

Genesis and Formation Conditions of Deposits in the Unique Strel'tsovka Molybdenum–Uranium Ore Field: New Mineralogical, Geochemical, and Physicochemical Evidence

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Abstract—The ambiguity of genetic interpretations of uranium ore formation at Mo–U deposits of the Strel'tsovka ore field led us to perform additional geochemical, mineralogical, and thermobarogeochemical studies. As a result, it has been established that closely related U and F were progressively gained in the Late Mesozoic volcanic rocks from the older basic volcanics (170 Ma) to the younger silicic igneous rocks (140 Ma). The Early Cretaceous postmagmatic hydrothermal epoch (140–125 Ma) is subdivided into preore, uranium ore, and first and second postore stages. The primary brannerite–pitchblende ore was formed in association with fluorite. At the first postore stage, this assemblage was replaced by a U–Si metagel, which was previously identified as coffinite. The metagel shows a wide compositional variation; its fine structure has been studied. The preore metasomatic alteration and related veined mineralization were formed under the effect of sodium (bicarbonate)–chloride solution at a temperature of 250–200°C. The uranium ore formation began with albitization and hematization of rocks affected by supercritical fluid at 530–500°C; brannerite and pitchblende precipitated at 350–300°C. The chondrite-normalized REE patterns of pitchblende hosted in trachybasalt, trachydacite, and granite demonstrate a pronounced Sm–Nd discontinuity and a statistically significant tetrad effect of W type. These attributes were not established in REE patterns of rhyolites derived from the upper crustal magma chamber. This circumstance and a chronological gap of 5 Ma between silicic volcanism and ore formation do not allow us to suggest that uranium was derived from this magma chamber. According to the proposed model, the evolved silicic Li–F magma was a source of uranium. U^{4+} , together with REE, was fractionated into the fluid phase as complex fluoride compounds. The uranium mineralization was deposited at a temperature barrier. It is suggested that hydromica alteration and the formation of molybdenum mineralization were genetically unrelated to the uranium ore formation.

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INTRODUCTION

In the 1950s, F.I. Wolfson, while analyzing the geology of the eastern Transbaikalian region, concluded that this territory was promising for hydrothermal uranium deposits and recommended that prospecting works be performed here, which resulted in the discovery of the Strel'tsovka ore field (SOF) in the early 1960s.

In the over 35 years since this moment, 19 Mo–U deposits containing more than 250 kt of total uranium reserves have been explored in the Strel'tsovka caldera, 140 km² in area, and this caldera was admitted to be a unique ore field (Ishchukova et al., 1998). After the breakup of the Soviet Union in the early 1990s, the deposits of the SOF, mined by the Near-Argun Mining and Chemical Industrial Corporation (PPGKhO JSC), turned out to be the only source of natural uranium in Russia.

The geology of the ore field, the geological and structural conditions of ore localization, the mineral

composition of ore, wall-rock metasomatic alteration, and the physicochemical conditions of ore and wall rock formation were subjects of investigations by territorial, industry-related, and academic institutions, including the Geological Exploration Expedition no. 324 of Sosnovgeologiya Enterprise; PPGKhO JSC; the Transbaikalian Research Institute; the All-Russia Research Institute of Geology (VSEGEI); the All-Russia Research Institute of Mineral Resources (VIMS); the All-Russia Research Institute of Chemical Technology (VNIKhT); the Institute of Geochemistry and Analytical Chemistry (GEOKhI); and the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), Russian Academy of Sciences (RAS). An extensive set of factual data was collected and analyzed. The team of the First Expedition of IGEM RAS, headed by Professor Wolfson, provided important insights into the uranium ore formation within the SOF. Under the guidance of Wolfson and with his participation, a wide circle of problems was studied, from the evolution of magmatism and localization of ore mineralization in the ore field to the mineral

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assemblages and fluid inclusions (FIs) in minerals. On the basis of this knowledge, a genetic model of these unique deposits was proposed.

The results obtained by different research teams have much in common as concerns the geology of the ore district and ore field and their evolution, the localization of orebodies, the distribution of uranium and associated elements in host rocks, the staged hydrothermal activity, the physicochemical conditions of ore formation, the species of uranium transport, and the factors that controlled the deposition of uranium ore. However, the treatments of some features are ambiguous and in some cases alternative. In particular, there are divergent views concerning the sequence of veined and metasomatic mineral formation and interpretation of isotopic ages of igneous rocks and hydrothermal mineralization. The difference in opinions is caused by the complex, multistage character of magmatism and hydrothermal activity. There are at least three competitive genetic models of economic uranium mineralization known to date, differing in the inferred source of uranium.

The adherents of one of the hypotheses suppose that the main mass of uranium concentrated in orebodies was leached from host rocks in the process of intense preore metasomatic alteration (Modnikov et al., 1984; Naumov et al., 1985; Ishchukova et al., 1991; Chabiron et al., 2003). According to another concept (Ishchukova et al., 1998), the upper mantle was the main source of uranium and leaching of uranium from the host rocks is regarded as a local phenomenon that does not affect the formation of economic ore. The hypothesis developed by Wolfson and his team considered an upper crustal source of silicic magma as the most probable initial reservoir of uranium ore. Since many aspects of the mineral formation sequence, the dating of igneous rocks and hydrothermal processes, the behavior of uranium in these processes, and the genetic interpretations remain questionable, it was necessary to perform additional investigations using modern precision methods.

RESEARCH METHODS

In the course of fieldwork at the Strel'tsovka, Antei, Oktyabrsky, Luchisty, Tulukui, and Krasny Kamen deposits and elsewhere in the ore field, about a thousand specimens and core samples of Mo–U ore, metasomatic rocks, and unaltered host rocks were collected and about 1500 thin sections were examined in transmitted and reflected light under an optical microscope.

To determine the chemical compositions of uranium minerals, sulfides, silicates, and carbonates, more than 3000 analyses were made on Cameca SX-50 and SX-100 microprobes at the Henri Poincaré University, Nancy, France, and a few hundred analyses, on a Hitachi S-2500 SEM equipped with a Kevex EDS (analyst A. Koehler, Henri Poincaré University) and a Jeol JSM-5300 SEM equipped with a Link ISIS EDS (ana-

lyst O.A. Doinikova, IGEM RAS). The fine structure of a U–Si metagel previously identified as coffinite was studied on a Philips CM-20 high-resolution TEM with microdiffraction and a Princeton PGT EDS (analyst J. Ghanbaja, Henri Poincaré University). The REE contents in pitchblende were determined on a Cameca IMS-3f ion microprobe (analyst J. Bonhoure, CRPG, Nancy).

