
MINERALS
AND MINERAL PARAGENESES

Compositional Variations of Pyrochlore Group Minerals in Ongonite and Zwitter of the Verkhneurmisky Pluton, Russian Far East

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Abstract—The pyrochlore-group minerals in ongonite and zwitter of the Verkhneurmisky granite pluton in the Badzhal district, Russian Far East are reported. The composition, genesis, and crystallization sequence are characterized. Three rare species of pyrochlore, pyrochlore-I and pyrochlore-II in ongonite, and pyrochlore-III in zwitter are found for the first time in the Russian Far East. Pyrochlore-I is a possible new member of the pyrochlore group, bismuth-bearing “oxyferropyrochlore”; pyrochlore-II is an uranium-bearing and iron-bearing hydrokenopyrochlore; and pyrochlore-III is a lead- and iron-bearing hydrokenopyrochlore. All three pyrochlore species result from an alteration of early accessory minerals: niobium wolframite, samarskite, ishikawaite, wolframoixiolite, scheelite, and fergusonite. The Far East pyrochlore is characterized by extremely high Ta, W, and Fe contents. Compositional variations in pyrochlore are caused by substitution of Nb, Ta, W at the *B* site of the crystal structure and exchange of U, Pb, Bi, and Fe at the *A* site. The Ta, Bi, and Th concentrations decrease during transition from the late magmatic to greisen stage; the mineral forming significance of Nb, W, U, Y, Pb, and H₂O increases as followed: Ta, Nb, Bi, Fe, Th, As, P, Ca, Ti → Nb, Ta, W, U, Fe, HREE, Sc, Mn, Na, H₂O → Nb, Pb, W, Fe, Y, H₂O.

Keywords: pyrochlore group, bismuth-bearing oxyferropyrochlore, uranium-bearing hydrokenopyrochlore, lead-bearing hydrokenopyrochlore, ongonites, zwitters, Verkhneurmisky granite massif, the Russian Far East

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INTRODUCTION

Pyrochlore, $A_{2-m}B_2O_{6-w}(OH, F, O, \square, H_2O)_{1-n}$ ($m = 0-1.7$, $w = 0-0.7$, $n = 0-1$), is known by its compositional variations reflecting specific features of its structure (Atencio et al., 2010). Large cavities $A^{[8]}$ like zeolite retaining vacancies and providing exchange of cations Na, Ca, Sr, Pb, Bi, Y, REE, U, Th, and Fe²⁺, as well as H₂O, are present in the rigid framework of the $B^{[6]}$ octahedra (cations Nb, Ta, Ti, W, Fe³⁺) (Gorzhevskaya et al., 1974; Voloshin, 1993; Lapin and Kulikova, 2000). An abundance in nature, multiple nucleation and transformation in various environments, and isomorphic capacity in regard to incompatible elements (Nb, Ta, U, Th, Y, REE) make the pyrochlore-group minerals by important indicators of petrogenesis of rare metal mineralization (Kuzmenko and Es'kova, 1968; Gorzhavskaya and Skorobogatova, 1989; Lumpkin and Ewing, 1995; Wall et al., 1996; Nasraoui and Bilal, 2000; Yaroshevsky and Bagdasarov, 2008; Zaitsev et al., 2012; Hogarth, 2016; Li et al., 2016; Melcher et al., 2017). The pyrochlore-group minerals are well studied in carbonatite, alkaline rocks, and pegmatites, whereas Ta minerals of the microlite group are predominantly examined in rare-

metal Li–F granite and greisen (Kuzmenko and Es'kova, 1968; Aleksandrov, 1973; Gorzhavskaya et al., 1974; Beskin et al., 1979, 1994; Vladyskin, 1983; Belkasmi et al., 2000; Semenov, 2001; Huang et al., 2002, 2015; Ercit et al., 2003; Rub A.K. and Rub M.G., 2006; Breiter et al., 2007; Yaroshevsky and Bagdasarov, 2008; Alekseev and Marin, 2015). Niobium mineralization was identified (Alekseev, 2014; Alekseev et al., 2015, 2018) and rare species of pyrochlore described in this paper were established during the investigation of ongonite and zwitter of the Verkhneurmisky granite pluton in the Russian Far East.

OBJECT AND EXPERIMENTAL

The Pravourmisky Complex of rare-metal Li–F granites containing ongonite dikes and accompanied by the outer-contact siderophyllite–quartz–topaz greisen, zwitter was identified within the Verkhneurmisky pluton of the Badzhal tin district in the Russian Far East (*Geodynamics ...*, 2006; Alekseev, 2014). Small Li–F granite intrusions and thin ongonite dikes intruded into biotite leucogranite of the Verkhneurmisky pluton and rhyolite ignimbrite of the Urmi caldera. In ongonite, fine-grained zinnwaldite–quartz–

