The ferberite–wolframioxiolite assemblage is of doubtless interest. The question of the genetic relation between the two minerals is still open. It is known that tungsten does not accumulate in the early granitic rocks of intrusive series and concentrates in the late rare-metal derivatives only seldom forming wolframite (Badanina, 2008). The contemporary data (Linnen, 1998, 2005; Keppler and Wyllie, 1999) point to the undersaturation of peraluminous granitic melts in tungsten. An accessory wolframite was described in W-bearing leucogranites of the Gorny Altai, the Urals, the North Caucasus region, Transbaikalia, Kazakhstan, and Korea (Lyakhovich, 1967; Marin, 2004). Wolframite is identified in heavy concentrates along

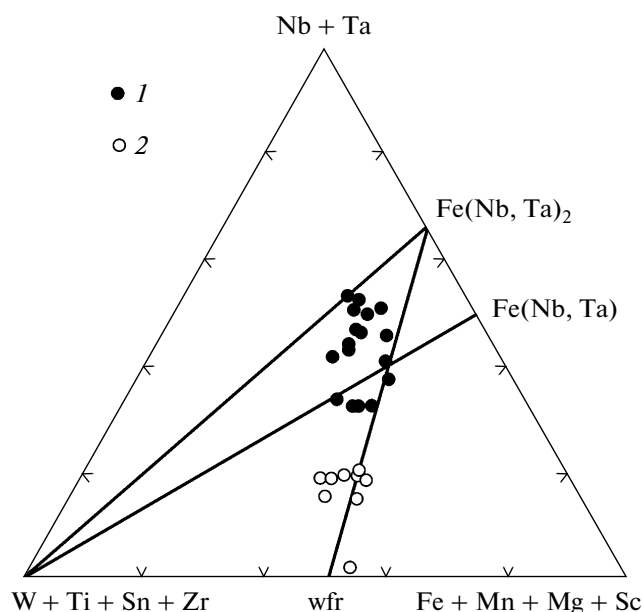


Fig. 4. Chemical compositions of wolframioxiolite and niobian wolframite from zinnwaldite granite of the Chukchi Peninsula. (1) Wolframioxiolite, (2) niobian wolframite.

with secondary anglesite, limonite, marcasite, etc. (Lyakhovich, 1967) providing evidence that at least some wolframites are postmagmatic in origin. The wolframite inclusions in granites at the Spokoininsky and Taptanai deposits in Transbaikalia reliably confirm their magmatic genesis (Syrtsso et al., 2008). Thus, the findings of accessory wolframite in granites and pegmatites are few in number in contrast to greisen, skarn, and quartz veins, which are the main concentrators of wolframite mineralization. Nb in hydrothermal wolframite is usually related to inclusions of Ta–Nb minerals.

At the same time, tungsten is certainly fixed in ixiolite, and the α - PbO_2 ixiolite structure can be transformed into the wolframite structure by the ordering of the cations of groups A (Fe, Mn) and B (W) along the layers formed by octahedron chains as in quitianlingite (Voloshin, 1993). The more precise methods that are used by mineralogists, the more distinct the genetic relation is displayed in the wolframioxiolite–wolframite couple. Ginzburg et al. (1969), having noted the similarity of wolframite and columbite structures and having suggested the statistic alternation or direct isomorphic substitution of $(NbO_6)^{7-}$ with $(WO_6)^{6-}$, also assumed their ordered intercalation. Kornetova et al. (1982) considered wolframioxiolite to be an exsolution product—a structured compound of the wolframite, columbite, and rutile mineral groups. Černý referring the formation of W-ixiolite to the exsolution of Nb-rutile in pegmatites from Colorado, the Urals, and Bohemia assumes its primary magmatic origin

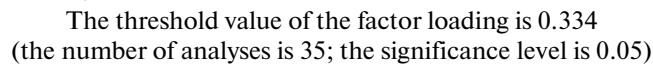


Fig. 5. Crystal chemical links of components in wolframioxiolite and wolframite inclusions from zinnwaldite granite of the Chukchi Peninsula (diagrams of factor loadings on component contents).