The FIs in quartz of several generations, fluorite, and calcite were studied at IGEM RAS with microthermometric methods (freezing study and homogenization) on a Linkam THMS600 heating and freezing stage, which works within a temperature range from –196 to +600°C. The compositions of gas and solid phases in the inclusions were determined with Raman microspectroscopy on a DILOR XY device (analyst T. Lhomme, Henri Poincaré University). Four hundred and twenty inclusions from 30 samples were studied with various methods.

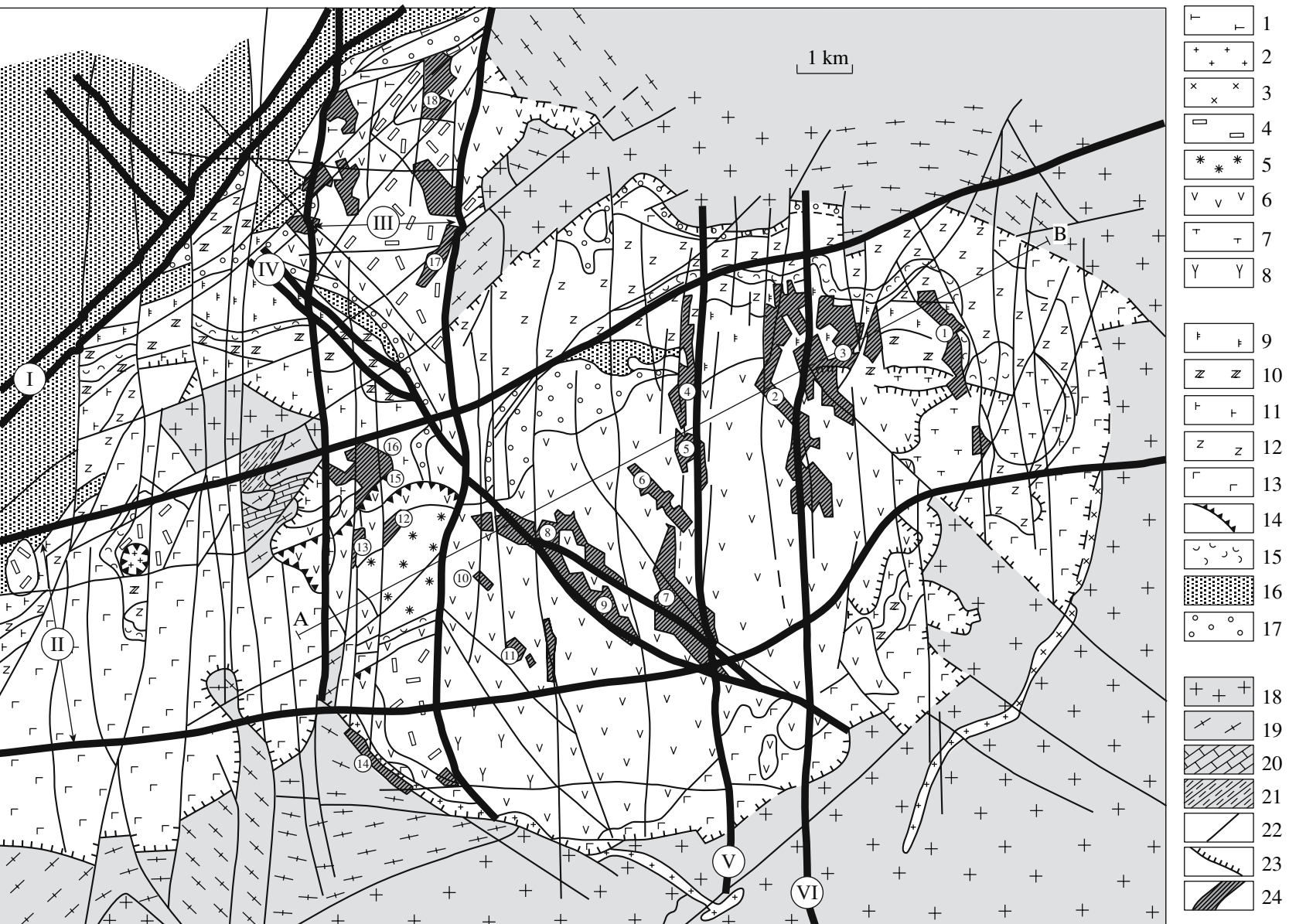
The uranium distribution in rocks and ores was studied with fission-track radiography, while the uranium content in mineral aggregates was determined from digital photomicrographs of detectors using software developed at IGEM RAS. The chemical composition of rocks and mineral separations were determined with ICP-AES and -MS at CRPG, Nancy, France, and at the Institute of Experimental Mineralogy (IEM) of the RAS, Chernogolovka, Russia; 240 samples were analyzed. More than 100 samples were analyzed with XRF and INAA at IGEM RAS.

GIS modeling was used for the 3D analysis of the spatial relations between the main structural elements of the upper crust near the SOF and the localization of uranium ore at the Antei and Oktyabrsky deposits. 3D geological models were created with the GeoSpline module, specially developed at IGEM RAS and functioning under the AutoCAD Map GIS editor. 3D numerical models of orebodies were created in the Cocad program (C. Le-Carlier, CRPG, France) and afterward were imported into AutoCAD Map for analysis.

GEOLOGY OF THE STREL'TSOVKA ORE FIELD

The Strel'tsovka caldera is situated in the southwestern portion of the Argun–Bureya Terrane in the Mongolia–Okhotsk Foldbelt (Zonenshain et al., 1990). The Urulyungui Block, which hosts the SOF, is distinguished from the neighboring blocks by metallogenic specialization for uranium and fluorine (Ishchukova et al., 1998; Rybalov, 2000).

The Strel'tsovka caldera was formed at the intersection of a near-meridional deep zone of increased magmatic permeability (Dukhovskiy et al., 1998) with the NE-trending East Urulyungui and Argun deep zones (Ishchukova et al., 1998). The formation of the caldera was caused by eruption of rhyolitic melt from the upper crustal magma chamber, which, as follows from geophysical data, is located at a depth of ~5 km beneath the



caldera. Many near-meridional, northeastern, north-western, and near-latitudinal faults are traced in the caldera and its framework. Some of these faults served as conduits for basaltic, dacitic, and rhyolitic melts.