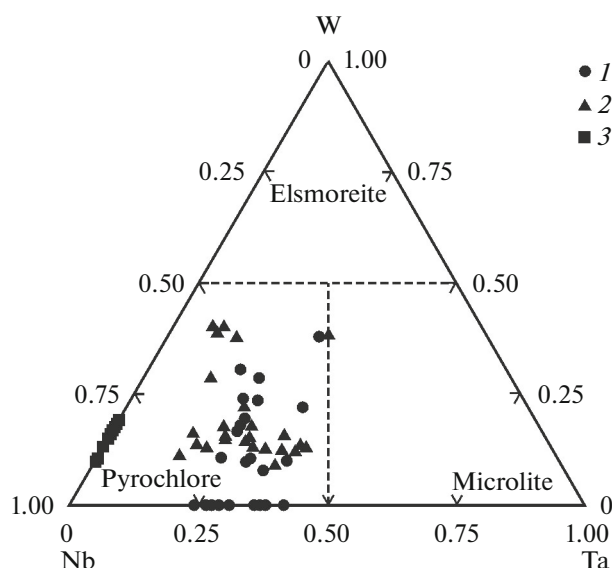


Fig. 1. Triangle plot in terms of Nb, W, and Ta occurring in crystal framework *B* of pyrochlore group minerals of Verkhneurmitsky pluton. (1) pyrochlore-I, (2) pyrochlore-II, (3) pyrochlore-III.

microcline—albite rock (Alekseev, 2014), a wide range of accessory minerals was identified: fluorite, cyrtolite, monazite, xenotime, niobium wolframite, wolframioxiolite, columbite, samarskite, ishikawaite, scheelite, chernovite, thorite, and uraninite. Zwitter is a massive siderophyllite—topaz—quartz altered rock with yttrifluorite, cassiterite, wolframite, arsenopyrite, and bismuthinite, which occurs as shallow-dipping and steep bodies of variable thickness; some of these bodies are W—Sn deposits and prospects (Pravourmiysky, Wolfram-Makit, Vysoky) (Semenyak, 1983; Marin et al., 1990; *Geodynamics* ..., 2006). In zwitter of the Verkhneurmitsky pluton, a St. Petersburg Mining University expedition supervised by Yu.B. Marin found rare-metal mineralization close in mineralogy to that of Li—F granites: ilmenorutile, monazite, yttrifluorite, niobium-bearing wolframite, wolframioxiolite, ishikawaite, fergusonite, and euxenite (Marin et al., 1990; Alekseev and Marin, 2015; Alekseev et al., 2018).

The representative samples of granitoids and zwitter were collected at the rare-metal mineralized locations identified with geochemical surveys. Sampling was terminated by a petrographic description of rocks and their geochemical study (ED-2000, XRF-1800, ICPE-9000, AA6300, AAS5EA) at the Common Use Center of the St. Petersburg Mining University.

Samples with elevated contents of trace elements were studied with optical and electron microscope to find their mineral carriers (JSM-6460LV, JSM-7001F, JIB-4500, Cameca MS-46; St. Petersburg University, VSEGEI, St. Petersburg). The data obtained were interpreted with the INCA Energy (Oxford) software

package. An investigation of the ongonite and zwitter accessory minerals was focused on the structure of individuals, trace elements, composition of mineral-prisoners and their distribution in crystals (Brodskaia and Marin, 2016). The chemical composition of minerals was determined in monomineralic samples using bulk chemical analysis, ICP-MS, and AAS. The composition of tantaloniobates was determined on a Cam-Scan MV2300 electron microscope and JXA-8320 electron microprobe equipped with WDS at Russian Geological Research Institute and St. Petersburg State Mining University, respectively. Micrograins of the pyrochlore-group tantaloniobates were identified as a result of a detailed study of the W and Nb minerals in ongonite and zwitter.

PYROCHLORE-GROUP MINERALS OF VERKHNEURMIYSKY PLUTON

The relationship of the mineral-forming elements (Nb, Ta, W, U, Pb, Bi, Th, Fe, Y, REE, Ca) allows the attribution of minerals found in the Verkhneurmitsky pluton to three pyrochlore species different in the composition of extraframework cations, Bi, U, and Pb (Skorobogatova et al., 1966; Chukanov et al., 1999; Chakhmouradian and Mitchell, 2002; Hogarth, 2016). Previously, similar minerals were named as bismutopyrochlore, uranpyrochlore, and plumbopyrochlore, respectively (Hogarth, 1977; Voloshin and Pakhomovsky, 1986; Gorzhevskaya and Skorobogatova, 1989; Krivovochev, 2008; Yaroshevsky and Bagdasarov, 2008). Presently, these minerals are discredited (Atencio et al., 2010). In this study, the pyrochlore-group minerals are divided into three subgroups different in the chemical composition and conditions of formation: pyrochlore-I and pyrochlore-II identified in ongonite, and pyrochlore-III present in zwitter (Fig. 1).