and also notes that the W-richer varieties are similar to Nb-wolframite from Mozambique and the Czech Republic (Černý et al., 1999, 2001, 2007). In his opinion, the metastable mineral formation occurs against the background of the unordered occupancy of the ixiolite structure with heterovalent cations: $(\text{Fe}_3^{2+}\text{W}_3^{6+})_{+1}(\text{Fe}_2^{2+}\text{Nb}_4^{5+})_{-1}$ and $(\text{Fe} > \text{Sc})_{+3}^{3+}$ ($\text{Fe} \gg \text{Mn, Mg, Ca})_{-2}^{2+}(\text{Nb} > \text{Ta})_{-1}^{5+}$.

The joint occurrences of wolframoixiolite and wolframite are also known. Ginzburg et al. (1969) noted the wolframite inclusions in the wolframoixiolite described by these authors for the first time. Marignac et al. (2001) described the Nb-wolframite inclusions in wolframoixiolite from the Zrari topaz–zinnwaldite granite in Mozambique, fibrous wolframoixiolite in ferberite from the Beauvoir stockwork in France, and the consecutive crystallization of zinnwaldite-1 with wolframoixiolite inclusions and zinnwaldite-2 with wolframite in the Tin Amzi Granite in Algeria. The replacement of wolframite with wolframoixiolite and W-bearing manganocolumbite was observed in quartz veins of the Dajishan deposit in South China (Zhang et al., 2003). Novák et al. (2008) reported wide isomorphic substitutions in wolframoixiolite from pegmatites of the Czech Republic and rhythmically zoned intergrowth of wolframoixiolite with Nb-ferberite and proposed an isomorphic exchange scheme: $(\text{R}^{3+})_8(\text{R}^{4+})_6(\text{R}^{5+})_{16}(\text{R}^{2+})^{-13}(\text{R}^{6+})^{-17}$, where $\text{R}^{2+} =$

$\text{Fe}^{2+} > \text{Mn, Ca}$; $\text{R}^{3+} = \text{Fe}^{3+} > \text{Sc, Al}$; $\text{R}^{4+} = \text{Ti} > \text{Zr, Si}$,
 U ; $\text{R}^{5+} = \text{Nb} > \text{Ta, P}$; $\text{R}^{6+} = \text{W}$.

Our data confirm the possible cocrystallization of the aforementioned minerals in granites. It is hard to imagine ferberite inclusions in wolframoixiolite as embryonal nuclei of the latter. More likely, these are exsolution products of the metastable phase evolving in the course of cooling. This is confirmed by the stable relationships between the tungsten phases, including the constant relative amounts of the inclusions (about 5–10% of the area occupied by the host mineral) and the localization of them in axial zones and at apices of the host mineral. It may be concluded that the ixiolite crystal structure chemically restricts the substitution of Nb with W. The formula of the primary mineral subjected to exsolution during crystallization of the Chukchi granites might have looked like $(\text{Fe}_{0.54}\text{Nb}_{0.32}\text{Mn}_{0.1}\text{Sc}_{0.06})_{1.09}(\text{Nb}_{0.34}\text{W}_{0.43}\text{Ta}_{0.11}\text{Ti}_{0.12})_{1.00}\text{O}_{4.00}$. A hypothetical mineral was similar to the studied wolframoixiolite while differing in excess W and Fe from the latter.

Petrologic and metallogenic implications. The finding of wolframoixiolite in two consecutive intrusive phases—microcline–albite granite and ongonite—^{1 2} indicates that this mineral likely crystallized from an ongonitic melt. Thus, the ore potential of granitic rocks can be estimated using wolframoixiolite and Nb-ferberite as index minerals of rare-metal magmatism. In our case, the zinnwaldite granite and ongonite ^{3 2}

Table 2. Chemical composition (wt %) and crystal chemical formulas of wolframite in association with wolframioixiolite