The basement of the caldera is composed of Early Paleozoic granite gneiss and Late Paleozoic granite with xenoliths of ancient gneiss, schist, amphibolite, and marble. The caldera is filled with a Late Mesozoic volcanic-sedimentary sequence up to 1200 m in total thickness, which is subdivided into two formations. The Argun Formation rests upon the eroded surface of older granite. The lower portion of this formation, dated at 170 Ma (Bocharov et al., 1978), consists of trachybasalt and basaltic trachyandesite. The middle portion is made up of trachydacite flows separated by tuff units (165–155 Ma); the section is completed by trachybasalt flows intercalated with tuffstone, gravelstone, and conglomerate. The overlying Turga Formation is composed of rhyolite flows (140–145 Ma) alternating with tuffaceous and sedimentary rocks and thin trachybasalt flows. The thickness of separate trachybasalt, basaltic andesite, trachydacite, and rhyolite units reaches hundreds of meters. Rhyolite yields to trachybasalt and trachydacite in volume. The measured isotopic ages of volcanic rocks indicate that the collapse caldera actively functioned for 30–40 Ma.

The ore field is dissected by numerous N–S-, NW-, W–E-, ENE-, and NNE-trending faults (Fig. 1). Low-angle detachments along contacts of lava flows and tuffaceous and sedimentary units are widespread. NE-trending and near-latitudinal faults are more abundant in the basement. Faults oriented 20°–30° NE control uranium mineralization hosted in granite at the Antei deposit. Meridional and NW-trending faults are largely traced in the volcanic fill of the caldera, where they control the localization of most deposits.

The localization of ore mineralization in virtually all sedimentary and volcanic rocks, as well as in metamorphic and granitic rocks of the basement, distinguishes the SOF from other Mo–U deposits. The uranium reserves of the Antei and Argun deposits, hosted in the basement rocks, amount to about a quarter of the total reserves known from the ore field. In the sedimentary–volcanic sequence, orebodies concentrate within a depth range of 100–600 m, whereas in the basement they occur at a depth of 400–900 m.

The ore mineralization is mainly controlled by steeply dipping faults. The most typical structural conditions of ore localization are related to screening of steeply dipping faults from above and below by low-angle bedding-plane detachments; screening of certain faults (often NW-trending) by other, near-meridional and near-latitudinal faults; intersections and bends of faults; and horsetail fracture systems.

The direction of ore-bearing solution flow was deduced from the morphology of orebodies and their structural position within the caldera, zoning of mineral assemblages and geochemical halos, and orientation of carbonate axes (Ishchukova et al., 1998). It has been established that the ascending solutions penetrated into the bedded fill of the caldera from the basement mainly in the area of the Krasny Kamen paleovolcano controlled by the Meridional Fault Zone and along large meridional faults in the eastern part of the caldera. On reaching the sedimentary–volcanic sequence, solutions spread along low-angle detachments, forming multi-stage systems of orebodies.

EPOCHS OF MESOZOIC MAGMATISM AND BEHAVIOR OF URANIUM AND FLUORINE

Because many researchers suggest genetic links between uranium ore mineralization in the SOF and magmatism, the distribution of uranium and associated elements in igneous rocks of different ages attracts keen interest. Four epochs of Late Mesozoic magmatism are recognized in the eastern Transbaikalian region (Andreeva et al., 1996). The first epoch (208–187 Ma) was not intense and did not develop near the SOF. During the second epoch (178–154 Ma), granodiorite–granite–leucogranite plutons were emplaced a few hundred kilometers north of the SOF and trachybasalt and trachydacite of the Argun Formation were erupted at the site of the future Strel'tsovka caldera.

The third epoch of magmatism (150–138 Ma) is the most important in terms of uranium ore formation because the SOF was formed after crystallization of intrusive and volcanic rocks pertaining to this epoch. These rocks are distinctly specialized in Ta, Nb, W, Be, and U. Minor hypabyssal intrusions of Li–F leucogranite and subvolcanic ongonite intrusions were emplaced in this epoch in the eastern Transbaikalian region. Most of

Fig. 1. Geological map of the Strel'tsovka ore field, after Ishchukova et al. (1998). (1–13) Upper Jurassic–Lower Cretaceous volcanic sequence filling the caldera: (1) basalt, (2) dikes and subvolcanic bodies of rhyolite with small phenocrysts, (3) syenite and syenite and granosyenite porphyries, (4) upper flow of rhyolites with small and large phenocrysts, (5) cream-colored spherulitic rhyolite, (6) massive and fluidal felsite and quartz porphyry, (7) andesite, (8) lower flow of spherulitic and thin fluidal glassy rhyolite, (9) upper flow of basalt and basaltic andesite, (10) upper flow of trachydacite, (11) middle flow of basalt, (12) lower flow of trachydacite, (13) lower flow of basaltic andesite; (14) paleovolcanoes; (15–17) tuffaceous and sedimentary rocks: (15) tuff, (16) sandstone with siltstone interbeds, (17) conglomerate and gravelstone; (18–21) Paleozoic basement of the caldera: (18) Variscan coarse- and medium-grained granites, (19) Caledonian gneissose granite, (20) marble, (21) siltstone, phyllite, quartz-sericite schist, and quartzite; (22) steeply dipping faults; (23) gently dipping faults; (24) contours of deposits (numerals in circles): 1, Shirondukui; 2, Strel'tsovka; 3, Antei; 4, Oktyabrsky; 5, Luchisty; 6, Martovsky; 7, Lesser Tulukui; 8, Tulukui; 9, Yubileiny; 10, Vesenny; 11, Novogodny; 12, Pyatiletny; 13, Krasny Kamen; 14, Southwestern; 15, Zherlovoy; 16, Argun; 17, Bezrechny; 18, Dal'ny. Fault zones (numerals in circles): I, Urulyungui; II, Argun; III, Meridional; IV, Tulukui; V, Lesser Tulukui; VI, Central.

