

Formation Conditions of the Ore-Bearing Lithium–Fluoride Granites of the Shumilov Tungsten Deposit, Central Transbaikalia

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Abstract—Silicate melt inclusions were studied in the quartz phenocrysts from the Li–F granite porphyry of the Shumilov Massif, which are considered to be the sources of ore-bearing fluids of the Shumilov tungsten deposit. The estimated water content in the granite melt was 2.1–7.6 wt %, at a water pressure in the magmatic chamber of 3.1–5.2 kbar. It was concluded that the fluid–magmatic systems of the Shumilov and Spokoinoe tungsten deposits were formed at similar physicochemical conditions.

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INTRODUCTION

Data on the composition and content of volatiles in the ore-bearing granitoid melts are crucial for estimating the ore potential of the granitoid fluid–magmatic systems (Reyf and Bazheev, 1982; Reyf, 1990). The water fluid pressure and water content were estimated for the first time in the melt of Li–F granites of the Shumilov Massif, the source of the Shumilov tungsten deposit (Getmanskaya et al., 1986; Bubnov, 1995; Gaivoronskii, 1995).

BRIEF GEOLOGICAL CHARACTERISTICS OF THE SHUMILOV DEPOSIT

The deposit is located in the southern part of central Transbaikalia, 70 km south of the latitudinal segment of the Chikoi River (Fig. 1), and is confined to the area of Mesozoic activation of the Proterozoic–Paleozoic folded basement of the Mongol–Okhotsk collisional belt. The deposit is localized in the central dome of the large Middle Jurassic Asakan–Shumilov granite intrusion (170 Ma), exposed over an area of 300 km² (Gaivoronskii, 1995). The Asakan–Shumilov ore district also contains other W, Sn–W, and Mo–W deposits and occurrences, as well as non-economic Ta, Nb, and Be mineralization.

The Asakan–Shumilov Massif consists of the granites of three subsequent phases (Fig. 2, Table 1). The first phase is made up of the biotite porphyritic fine- to

medium-grained massive, occasionally gneissic granites and less common granodiorites. The second phase comprises leucocratic equigranular porphyritic fine- to coarse-grained granites and granite porphyries. The third phase includes fine and medium-grained Li–F granites and granite porphyries, which host the tungsten-bearing greisens of the Shumilov deposit.

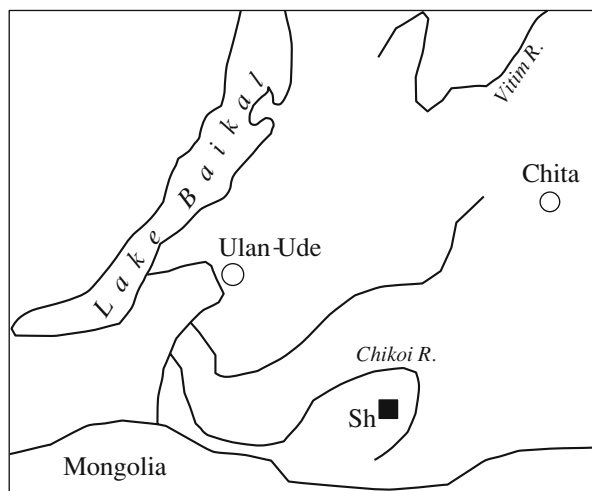


Fig. 1. Geographic position of the Shumilov Massif (Sh).