Pyrochlore-I occurs as anhedral metasomatic segregations of n to $n \times 10 \mu\text{m}$ in size in accessory W and Nb minerals from ongonite. It is distributed throughout the grains of the minerals using microinclusion boundaries, pores, and fractures resulted from heterometry (Figs. 2a, 2b). Protominerals for the pyrochlore-I formation were (in order of occurrence): niobium wolframite, ishikawaite, wolframioxiolite, samarskite, and scheelite. Grains of pyrochlore-I are observed along cleavage of rock-forming minerals, zinnwaldite, albite, and microcline.

The major components of the pyrochlore-I composition are, wt %: 11.7–31.3 Nb₂O₅, 9.5–34.6 Ta₂O₅, 7.2–19.4 Bi₂O₃, 5.4–25.8 ThO₂, 0–23.7 WO₃, 5.2–14.1 FeO, 1.7–12.6 UO₂. Minor concentrations are typical of CaO, P₂O₅, TiO₂, MnO, Sc₂O₃ (average 1.6, 2.6, 0.5, 0.5, and 0.1 wt %, respectively). Uncommon admixture As₂O₅ (0.76–4.41 wt %) in pyrochlore-I from ongonite (67% of all samples) should be noted. The REE content is relatively low and ranges from 0 to

Table 1. Chemical composition, wt % of pyrochlore-group minerals in ongonite (pyrochlore-I, II) and zwitter (pyrochlore-III) of Verkhneurmitsky pluton

Component	Pyrochlore-I			Pyrochlore-II			Pyrochlore-III		
	1	2	Av. (24)	3	4	Av. (26)	5	6	Av. (12)
Na ₂ O	—	—	—	0.00	0.00	0.04	—	—	—
P ₂ O ₅	5.32	0.00	2.58	—	—	—	—	—	—
CaO	2.88	0.00	1.57	0.00	2.20	1.02	—	—	—
Sc ₂ O ₃	0.00	0.00	0.13	1.03	0.86	0.93	—	—	—
TiO ₂	0.00	0.00	0.52	0.00	0.00	0.09	—	—	—
MnO	0.00	1.50	0.45	0.59	1.28	1.08	—	—	—
FeO*	11.53	10.02	10.83	0.67	1.33	3.50	6.50	6.57	6.25
As ₂ O ₅	0.00	0.87	1.85	—	—	—	—	—	—
Y ₂ O ₃	—	—	—	—	—	—	0.00	9.88	3.15
Nb ₂ O ₅	25.36	20.63	22.87	29.88	30.89	27.60	46.03	53.97	50.24
Ce ₂ O ₃	0.00	1.87	0.39	0.00	0.00	0.12	—	—	—
Nd ₂ O ₃	—	—	—	0.00	0.00	0.03	—	—	—
Dy ₂ O ₃	0.00	0.00	0.05	1.84	0.00	0.56	—	—	—
Er ₂ O ₃	—	—	—	1.45	0.00	0.58	—	—	—
Yb ₂ O ₃	0.00	0.00	0.07	3.02	1.74	1.98	—	—	—
Ta ₂ O ₅	17.55	26.80	17.70	16.91	18.32	20.01	—	—	—
WO ₃	0.00	18.31	6.81	15.47	13.17	15.77	18.54	10.34	15.27
PbO	—	—	—	6.03	5.81	6.29	20.04	10.14	16.92
Bi ₂ O ₃	14.13	7.66	12.92	0.00	0.00	0.61	—	—	—
ThO ₂	14.18	5.81	12.96	3.78	0.00	3.00	—	—	—
UO ₂	5.26	5.16	5.55	18.24	22.92	15.76	7.73	7.90	7.05
Total	96.20	98.64	97.24	98.71	98.49	98.90	98.83	98.80	98.89
Formula coefficients calculated on the basis of (Nb + Ta + Ti + W + P + As = 2)									
Na				0.00	0.00	0.01			
Ca	0.30	0.23	0.16	0.00	0.21	0.10			
Sc	0.00	0.00	0.01	0.08	0.07	0.07			
Mn	0.00	0.00	0.04	0.05	0.10	0.08			
Fe	0.93	0.80	0.89	0.05	0.10	0.27	0.42	0.41	0.39
Y							0.00	0.39	0.13
Ce	0.00	0.00	0.01	0.00	0.00	0.00			
Dy	0.00	0.00	0.00	0.05	0.00	0.02			
Er				0.04	0.00	0.02			
Yb	0.00	0.00	0.00	0.08	0.05	0.05			
Pb				0.15	0.14	0.15	0.42	0.20	0.34
Bi	0.35	0.45	0.33	0.00	0.00	0.01			
Th	0.31	0.26	0.29	0.08	0.00	0.06			
U	0.11	0.13	0.12	0.37	0.46	0.32	0.13	0.13	0.12
Total A	2.00	1.87	1.85	0.95	1.12	1.17	0.98	1.13	0.98
P	0.43	0.43	0.21						
Ti	0.00	0.10	0.04	0.00	0.00	0.01			
As	0.00	0.17	0.09						

Table 1. (Contd.)