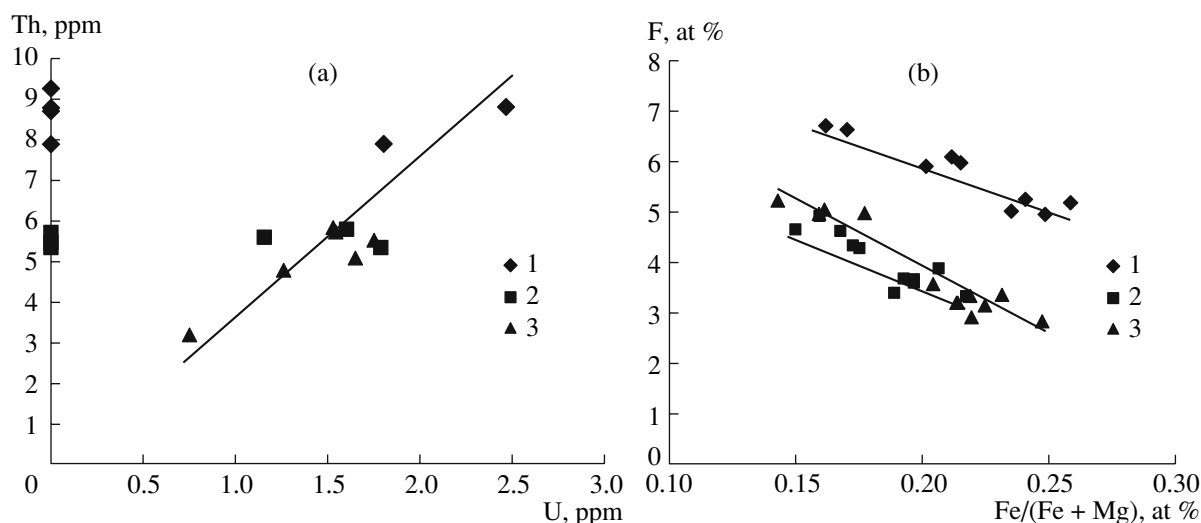


Fig. 2. (a) Uranium and thorium contents in basalts and (b) fluorine content in biotite. (1) Lower and (2) upper basalts of the Argun Formation, (3) basalt of the Turga Formation. Dots on the y axis in panel (a) denote Th content in the samples where U was not analyzed.

these intrusions were formed 144–138 Ma ago (Badanina et al., 2004, 2006; Kuznetsov et al., 2004; Andreeva et al., 1996). Silicic volcanics of the Turga Formation enriched in U (15–25 ppm) were erupted in the Strel'tsovka caldera. According to the data of P.S. Kozlova and colleagues (IGEM RAS), similar U contents were established in the rare-metal leucogranite of the Kir-Kirin pluton (12–30 ppm U), located 50 km north of the SOF; the Sektui pluton (9.6–28 ppm U), 130 km northwest of the SOF; and the Khangilai pluton (10.8 ppm U, on average), 250 km northwest of the SOF.

The fourth epoch (126–117 Ma) is characterized by waning magmatic activity. At that time, the Kondui pluton of monzon-bearing leucogranite, dated at 125–120 Ma (Andreeva et al., 1996), was emplaced 50 km northwest of the SOF and silicic lavas were erupted 100 km northeast and 20 km southeast of the SOF 120–118 Ma ago.

The available information on U contents in igneous rock is rather extensive (Ishchukova et al., 1998; Andreeva et al., 1990, 1996). However, these results were obtained with the radiometric method or XRF, with a detection limit of 1.2 ppm, which is twice as high as the average U content in basalts. We carried out additional study of the behavior of uranium in the magmatic process using more precise analytical methods (ICP-MS and INAA). The syngenetic character of uranium distribution in samples was controlled with fission-track radiography.

The distribution of U and other elements in trachybasalts from the Strel'tsovka caldera was studied at several stratigraphic levels. The lower trachybasalt flows of the Argun Formation were sampled at the Strel'tsovka deposit, and the upper flows of the same formation, at the Tulukui deposit. The younger flows of

the overlying Turga Formation were sampled near the Dal'ny deposit.

It has been established that trachybasalt of the lower flow is characterized by the highest U content (1.8–2.5 ppm) (Fig. 2a); the overlying trachybasalt flows from the Argun and Turga formations contain 1.0–1.8 ppm U. These results are broadly consistent with the range of U contents in basalts of the Strel'tsovka caldera obtained from radiometric analysis and fission-track radiography (1.2–2.8 ppm, according to data of P.S. Kozlova, B.M. Sel'tsov, V.V. Viktorov, and other authors from IGEM RAS).

Some slightly altered samples from the lower flow are marked by elevated superimposed U contents (>3 ppm), which are not shown in Fig. 2a. Therefore, the radioactivity of these samples was measured by Th as a less mobile element. As can be seen from Fig. 2a, the Th content in basalts of the lower flow (8.0–9.5 ppm) is higher than in basalts of the upper flows (5.2–6.0 ppm). These results raise the statistical significance of the elevated U content in the lower basalts.

The close association of uranium with fluorite at many uranium deposits made it necessary to determine F contents in igneous rocks of the SOF. The concentration of F in rocks was estimated from its content in biotite determined with microprobe analysis and in melt inclusions from rhyolite (Chabiron et al., 2003).

The distribution of fluorine in biotite from the studied trachybasalt flows shows the same trend as for uranium. Biotite from the lower flow is characterized by the highest F content, up to 5.7 wt % (6.6 at %, Fig. 2b). The F content in biotite is inversely correlated with the Fe mole fraction (Reviews..., 1984), as is clearly seen from Fig. 2b. The F content in biotites from the upper flows in the Argun and Turga formations is lower than in biotite from the lower flow of the Argun Formation.

The F content in basaltic magma was estimated at 0.29 wt % on the assumption that this element mostly concentrates in biotite and fluorapatite. The same average F content (0.299 wt %) in basalt with >1.3 wt % K₂O was calculated by Naumov et al. (1998) from F concentrations in melt inclusions and quenched basaltic glasses.

The U and F contents in silicic melt from the upper crustal magma chamber as a source of rhyolite of the Turga Formation were estimated from data on melt inclusions (Chabiron et al., 2001). It has been established that the melt contained 14–23 ppm U and 1.4–3.2 wt % F. These results support previously obtained data on high U contents in silicic volcanic glasses in the SOF (Andreeva et al., 1996).

Unfortunately, we failed to find unaltered biotite grains or melt inclusions in quartz phenocrysts from trachydacite, which would be fit for estimation of U and F contents. According to Andreeva et al. (1990), the average U content in the least altered trachydacite is 9.8 ppm; the primary character of the U distribution in this rock was corroborated by fission-track radiography. Our unpublished data coincide with this estimate and indicate that the concentration of U in trachydacite and other volcanic rocks in the Strel'tsovka caldera is three to four times higher than the global uranium average in the same rocks.