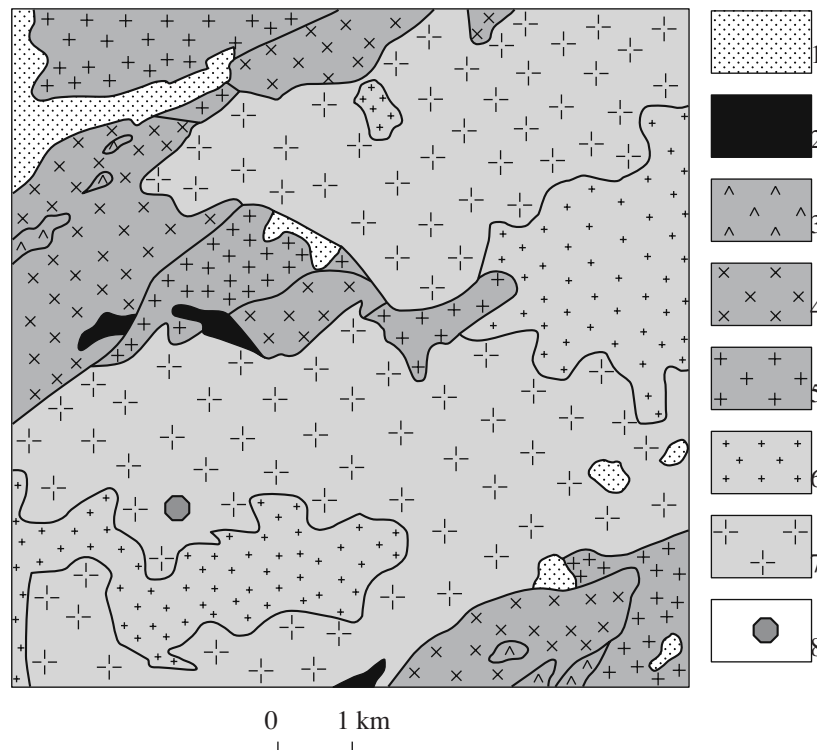


Fig. 2. Schematic geological map of the Shumilov deposit (prepared using materials of Dvoryadkin et al., 1975).

(1) Terrigenous deposits of the Ingoda Group, C_{1-2} ; (2) subvolcanic complex (dacitic porphyrites, quartz porphyries), $\lambda\pi\text{-}\alpha\beta\pi\text{PZ}_3$; (3–5) Daur granitoid complex, $\gamma\text{-}\delta\text{T}$ ((3) phase 1 biotite–hornblende diorite, (4) phase 2 granodiorite, (5) phase 3 porphyritic biotite granites); (6–8) Asakan–Shumilov granitoid massif, $\gamma_1\text{-}\gamma_2\text{J}_2$ ((6) phase 1 biotite porphyritic granite and granodiorite, (7) phase 2 leucocratic porphyritic granite and granite porphyry, (8) phase 3 Li–F granites).

MINERALOGY AND GEOCHEMISTRY OF THE SHUMILOV DEPOSITS

The Shumilov greisen tin–tungsten deposit (Getmanskaya et al., 1986; Bubnov, 1995; Gaivoronskii, 1995) is the largest ore deposits in the region. The main greisen ore lode of the deposit is situated at a depth of 70–120 m from the surface of a dome of medium-grained biotite leucogranites and forms a thick (up to 100 m) gently dipping body 500 × 600 m in area (Getmanskaya et al., 1986, 1995; Gaivoronskii, 1995). In terms of morphology, the ore lode is ascribed to the economic type of greisenized granite domes. The deposit is unusual in that the economic greisen ore body is situated at a certain depth instead of the typical position in the apical part of the granite pluton. This is because their sources were not the host porphyritic leucogranites of the early phases but the fine-grained Li–F granite stock of the final stage of the Asakan–Shumilov intrusive complex, with these rocks recovered from a depth of 120–140 m below the early phase (Bubnov, 1995).

The apical part of the Li–F granite stock and, partially, biotite leucogranites of the roof are transformed into a greisen body with economic tungsten mineralization, which composes the main ore lode of the Shumilov deposit. This is referred to as a dome-in-dome

structure (Tischendorf, 1989). The deposit contains widespread mica–quartz, mica–topaz–quartz, and topaz–quartz greisens. The main ore mineral, wolframite, forms fine uneven disseminations in the greisens, as well as small pockets and veinlets in association with other ore minerals: cassiterite, sphalerite, arsenopyrite, pyrite, chalcopyrite, molybdenite, galena, and bismuth minerals. Quartz, feldspar, lithium micas (protolithionite and zinnwaldite), and topaz (Getmanskaya et al., 1986) are gangue minerals.

The medium-grained porphyritic biotite granites (leucogranites) of the main phase of the massif are built up of quartz, microcline, oligoclase, and biotite. The phenocrysts are microcline. In terms of accessory minerals, the granites are ascribed to the monazite–ilmenite type, which are enriched in Cs, Rb, Li, As, Be, Sb, W, Ta, Th, U, and Pb, and depleted in Ba, Sr, V, Cu, Mo, Cr, Ni, Co, V, Nb, Zr, Hf, Y and most REE as compared to the average upper continental crust. The later fine-grained Li–F granites of the internal stock consist of quartz, microcline, albite, protolithionite, and subordinate topaz. As compared to the biotite leucogranites, they are even more enriched in many lithophile and ore metals: Bi, Cd, W, Mo, Be, Sn, Ta, Nb, Hf, Zr, Li, Rb, Cs, Tl, Zn, Pb, Cu, As, Ga, and U (Fig. 3).