Component	Pyrochlore-I			Pyrochlore-II			Pyrochlore-III		
	1	2	Av. (24)	3	4	Av. (26)	5	6	Av. (12)
Nb	1.11	0.94	1.01	1.22	1.25	1.13	1.62	1.80	1.70
Ta	0.46	0.36	0.47	0.42	0.45	0.49			
W	0.00	0.00	0.17	0.36	0.31	0.37	0.38	0.20	0.30
Total <i>B</i>	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00

Representative (1–6) and average (Av.; number of sample *s* in parentheses) electron microprobe data for pyrochlore (Common Use Center, St. Petersburg Mining University). Dash denotes that the element was not detected. FeO* is FeO + Fe₂O₃.

4.6 wt %; Ce and Yb maximums are typical (see Table). The pyrochlore-I grains are extremely heterogeneous in composition: variation coefficients of the Nb, Ta, Bi, U, Th, and Fe content are 24 to 41%; variations in the contents of minor Ti, W, Mn, P, and Ca are very significant (>100%); Ce, Yb, Dy, Sc (>200%).

Pyrochlore-I is one of the most stoichiometric pyrochlore-group minerals studied here: average formula coefficients of Nb, Ta, W are 1.01, 0.47, and 0.17, respectively; total cations at site *A* is 1.85, including Bi, Th, and Fe 0.33, 0.29, and 0.89, respectively. The replacement of the complex Ta–Nb–W minerals by pyrochlore-I results in an unusual property of the latter. It has an extremely high proportion of Ta and W, apfu: 0.26–0.81 and 0.00–0.73, respectively (average mole fractions at site *B* are 0.025 and 0.09). The

Nb/Ta ratio is 1.1–3.2 (average 2.0). Tungsten- and Bi-bearing pyrochlore very close to tungsten microcline-Bi (Hogarth, 1977; Yaroshevsky and Bagadasarov, 2008; Hatert et al., 2013) was identified in one sample (Fig. 1).

With all exotism of cations at site *A*, Fe is defining in pyrochlore-I: (Fe_{0.89}Bi_{0.33}Th_{0.29}Ca_{0.16}U_{0.12}Mn_{0.04}Sc_{0.01}Ce_{0.01}□_{0.15})_{2.00}(Nb_{1.01}Ta_{0.47}P_{0.21}W_{0.17}As_{0.09}Ti_{0.04})_{2.00}O₆O. The pyrochlore-I studied here is an unknown phase taking into the classification of the Commission on New Minerals, Names, and Classification, International Mineralogical Association (Atencio et al., 2010; Hatert et al., 2013; Updated list of IMA-approved minerals (September 2017)) and its possible new pyrochlore-group member, Fe₂Nb₂O₆O with conditioned name Bi-bearing “oxyferropyrochlore”

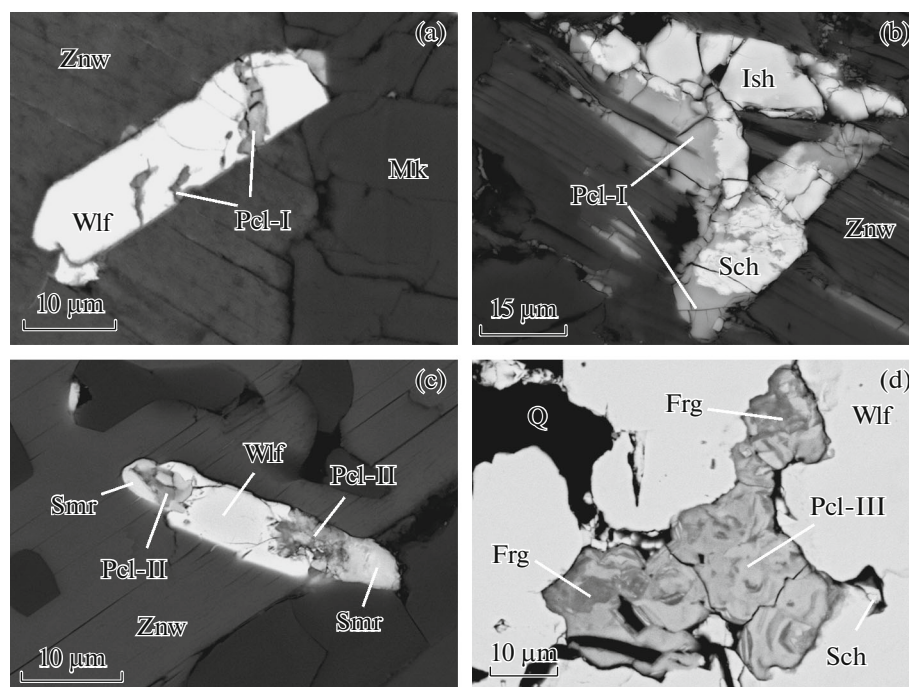


Fig. 2. Back-scattered electron images (JSM-7001F, Common Use Center, St. Petersburg Mining University) of pyrochlore group minerals in ongonite and zwitter of Verkhneurmitsky pluton. Frg, fergusonite; Ish, ishikawaite; Mk, microcline; Pcl, pyrochlore; Q, quartz; Smr, samarskite; Sch, scheelite; Wlf, wolframite; ZnW, zinnwaldite.