Thus, the general trend is the enrichment of volcanic rocks in U and F from the older basic rocks (2.0–2.5 ppm U and 0.3 wt % F) through the intermediate and moderately silicic rocks (10 ppm U and ? F) to the younger highly silicic rocks (15–25 ppm U and ~3 wt % F). Thus, we are dealing with a U–F geochemical association of Late Mesozoic igneous rocks, which indirectly testifies to the postmagmatic nature of the pitchblende–fluorite mineral assemblage of ore.

SEQUENCE OF LATE MESOZOIC HYDROTHERMAL MINERAL FORMATION AND TYPOMORPHISM OF MINERALS

The staged mineral formation at the SOF deposits has been studied by V.P. Rogova, M.V. Vampilov, I.V. Mel'nikov, I.V. Chernykh, K.V. Skvortsova, N.S. Trofimov, L.P. Ishchukova, and other researchers (Ishchukova et al., 1998). The following stages of the Late Mesozoic hydrothermal activity have been established: (1) widespread preore argillic alteration with the subsequent formation of sulfide-bearing cryptic quartz veins; (2) uranium ore formation expressed in deposition of brannerite–coffinite–pitchblende mineralization and molybdenite along with development of wall-rock albitization and hematitization; (3) formation of a postore quartz–fluorite–molybdenite assemblage; and (4) formation of the youngest quartz carbonate–fluorite veins with kaolinite selvages. Over the last ten years, we obtained new data that allowed us to refine this scheme.

In our opinion, the Late Mesozoic (Early Cretaceous) hydrothermal activity that developed after the third magmatic epoch may be divided into four stages: preore, uranium ore, and first and second postore (Fig. 3).

The preore stage was characterized by metasomatic alteration of both metamorphic and granitic rocks of the basement and volcanic and sedimentary rocks filling the Strel'tsovka caldera. This postvolcanic pervasive alteration was not intense but affected virtually the entire body of host rocks. In contrast to the postore alteration, which, as a rule, is intense and controlled by faults, the halos of preore metasomatic alteration are visually vague and have diffuse boundaries.

The alteration is expressed in development of hydromica in association with carbonates (siderite, ankerite, and calcite), chlorite, leucoxene, and quartz. Some authors suppose that kaolinization at the deposits in the western portion of the ore field pertains to the preore alteration as well (Andreeva and Golovin, 1998; Ishchukova et al., 1998).

In granite and phenocrysts of trachydacite and rhyolite, plagioclase is replaced by hydromica (illite or illite-smectite), carbonate, and albite. Biotite is partly replaced by chlorite, carbonate, and hydromica. The groundmass of trachydacite and rhyolite is replaced by leucoxene and hydromica; decomposition of hematite results in bleaching of rocks. Olivine phenocrysts in trachybasalt are partly or completely replaced by calcite; pyroxene is more stable. The groundmass of trachybasalt is insignificantly replaced by calcite and illite-smectite; titanomagnetite is partly replaced by leucoxene, and, as a result, the rock is slightly bleached. Silification is predominant in silicic volcanics and carbonation is typical of basalts. Very thin veinlets composed of the newly formed minerals are universally abundant.

Veins, veinlets, and breccia cement consisting of cryptocrystalline and less frequent fine-grained quartz with fine disseminations of pyrite, amorphous molybdenum sulfide (jordisite), and low-Fe sphalerite (cleiophane) were also formed at the preore stage. Native copper occurs in thin carbonate–cryptocrystalline quartz veinlets cutting basalt.

The sulfide–carbonate–cryptocrystalline quartz veins and veinlets pertain to the preore stage because they are widespread in altered rocks and their composition is close to the newly formed mineral assemblage of rocks affected by argillic alteration. The lower chronological boundary of the preore mineral complex¹ is determined by the age of the late syenite porphyry dikes (139–140 Ma) pertaining to the third epoch of Mesozoic magmatism and affected by argillic alteration. The upper boundary is the age of uranium mineralization (135 ± 2 Ma) established from U–Pb dating of pitchblende (Chernyshev and Golubev, 1996). A part of

¹ A mineral complex is a set of minerals formed during a certain stage of the hydrothermal process.