Table 1. Chemical composition (wt %) of granitoids of the Asakan–Shumilov intrusive complex (after Dvoryadkin et al., 1975; Syritso, 2002)

Component	1	2	3	4	5	6	7	8	9
SiO ₂	72.82	73.64	72.64	71.66	75.38	75.84	75.98	76.06	72.15
TiO ₂	0.55	0.10	0.29	0.25	0.18	0.21	0.16	0.21	0.01
Al ₂ O ₃	14.07	12.89	13.10	13.80	12.80	13.00	11.58	10.95	15.90
Fe ₂ O ₃	–	0.12	0.72	0.84	0.42	0.42	0.68	1.46	0.36
FeO	0.06	2.66	2.35	2.87	1.15	1.07	0.65	0.93	1.17
MnO	0.39	0.043	0.051	0.057	0.03	0.02	0.04	0.07	0.09
MgO	0.82	0.24	0.35	0.39	0.22	0.18	0.16	0.76	0.23
CaO	3.80	0.77	1.04	0.99	0.25	0.67	0.44	0.86	0.26
Na ₂ O	4.70	4.40	4.15	3.95	3.85	3.15	3.95	3.24	5.76
K ₂ O	4.40	4.90	4.60	4.30	4.70	4.60	4.80	5.00	3.26
P ₂ O ₅	0.95	0.14	0.13	0.05	0.06	0.06	0.01	0.04	0.01
L.O.I.	0.13	0.05	0.35	0.65	0.58	0.34	0.84	2.91	nd
Total	98.70	100.00	99.77	99.81	99.62	99.57	99.30	99.49	99.20

Note: (1–4) phase 1: (1, 2) Ust'-Shumilov Massif, (3, 4) Verkhniy Marfa Massif; (5, 8) phase 2: (5, 6) Shumilov Massif, (7, 8) Yasytai Massif; (9) phase 3 (Shumilov deposit).

Relative to the Li–F granites, the greisens are enriched in elements incorporated into the minerals of the major ore assemblages of the deposit: W, Sn, Bi, Cu, Zn, Pb, As, and rare alkalis (Li, Rb, and Cs) are accommodated in Li micas, as well as all REE and Y that form own minerals, monazite and xenotime, in the ores of the deposit (Table 2). The similar geochemical

specifics of the greisens and Li–F granites makes it possible to consider the latter to be the source of the greisen- and ore-forming fluids. Therefore, the study of physicochemical conditions under which the Li–F granites and related aqueous fluids at the Shumilov deposit were produced appears to be of a first-priority significance.

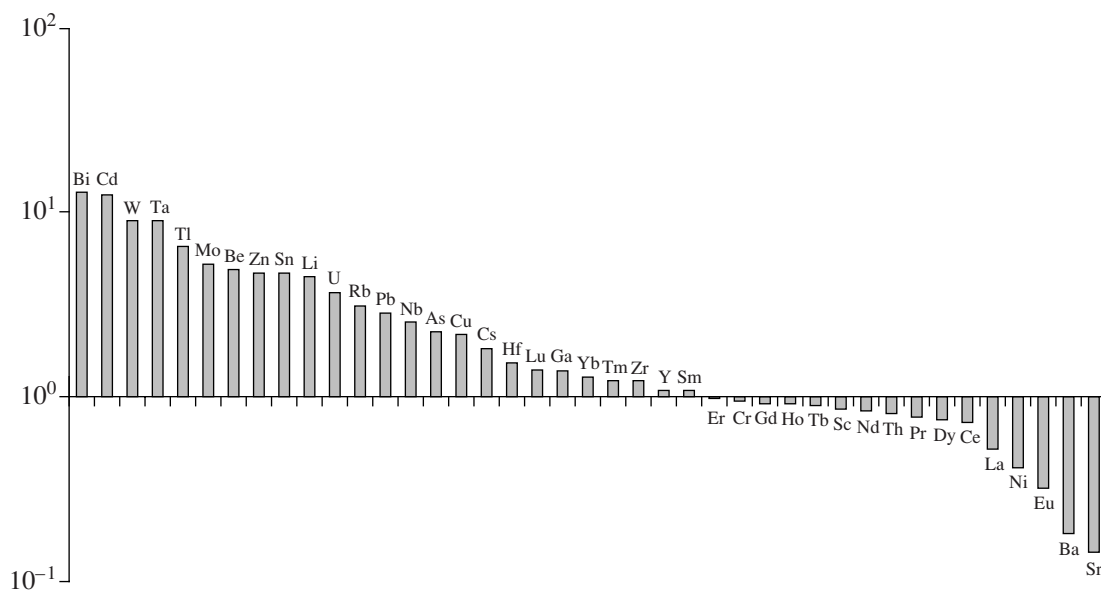
**Fig. 3.** Enrichment and depletion of Li–F granites of the Shumilov deposit in various trace elements relative to the parent leucogranites of the Asakan–Shumilov Massif.