Component	Niobian wolframite, Chukchi Pen.				Wolframite from other regions			
	1a	2a	3a	4	5	6	7	8
Sc ₂ O ₃	—	5.48	—	1.23	0.40	—	1.33	—
TiO ₂	—	3.47	4.64	1.32	1.93	1.20	4.75	4.50
MnO	—	5.43	6.31	5.08	7.46	2.04	3.28	6.31
FeO*	17.36	13.91	14.18	16.35	14.37	24.78	16.90	13.57
Nb ₂ O ₅	18.34	16.50	20.43	16.66	31.25	7.86	19.13	27.54
Ta ₂ O ₅	—	—	—	—	3.12	0.70	2.55	5.56
WO ₃	64.30	55.21	54.44	59.36	41.56	63.01	49.00	37.77
SnO ₂	—	—	—	—	0.37	0.26	0.40	1.13
Total	100.00	100.00	100.00	100.00	100.50	99.85	99.06	99.39
Formula coefficients								
Sc	—	0.21	—	0.04	0.02	—	0.05	—
Ti	—	0.12	0.16	0.06	0.07	0.04	0.16	0.15
Mn	—	0.20	0.24	0.20	0.28	0.08	0.12	0.24
Fe	0.68	0.52	0.53	0.62	0.53	1.00	0.63	0.50
Nb	0.39	0.33	0.41	0.35	0.62	0.17	0.39	0.55
Ta	—	—	—	—	0.04	0.01	0.03	0.10
W	0.78	0.63	0.63	0.71	0.47	0.79	0.57	0.43
Sn	—	—	—	—	0.01	0.01	0.01	0.02

Note: (1a–3a) Representative microprobe analyses of niobian wolframite from granites of the Chukchi Peninsula, see Figs. 2a–2c; (4) average composition of niobian wolframite from the Chukchi Peninsula (10 analyses); (5–8) niobian wolframites from: (5) Zrari topaz granites (the sum includes 0.04 wt % UO₂) (Marignac et al., 2001), (6) Volhyn miarolitic pegmatite (Tsareva et al., 1993); (7) Bohemian pegmatite (the sum includes 1.34 wt % ZrO₂, 0.11 wt % UO₂, 0.07 wt % HfO₂, 0.06 wt % Bi₂O₃, 0.06 wt % MgO, 0.03 wt % ThO₂, and 0.02 wt % CaO) (Černý et al., 2008), (8) Siberian pegmatite (Kornetova et al., 1982). FeO* is the total FeO + Fe₂O₃. The empiric formulas are recalculated to 4 atoms of oxygen.

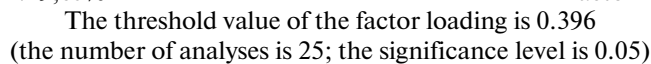
undoubtedly have rare-metal specialization and cardinally differ from the biotitic granites widespread in the region. The appearance of accessory minerals as direct witnesses of this specialization is related to the moderate F content in the initial melt, which diminishes the migration ability of tungsten and hampers its partitioning into the fluid.

In this regard, it is important to note that the high-grade tin mineralization hosted in the metasomatic rocks of the tourmaline stage is spatially related to the studied granites of the Chaun ore district. The tungsten mineralization reflected in the accessory minerals could have been formed at the earlier greisen stage, the products of which occur at the deeper levels. This allows us to positively estimate the prospectivity for

tungsten mineralization in the Kuiviveem–Pyrkakai ore district.

CONCLUSIONS

Accessory wolframioixiolite was found for the first time in zinnwaldite granitic rocks of the Chaun region of the Chukchi Peninsula. The presented data, along with the results of other contemporary studies of wolframioixiolite, refute the opinion about its polyphase composition. Although the wolframioixiolite from the Chukchi Peninsula contains ferberite inclusions, it is distinguished by its individuality in crystal morphology and chemical composition and most likely is a homogeneous metastable variety of ixiolite. Its origin is related to the crystallization of an ongonitic melt enriched in Nb, Ta, and W with the formation of the



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SPELL: 1. microcline, 2. ongonite, 3. zinnwaldite

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