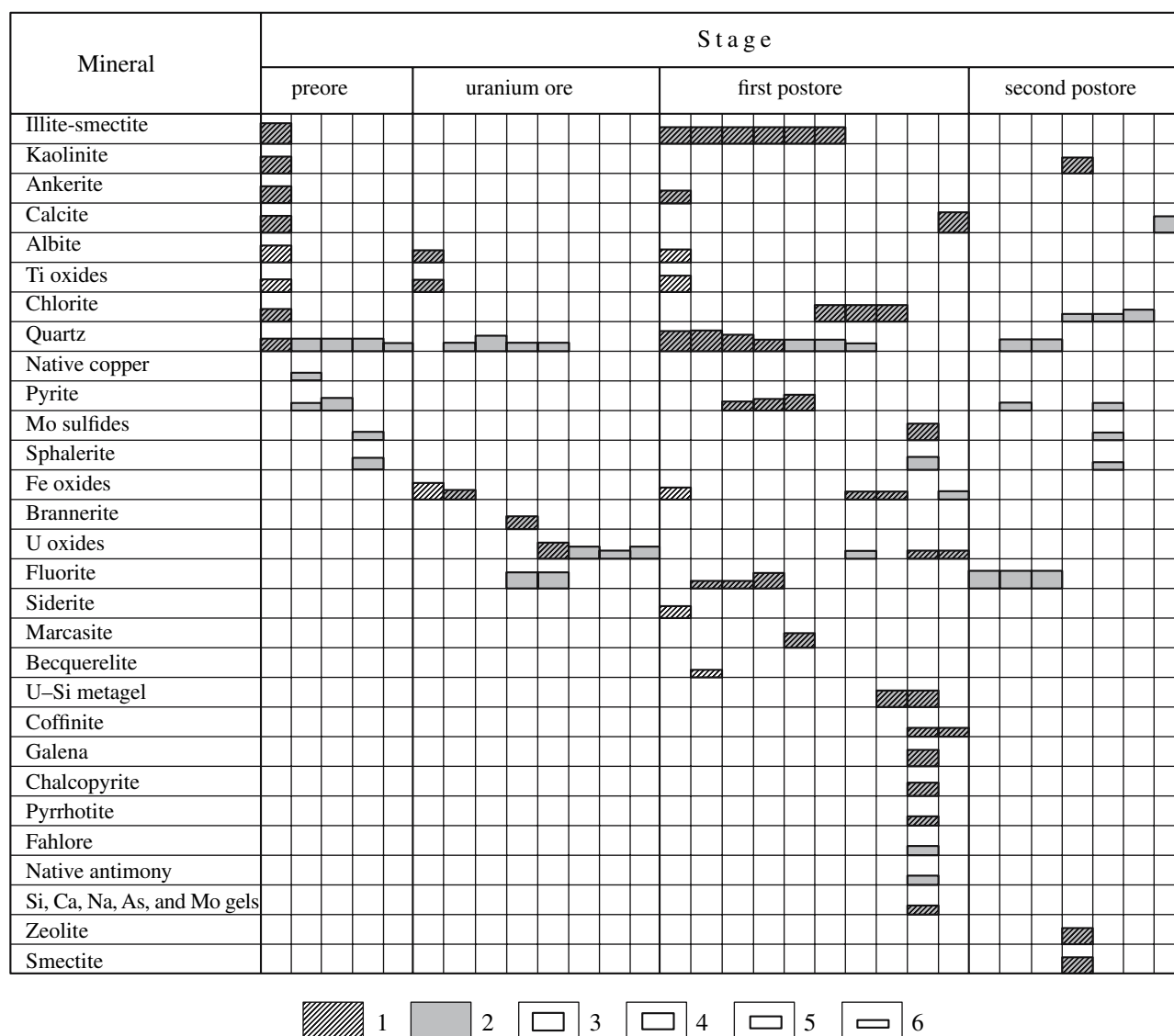


Fig. 3. Sequence of mineral formation at the deposits of the Strel'tsovka ore field, after Ishchukova et al. (1998) and Andreeva and Golovin (1998). (1–6) Minerals: (1) metasomatic, (2) veined, (3) highly abundant, (4) abundant, (5) not abundant, (6) rare.

hydromicas has an isotopic age of 139–135 Ma (Andreeva et al., 1996).

The mineral complex of the *uranium ore stage* developed more locally in comparison with the pre- and postore mineral complexes. The veined and disseminated brannerite–pitchblende mineralization, accompanied by narrow halos of wall-rock alteration, is controlled by faults. Three main structural types of ore are recognized: veins in fissures, ore breccia in crush zones, and stringer–disseminated ore in cataclase zones.

Metasomatic albite and hematite accompany ore formation. The areas of mineralized aluminosilicate rocks almost always are accompanied by halos of hematitization that develops somewhat wider than orebodies. The thickness of hematite-rich selvages near

separate fractures and tectonic sutures is not greater than a few decimeters, while in ore stockworks these selvages merge into zones a few tens of meters thick. At the Argun deposit, the orebodies hosted in marmorized limestone are not accompanied by hematitization. Albitization develops sporadically and more locally than hematitization. Albite occurs in metasomatic rocks, in selvages of veinlets, and in the cement of breccia. Albite and hematite were formed before the deposition of uranium minerals. Bipyramidal quartz and fluorite crystallized later than albite and hematite but earlier than ore minerals.

Two generations of quartz are recognized in the uranium ore mineral complex. Quartz 1 is not abundant and occurs as fine-grained aggregates saturated with dispersed iron oxides (Fig. 4a). Quartz 2 is more widespread as short-prismatic, often bipyramidal crystals of

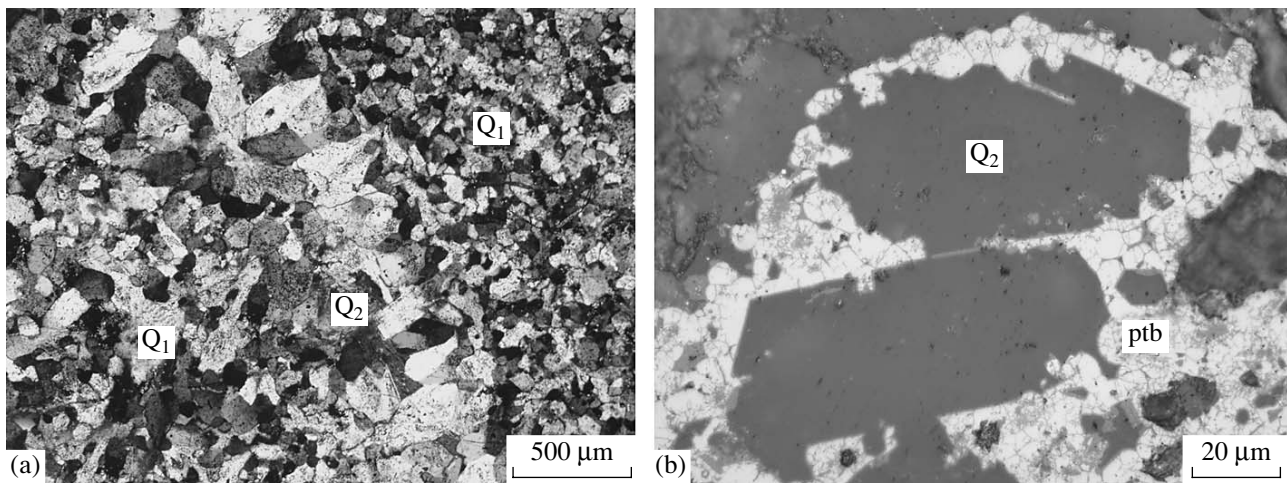


Fig. 4. Generations of quartz formed at the uranium ore stage. Polished thin sections. (a) Micrograined quartz 1 (Q_1) is crossed by a veinlet of coarser grained quartz 2 (Q_2), the Strel'tsovka deposit (transmitted light, crossed polars); (b) bipyramidal and short-prismatic quartz 2 (Q_2) with pitchblende (ptb) spherulites, the Antei deposit (reflected plane light).