Table 2. Rare and REE composition (in ppm) of Li–F granites and ore-bearing greisens of the Shumilov deposit

Element	Li–F granite	Greisen after granite	Element	Li–F granite	Greisen after granite
Li	307	902	La	8.2	12.6
Be	22.5	6.1	Ce	26.9	33.7
Sc	1.2	1.8	Pr	3.5	4.6
Cr	16.8	90.9	Nd	14.4	18.6
Co	–	–	Sm	4.8	6.2
Ni	–	1.4	Eu	–	–
Cu	4.5	614	Gd	3.8	4.3
Zn	211	4275	Tb	0.58	0.59
Ga	29.3	25.9	Dy	2.7	3.4
As	12.9	129	Ho	0.55	0.55
Rb	1231	1693	Tm	0.21	0.23
Sr	9.2	4.7	Yb	1.6	1.9
Y	15.0	21.9	Lu	0.23	0.29
Zr	97.5	53.3	Hf	5.1	3.9
Nb	39.7	22.6	Ta	17.2	7.0
Mo	1.9	0.8	W	4.3	13.8
Ag	1.1	6.5	Tl	17.8	5.5
Cd	1.5	19.4	Pb	94	863
Sn	43.6	243	Bi	3.1	21.8
Cs	33.7	37.7	Th	31.5	39.2
Ba	29.1	36.4	U	32.4	14.7

MELT INCLUSIONS

Samples were taken from the contact zone of a Li–F granite stock showing no traces of greisenization or other hydrothermal alterations (borehole 73, depth 401 m). The Li–F granites vary from medium-grained (in the central part of the stock) to finer grained rocks with porphyritic phenocrysts of tabular microcline and rounded quartz (3–5 mm) in the near-contact zone. The quartz phenocrysts contain primary silicate-melt inclusions 3–25 μm in size, which consist of anisotropic crystals of silicate minerals, a gas bubble, and aqueous solution in the interstices between crystalline phases (Fig. 4).

The silicate-melt inclusions (Table 3) were studied at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences. They were homogenized by quenching in a muffle with a platinum heater (Naumov, 1969), and the homogenization temperature was measured accurate to $\pm 10^\circ\text{C}$. The samples were heated for a long time (1–3 h) at a stable temperature, and then air quenched; the results of step heating were studied at room temperature. The temperature difference between the experiments was decreased with approaching phase transitions, which allowed us to accurately determine not only the homogenization temperature but also the temperature at which silicate phases begin to melt. It

should be noted that all high-water silicate glass inclusions, except for only the smallest individual ones, exploded at temperature above 550°C . We also analyzed the silicate-melt inclusions with a visible aqueous fluid phase (i.e., water-enriched melts) for fluid salinity using the ice melting temperatures and the volume proportions of phases, which are required for estimating

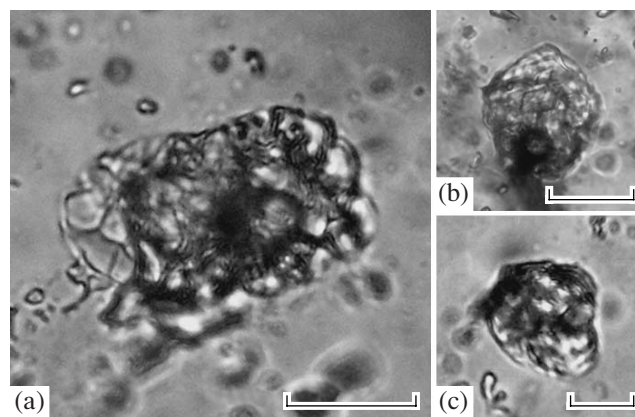


Fig. 4. Silicate melt inclusions (silicate phases, gas bubbles, and aqueous solution in interstices) in quartz phenocrysts from the porphyritic Li–F granites of the Shumilov Massif. Scale bar 10 μm .