According to the classification of Hogarth (1977) Bi-bearing “oxy-ferropyrochlore” refers to bismuth pyrochlore.

Pyrochlore-II is present in highly altered crystals of accessory wolframite from ongonite replaced by scheelite, wolframixiolite, russelite, ishihawaite, samarskite-(Yb), and pyrochlore-I. Pyrochlore-II replaces these secondary minerals predominantly with samarskite and less frequently with pyrochlore-I (Fig. 2c).

The contents of the mineral-forming constituents in pyrochlore-II are wt %: 12.4–41.5 Nb₂O₅, 5.9–33.4 Ta₂O₅, 5.3–23.1 UO₂, 0–32.1 WO₃. Substantial admixtures are wt %: 1.5–8.9 PbO, 0–7.3 Bi₂O₃, 0–13.6 FeO, 0–7.7 ThO₂, 0–7.4 CaO. Concentrations of MnO, Sc₂O₃, and TiO₂ are minor, averaging 1.1, 0.9, and 0.1 wt %, respectively. The rare-earth element content up to 8.7 wt % is the highest among pyrochlores of the district, with Y and Ce slope (see Table 1). Pyrochlore-II is heterogeneous in composition; variation coefficients in the Nd, Ce, Ti, and Bi concentrations are higher than 200%; those of the Er, Ca, Fe, and Mn contents are higher than 100%. Variation coefficients in the major component contents (Nb, Ta, W, U) are relatively low (20–51%).

Both pyrochlore-I and pyrochlore-II have high Ta and W; their formula coefficients are 0.16–0.79 and 0.00–0.81, respectively (average 0.49 and 0.37); the mole fraction at site *B* is 0.25 and 0.19, respectively. The Nb/Ta value ranges from 1.2 to 4.7 (average 2.3). Pyrochlore-II is close in composition to the microlite- and elsmoreite-group minerals (Williams et al., 2005; Atencio et al., 2010). In one case, W–Nb microlite-U was observed (Belkasmı et al., 2000; Huang et al., 2002, 2015; Rub A.K. and Rub M.G., 2006; Breiter et al., 2007; Melcher et al., 2017) (Fig. 1). Pyrochlore-II is composed of the extraframework cations U, Fe, Pb, Ca (0.32, 0.27, 0.15, and 0.10 apfu, respectively) and in contrast to pyrochlore-I, it has a high vacancy proportion at site *A* (up to 1.32 apfu) that facilitates the incorporation of water molecules at this site.

According to the conventional classification, pyrochlore-II, $(\square_{0.83}\text{U}_{0.32}\text{Fe}_{0.27}\text{Pb}_{0.15}\text{Ca}_{0.10}\text{Mn}_{0.08}\text{Sc}_{0.07}\text{Th}_{0.06}\text{Yb}_{0.05}\text{Dy}_{0.02}\text{Er}_{0.02}\text{Na}_{0.01}\text{Bi}_{0.01})_{2.00}(\text{Nb}_{1.13}\text{Ta}_{0.49}\text{W}_{0.37}\text{Ti}_{0.01})_{2.00}\text{O}_4(\text{OH})_2(\text{H}_2\text{O})$, is U- and Fe-bearing hydrokenopyrochlore $\square_2\text{Nb}_2\text{O}_4(\text{OH})_2(\text{H}_2\text{O})$ (Hålenius et al., 2017). In the previous classifications of Hogarth (1977), Gorzhevskaya and Skorobogatova (1989), and Yaroshevsky and Bagdasarov (2008), this mineral was referred to uranpyrochlore (Chakhmouradian, Mitchell, 2002; Krivovichev, 2008; Hogarth, 2016), which is discredited (Atencio et al., 2010).

Pyrochlore-III replaces fergusonite in zwitter to form partial or complete pseudomorphs. Association with Nb-bearing wolframite and scheelite (Fig. 2d) is typical. Pyrochlore-III is distinguished by an elevated content of Nb₂O₅ (44.6–56.2 wt %), PbO (6.8–21.6 wt %), and Y₂O₃ (0–14.0 wt %); Ta, Bi, Ca, Sc,

Mn, Ti, REE, and Th typical of pyrochlore from ongonite are absent in this pyrochlore. Similar to accessory pyrochlore-II, pyrochlore-III in zwitter is enriched in WO₃ and UO₂, 10.3–18.5 and 3.9–11.2 wt %, respectively. A presence of Pb (0.30–0.48 apfu) in its structure is combined with Fe (0.39 apfu), Y (0.13 apfu), and U (0.12 apfu) at site *A*. The crystal structure of pyrochlore-III has a high vacancy proportion (1.02 apfu): $\square_{1.02}\text{Fe}_{0.39}\text{Pb}_{0.34}\text{Y}_{0.13}\text{U}_{0.12})_{2.00}(\text{Nb}_{1.70}\text{W}_{0.30})_{2.00}\text{O}_6(\text{OH})_2(\text{H}_2\text{O})$. Pyrochlore-III is Pb- and Fe-bearing hydrokenopyrochlore (Hålenius et al., 2017). According to the previous classifications of Hogarth (1977), Gorzhevskaya and Skorobogatova (1989), and Yaroshevsky and Bagdasarov (2008), this mineral is close to plumbopyrochlore (Skorobogatova et al., 1966; Voloshin and Pakhomovsky, 1986; Krivovichev, 2008), which is discredited (Atencio et al., 2010).