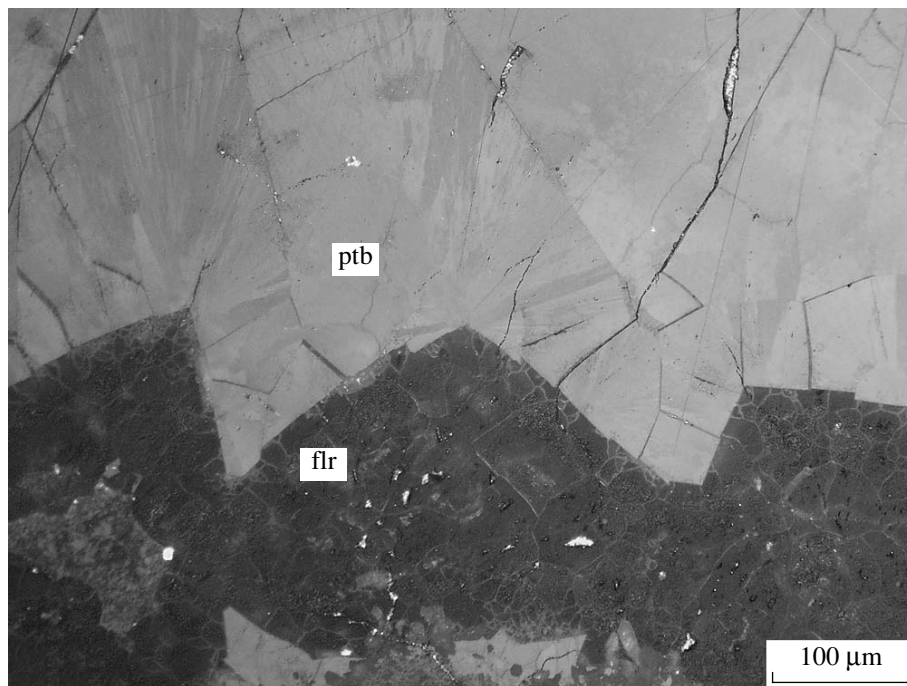


Fig. 5. Anisotropic pitchblende (ptb) of the large spherulitic generation overgrown on octahedral fluorite (flr) crystals, the Strel'tsovka deposit. Polished thin section in reflected light, crossed polars.

50 μm to a few millimeters in size. The paragenetic mineral assemblage quartz 2 + pitchblende is indicated by overgrowth of euhedral quartz crystals by pitchblende and encrustation of outer growth zones of quartz 2 by minute pitchblende spherulites with formation of induction surfaces (Fig. 4b).

Dark violet and dark brown fluorite was formed before the large spherulites of pitchblende. The paragenesis of both minerals is confirmed by the occur-

rence of large pitchblende spherulites on edges and apices of octahedral fluorite crystals with indications of their joint growth (Fig. 5). The amount of synore fluorite was much greater than is observed now because a considerable part of this fluorite was subsequently replaced by quartz, hydromica, carbonate, and chlorite in the course of postore hydrothermal alteration.

Pitchblende is the most abundant primary ore mineral at the SOF deposits. Four generations of pitch-

blende are separated by tectonic motions: (1) early small spherulites from 5 to 30 μm in size, (2) large spherulites up to a few centimeters in size, (3) medium-size spherulites, and (4) small spherulites (Aleshin et al., 2002). Pitchblende 1 occurs as thin veinlets and disseminations in rocks, and the other generations as veinlets and cement of breccia. Depending on crystallization conditions, uraninite is formed instead of pitchblende in some cases; the split cubic uraninite crystals grade into pitchblende. Pitchblende spherulites, in turn, are occasionally overgrown by rims of fine-crystalline uraninite. In some samples, the large and the late small spherulites of pitchblende show distinct anisotropy (Fig. 5), probably owing to the formation of the tetrahedral phase of uranium oxide.

The compositional dependence of pitchblende on the composition of host rocks indicates that ore-bearing fluid interacted with host rocks. The most distinct relationship is revealed with respect to Ca. Pitchblende hosted in basalt is distinguished by the highest Ca content (1.4 wt %, on average), whereas the lowest Ca content (1.04 wt %) was detected in pitchblende from granite; pitchblende from dacite contains 1.24 wt % Ca. A similar relationship was established for REE (see below).

Brannerite together with pitchblende commonly occurs as pseudomorphs after Ti-bearing accessory minerals and biotite in zones of hematitization and is noted less frequently in thin quartz veinlets. The composition of unaltered brannerite is stable and generally corresponds to the stoichiometry of this mineral $[(\text{U}_{0.91}\text{Ca}_{0.17})_{1.08}(\text{Ti}_{1.97}\text{Fe}_{0.08})_{2.05}\text{O}_6]$ (average of 29 microprobe analyses). The overgrowth of pitchblende spherulites on prismatic brannerite crystals without a tectonic break or corrosion testifies to paragenetic relations of these minerals. Brannerite is inferior to pitchblende in abundance (5–10% of the volume of pitchblende). At the lower levels of the Antei deposit, brannerite becomes prevalent due to the decreasing pitchblende content (Ishchukova et al., 1998).

The first postore stage is marked by the formation of quartz veinlets with dark violet fluorite of cubic habit, carbonate, hydromica, chlorite, and sulfides. Veinlets are, as a rule, accompanied by local halos of bleaching of wall rocks. The bleaching was caused by breakdown of finely dispersed iron oxides and development of hydromica, carbonate, quartz, and chlorite. The thickness of bleached zones varies from a few centimeters to a few meters. According to the available estimates, 20–30 vol % of rocks were affected by intense postore alteration; near orebodies, the percentage is even higher. The mineral composition of metasomatic alteration pertaining to the first postore stage is the same as at the preore stage, but its intensity is higher.

The frequently observed crosscutting relations between quartz–pitchblende aggregate and hydromica–carbonate–quartz veinlets and removal of hematite under the effect of superimposed quartz–chlorite–car-

bonate–hydromica alteration clearly indicate that the latter was formed after the brannerite–pitchblende ore mineralization. The encrustation of the postore comb quartz by hydromica and its occurrence in FIs in quartz as a solid phase, confirmed by Raman spectroscopy, testify to a paragenetic relationship of these minerals. Hydromicas from quartz–illite veinlets superimposed on the uranium ore mineralization and from metasomatic rocks are similar in composition (illite containing 6–9 wt % K_2O , as established by microprobe analysis). Mica with a lower K_2O content (2–5 wt %) is less abundant and likely is mixed-layer illite-smectite.

The postore veinlets, which are much more widespread than orebodies, are composed of comb-shaped quartz and less frequent rhythmically zoned chalcedony-like and cryptocrystalline quartz, dark violet fluorite, carbonates (siderite, ankerite, and calcite), chlorite of several generations, and sulfides (a few percent). Pyrite is the most abundant sulfide, and galena (mainly within orebodies), marcasite, jordisite with sporadic flakes of molybdenite, chalcopyrite, cleiophane, pyrrhotite, and fahlore are of subordinate importance. All sulfides occur in veinlets and as disseminations in metasomatic rocks enriched in hydromica. Postore quartz veinlets are predominant in granite, and carbonate veinlets, in basalts.