Table 3. Estimations of water pressure and H₂O and Cl contents in silicate melt inclusions from quartz of Li–F granites of the Shumilov Massif

Conditions	Run 1	Run 2	Run 3	Run 4	Run 5
<i>n</i>	3	2	2	4	3
<i>T</i> _{fl. hom.} , °C	204	169	285	243	232
<i>T</i> _{fl. eut.} , °C	–20	–19	–5	–20	–18
<i>T</i> _{ice melt.} , °C	–2.2	–1.8	–1.2	–1.4	–1.6
<i>C</i> _{salt} , equiv. wt % NaCl	3.7	3.1	2.1	2.4	2.7
<i>V</i> _{gas} , vol %	3.8	3.9	2.6	3.6	2.0
<i>V</i> _{fl} , vol %	14.6	19.5	10.8	10.3	6.3
<i>d</i> _{fl} , g/cm ³	0.89	0.92	0.75	0.83	0.85
<i>dP/dT</i> , bar/°C	13.3	13.7	11.6	12.5	13.2
<i>P</i> _{H₂O} , kbar (550°C)	4.6	5.2	3.1	3.8	4.2
<i>C</i> _{H₂O} , wt %	5.3	7.6	3.3	3.4	2.1

Note: (*n*) is the number of inclusions in the studied group; (*T*_{fl. hom.}) is the homogenization temperature of fluid into a liquid phase; (*T*_{fl. eut.}) is the eutectic temperature of the aqueous fluid; (*T*_{ice melt.}) is the temperature of ice melting in fluid; (*C*_{salt}) is the salinity of the fluid; (*V*_{gas}) is the volume of gas phase in the silicate melt inclusion; (*V*_{fl}) is the volume of the aqueous fluid in the silicate melt inclusions; *dP/dT* is the increase in the pressure of homogenous fluid at a temperature increase by 1°C; (*P*_{H₂O}) is the water pressure of fluid at melt crystallization temperature of 550°C, (*d*_{fl}) is the fluid density; *C*_{H₂O} is the water content in the melt.

the water content in the melt by the technique (Naumov, 1979).

The aqueous fluid of the melt inclusions was studied on a measurement complex consisting of a THMSG-600 Linkam heating–freezing stage, an Amplival microscope equipped with a long-distance objectives (including an Olympus 80× objective), a videocamera, and a controlling computer. The complex allows one to measure phase transition temperatures from –196 to +600°C on-line, monitor this process at great magnifications, and take digital photomicrographs. The salinity was estimated from the ice melting temperature, using data from (Bodnar and Vityk, 1994).

The aqueous solution of the melt inclusions mainly had chloride–sodic (eutectic temperature from –18 to –20°C), and, occasionally, sodium fluorides (eutectic temperature about –5°C) compositions and a low salinity (2.1–3.7 equiv wt % NaCl). The gas phase disappeared at 169–285°C (homogenization into liquid). The inclusions exploded at heating above 550°C, indicating a high internal fluid pressure. Only a few smallest inclusions reached homogenization at 930–950°C. Conceivably, some inclusions may have higher homogenization temperatures. The aqueous fluid pressure determined by the method (Naumov, 1979) at beginning-of melting-temperature of silicate phases (550°C) was 3.1–5.2 kbar, and the water content in the melt reached 2.1–7.6 wt %.

DISCUSSION AND CONCLUSIONS

The physicochemical conditions during the formation of the ore-bearing Li–F granites of the Shumilov deposit are similar to those determined in inclusions in

quartz from the Spokoineo Massif, which associates with eponymous tungsten deposit. The study of melt inclusions in quartz from the Li–F granites of the Orlovka Massif showed similar parameters: subliquidus temperatures of 660–700°C, an average water content in the melt of 6 wt %, and a salinity of the aqueous fluid in the inclusions of 3.8 equiv. wt % NaCl (Reyf et al., 2000). The strongly differentiated pegmatite melt of Volhynia shows subliquidus temperatures of 650–700°C, a water content of 7 wt %, and an aqueous fluid pressure of 2.6–3.0 kbar (Kovalenko et al., 1996). In the review of the physicochemical conditions of intermediate and acid magmas formed in different geodynamic environments (Kovalenko et al., 2000), intracontinental granites are characterized by an average water content of 2.8 wt % in the inclusions and 4.3 wt % in the quench glasses. The higher water contents established in the granites of the Shumilov Massif indicate a high degree of melt differentiation during the magmatic stage and the accumulation of large amounts of aqueous fluid, which could cause the high productivity of the Shumilov fluid–magmatic system. Our data are arguments calling for a revision of the tungsten reserves of the Shumilov deposit.

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