DISCUSSION

Pyrochlore composition. As aforementioned, the pyrochlore supergroup minerals in Li–F granite and ongonite of the rare-metal provinces in the world are microlite-group minerals. The pyrochlore-supergroup minerals are rare in the rare-metal Li–F granite: Orlovka and Etyka deposits in the Transbaikalian region (Aleksandrov, 1973; Beskin et al., 1994), and Cinovec, Czech Republic (Rub A.K. and Rub M.G., 2006). Pyrochlore, including U- and Pb-bearing varieties, is much more frequent in rare-metal alkali granite in Brazil (Bastos Neto et al., 2009; Melcher et al., 2017), Nigeria (Orajaka, 1986), Kazakhstan, Tuva, and other regions (Beskin et al., 1979; Grzhevskaya and Skorobogatova, 1989; Yaroshevsky and Bagdasarov, 2008; Melcher et al., 2017). Pyrochlore from ongonite was mentioned only in small intrusions of the Ukrainian shield (Marchenko and Kon'kov, 1988). We never see any description of pyrochlore from ongonite. However, taking into account the composition of ongonite from *type locality* in Mongolia (Štemprok, 1991), there are geochemical premises of crystallization in ongonite of pyrochlore enriched in Ta, W, Bi, U, and As. In particular, Dostal et al. (2015) reported Ta–Nb oxide (Nb/Ta = 5) enriched in W (2–8 wt %) from Ary-Bulak, Eastern Transbaikalian region.

In ongonite and zwitter of the Russian Far East, we established the pyrochlore-supergroup minerals for the first time. As shown in the aforementioned description, the typomorphic features of the pyrochlore-supergroup minerals in ongonite are: (1) substantial Ta and W admixture at site *B* (Fig. 1) and (2) constant Fe, U, and Bi at site *A* (Table 1). These parameters are inherited by postmagmatic pyrochlore of zwitter. In this case, Pb substitutes U at site *A* and Ta is substituted by Nb at site *B*. Thus, the composition of the pyrochlore-supergroup minerals from the Badzhal district reflects the tantalum specialization of ongonite, which is seen in the formation of tantalum

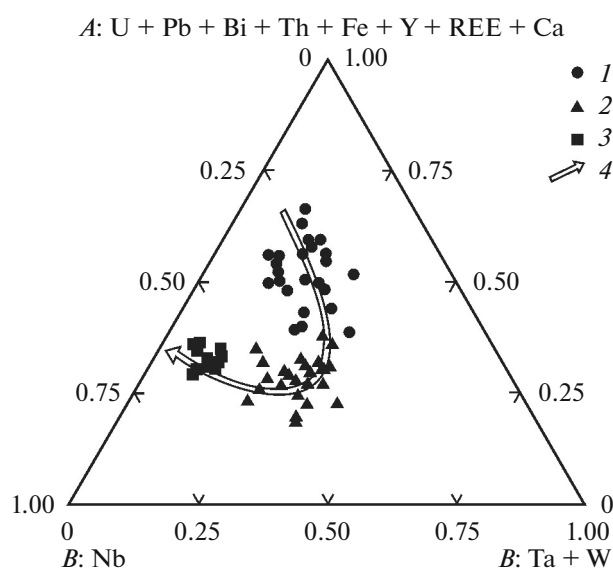


Fig. 3. Compositional evolution of pyrochlore-group minerals of Verkhneurmitsky pluton. (1) Pyrochlore-I; (2) pyrochlore-II; (3) pyrochlore-III; (4) direction of the compositional evolution. The diagram considers atomic amounts of elements with content reaching 5 wt %.

pyrochlore rather than in predominant microlite typical of Li–F granite (Kuzmenko and Eskova, 1968; Aleksandrov, 1973; Gorzhevskaya and Skorobogatova, 1989; Beskin et al., 1994; Lumpkin and Ewing, 1995; Belkasmi et al., 2000; Rub A.K. and Rub M.G., 2006; Breiter et al., 2007; Yaroshevsky and Bagdasarov, 2008; Huang et al., 2015), as well as bringing closer the Far East ongonite and alkali rare-metal granite. The high Ta_2O_5 content in pyrochlore-I and pyrochlore-II from ongonite of the Badzhalsky district (34.6 and 33.4 wt %, respectively) was not previously reported (Hogarth, 1977; Rub A.K. and Rub M.G., 2006; Atencio et al., 2010); niobium microlite-Bi and microlite-U are identified in sporadic samples (Fig. 1).

The high W concentration measured many times in the pyrochlore-supergroup minerals, especially in uranopyrochlore from Li–F granite, reaches 0.1–6.50 wt % (Kuzmenko and Eskova, 1968; Belkasmi et al., 2000; Rub A.K. and Rub M.G., 2006; Breiter et al., 2007; Harlaux et al., 2015; Huang et al., 2015). The WO_3 content in tantalum pyrochlore from granite pegmatites in the Pamir Mountains is 11.40 wt % (Konvalenko et al., 1982). However, the extremely high WO_3 content in pyrochlore-I, pyrochlore-II, and pyrochlore-III of the Verkhneurmitsky pluton (23.7, 32.1 and 18.5 wt %, respectively) was not mentioned in literature. Iron is important in the composition of all Far East pyrochlore species; the average FeO concentration is 10.8, 3.5, and 6.3 wt %, respectively (Table 1). The extreme W and Fe concentrations in pyrochlore are probably caused by early wolframite in the places of pyrochlore origin.

The bismuth admixture is characteristic of pyrochlore from rare-metal granite and pegmatites (Tindle and Breaks, 1998; Chukanov et al., 1999; Ercit, 2003; Yaroshevsky and Bagdasarov, 2008). The pyrochlore-supergroup minerals, microlite and tantalum pyrochlore, from Li–F granite and ongonite are typically enriched in U (Kuzmenko and Eskova, 1968; Gorzhevskaya and Skorobogatova, 1989; Belkasmi et al., 2000; Semenov, 2001; Huang et al., 2002; Ercit et al., 2003; Rub A.K. and Rub M.G., 2006; Yaroshevsky and Bagdasarov, 2008; Bastos Neto et al., 2009; Huang et al., 2015; Melcher et al., 2017). Lead-bearing pyrochlore-III found in zwitter frequently accompanies U- and Bi-bearing pyrochlore in rare-metal granite complexes (Voloshin and Pakhomovsky, 1986; Gorzhevskaya and Skorobogatova, 1989; Vasiliev et al., 2008; Yaroshevsky and Bagdasarov, 2008; Melcher et al., 2017), which was found for the first time in Li–F granite and altered rocks by Vladyskin (1983). Ercit et al. (2003) reported Pb-bearing pyrochlore associated with Bi-bearing pyrochlore from dikes of rare-metal leucogranite–pegmatite complex in Canada; in Li–F granites of Brazil, it is associated with U-bearing pyrochlore (Bastos Neto et al., 2009; Melcher et al., 2017).

Among minor admixtures, REE should be noted that their patterns with enrichment of HREE is similar to that in U- and Pb-bearing pyrochlore from subalkali rare-metal granites (Skorobogatova et al., 1966; Gorzhevskaya et al., 1974, 1989; Tindle and Breaks, 1998; Vladyskin, 1983; Semenov, 2001). It should be emphasized that all species of the Far East pyrochlore are compositionally variable in both individuals and aggregates. On the back-scattered electron images, pyrochlore is spotty that emphasizes variations in the contents of components (Fig. 2). The variation coefficients in the contents of the admixtures are 50–150% reaching 200% and higher for Ti, Sc, and REE.

Genesis and formation sequence of pyrochlore All mineral species of the pyrochlore group in the Badzhalsky district result from the alteration of earlier Nb-bearing minerals, chemical substitution of cations at site B (Nb, Ta, W) and cation exchange at site A (U, Pb, Bi, Fe) (Gorzhevskaya et al., 1974; Voloshin, 1993; Lumpkin and Ewing, 1995; Lapin and Kulikova, 2000; Yaroshevsky and Bagdasarov, 2008; Atencio et al., 2010). Pyrochlore from ongonite and zwitter is probably formed at the late magmatic and postmagmatic stages of the mineral-forming process in the sequence: pyrochlore-I → pyrochlore-II → pyrochlore-III (Fig. 3). The sequence of the mineral formation takes into account the crystallization order of proto-minerals, which are replaced by pyrochlore. In addition, the following facts give an indication of the mineral paragenetic sequence:

(1) Pyrochlore-I and pyrochlore-II were found in ongonite without any traces of hydrothermal alteration that demonstrates magmatic origin of these

pyrochlore species. Association of pyrochlore with ongonite indicates mineral formation as a result of crystallization of subalkaline leucogranite magma enriched in rare-metal fluids.

(2) Pyrochlore-I and pyrochlore-II are present in the same aggregates but are isolated and replace different protominerals; occasionally, pyrochlore-II replaces pyrochlore-I.

(3) If similar proto-minerals (wolframite, fergusonite, scheelite) replaced by the pyrochlore-group minerals are present in both ongonite and zwitter, the secondary pyrochlore-III is observed only in zwitter reflecting its pneumato-hydrothermal origin. It should be noted that crystallization in the order U-bearing pyrochlore-II $\rightarrow$ Pb-bearing pyrochlore-III was reported in Li–F granites of Brazil (Bastos Neto et al., 2009) and rare-metal altered rocks of the Polar Urals (Vasiljev et al., 2008).

The established compositional variations of the pyrochlore-supergroup minerals of the Verkhneurmiskiy pluton reflect geochemical and crystal chemical evolution of the minerals (Fig. 3). The geochemical evolution of pyrochlore is caused by the change in composition and physicochemical parameters of mineral-forming medium during transition from the late magmatic to pneumato-hydrothermal stage (temperature decreasing, increase of oxidizing potential, pH fluctuation) (Aleksandrov, 1973; Alekseev et al., 2018). The compositional evolution of the mineral-forming medium is described as follows: Ta, Nb, Bi, Fe, Th, As, P, Ca, Ti $\rightarrow$ Nb, Ta, W, U, Fe, HREE, Sc, Mn, Na, H₂O $\rightarrow$ Nb, Pb, W, Fe, Y, H₂O.

The crystal chemical evolution of pyrochlore is determined by the evolved mineral formation conditions. Early Bi-bearing “oxyferropyrochlore” replaces primary accessory minerals in ongonite, wolframite, scheelite, wolframixiolite, and ishiikawaite, by the coupled substitution of Nb, Ta, Bi, Th, P, As, and Ca for W and Fe (Figs. 1a, 1b). As a result, the crystal lattice with multicomponent framework *B* (Nb > Ta > W $\approx$ P > As > Ti) and completely occupied site *A*. Uranium-bearing hydrokenopyrochlore completes autometasomatic transformation of accessory minerals in ongonite: niobium wolframite $\rightarrow$ samarskite $\rightarrow$ hydrokenopyrochlore (Alekseev, 2014) (Fig. 1c). The mineral transformation is accompanied by two-step reconstruction of the layered crystal structure of wolframite to the structure of samarskite and then to that of pyrochlore (Voloshin, 1993). As a result, the mixed W–Ta–Nb framework of the mineral is formed and site *A* retains many vacancies and is occupied by H₂O (1.17 apfu). Postmagmatic Pb-bearing hydrokenopyrochlore replacing fergusonite is even more nonstoichiometric and structurally disordered most likely due to larger Pb ions. The eight-apex *A* sites in its predominantly niobium framework (85%) is only half occupied (0.98 apfu): Pb $\approx$ Fe > U $\approx$ Y (Fig. 3) that facilitates incorporation of the water molecule in this site.

Thus, the crystal chemical evolution of the Far East pyrochlore results in a stable structural framework through increasing Nb and Pb proportion at site *B* and exchange of heterovalent cations with increasing vacancy and water portion at site *A*: A^{2+} (Fe, Bi, Th, Ca, U) + B^{5+} (Nb, Ta, As, P) $\rightarrow$ A^{2+} (U, Fe, Pb, Ca, REE, Sc, H₂O, vacancy) + B^{5+} (Nb, Ta, W) $\rightarrow$ A^{2+} (Fe, Pb, U, Y, H₂O, vacancy) + B^{5+} (Nb, W) (Table 1). As demonstrated by the variations in the chemical composition, the Ta, Bi, and Th concentrations in pyrochlore studied here decrease during transition from the late magmatic to greisen stage, whereas mineral-forming importance of niobium, tungsten, uranium, yttrium, lead, and water increases.

CONCLUSIONS

(1) The specific features of the composition, genesis, and formation sequence of the pyrochlore-group minerals in ongonite are reported for the first time. Three rare pyrochlore species, pyrochlore-I, pyrochlore-II, and pyrochlore-III, are found in zwitter in the Russian Far East for the first time. Pyrochlore-I, a probable new mineral species of the pyrochlore group, is Bi-bearing “oxyferropyrochlore”; pyrochlore-II is U- and Fe-bearing hydrokenopyrochlore; pyrochlore-III is Pb- and Fe-bearing hydrokenopyrochlore.

(2) All three species of the Far East pyrochlore were formed by the multistage metasomatic replacement of the early accessory minerals: niobium wolframite, samarskite, wolframixiolite, scheelite, and fergusonite.

(3) The pyrochlore-group minerals from the Verkhneurmiskiy pluton are characterized by extremely high Ta, W, and Fe. Variations in the chemical composition of pyrochlore are caused by substitutions among Nb, Ta, and W in the *B* framework of the crystal structure and exchange among U, Pb, Bi, and Fe at site *A*.

(4) The compositional evolution of the pyrochlore-group minerals in the transition from the late magmatic to greisen stage of the Verkhneurmiskiy pluton reflects decreasing Ta, Bi, and Th concentrations and increasing mineral-forming significance of Nb, W, U, Y, Pb, and H₂O: Ta, Nb, Bi, Fe, Th, As, P, Ca, Ti $\rightarrow$ Nb, Ta, W, U, Fe, HREE, Sc, Mn, Na, H₂O $\rightarrow$ Nb, Pb, W, Fe, Y, H₂O.

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