The recognition of the first postore stage is substantiated by more widespread development of minerals belonging to this stage in comparison with the mineral complex of the uranium ore stage, their frequent spatial separation, and different physicochemical formation conditions (see below). According to the K–Ar and Rb–Sr ages of hydromica and ankerite, this stage developed 134–130 Ma ago (Andreeva et al., 1996).

Pitchblende and brannerite in orebodies are replaced everywhere and often intensely with a polyphase U–Si metagel,² which was previously identified as coffinite. Recent investigations have shown that this substance was formed as a gel with a variable U/Si ratio rather than a product of metamict breakdown of coffinite. This is supported by the absence of faced forms, abundant shrinkage cracks, primary zonal colloform structures of deposition of the polyphase gel (Fig. 6), a wide variation of the U/Si ratio (from 1/2 to 2/1 (in at %)), and the amorphous state of the overwhelming majority of particles studied with XRD and microdiffraction (Aleshin et al., 2005). In rare cases, in phases enriched in uranium relative to the normative coffinite composition, ultrafine (3–5 nm) uraninite crystallites and larger (up to 20–30 nm) sporadic coffinite nuclei were identified with TEM and microdiffraction. In one case, small (1 μm) prismatic coffinite crystals were found in association with calcite that was formed at the end of the postore stage, which evidences increased alkalinity of the solution.

² A metagel is a solidified colloid devoid of dispersed phase.

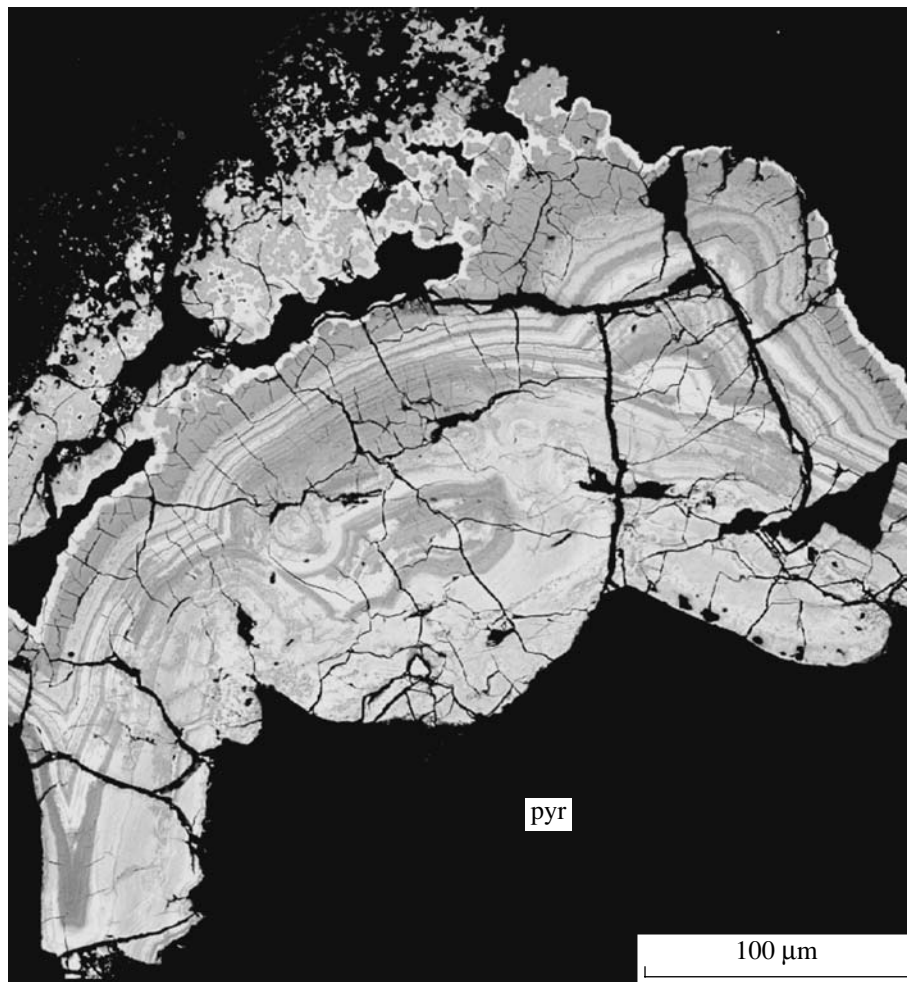


Fig. 6. Rhythmically zonal colloform U–Si metagel overgrowing pyrite (pyr) grains of the first postore mineral complex in a quartz veinlet, the Antei deposit. BSE image, Hitachi 2500 SEM.

The U–Si metagel is translucent and brown in thin chips and sections, with less frequently noted green hues. In high-grade ore, the color of the metagel changes from brown to orange and yellow with all transitional tints, indicating that U^{6+} prevails over U^{4+} in the composition of these gels.

The pseudomorphous replacement of pitchblende by U–Si metagel results in removal of uranium and its redistribution as the same metagel in immediate proximity to uranium oxide. The maximum distance of uranium transfer is a few centimeters. No segregations of U–Si metagel are observed beyond the limits of the area of primary uranium mineralization. Thus, uranium was not supplied with postore hydrothermal solutions and only was redistributed within orebodies.

The U–Si metagel was formed largely under reducing conditions, as follows from the association of this uranium silicate with chlorite, pyrrhotite, jordisite, and native antimony. The U–Si metagel is the uranium mineral second in abundance in the SOF. Its average content is 20–40%, increasing to 60–80% in some orebodies.

The preore and the first postore mineral complexes have much in common. First of all, this concerns the mineral composition of veins and metasomatic rocks: cryptocrystalline, chalcedony-like, and grained quartz; carbonates; chlorite; hydromica; mixed-layer illite-smectite; and sulfides (pyrite, sphalerite, and jordisite). The difference is the presence of fluorite, the U–Si metagel, galena, and some other minerals in the postore complex, obviously as a result of development of the preceding uranium ore stage. Both stages were characterized by colloidal mineral formation expressed in deposition of chalcedony-like and cryptocrystalline quartz, polyphase Mo–S gels (jordisite), U–Si, and complex Si–Na–Ca–Fe–Mo–Ba–As gels.

The similarity of the preore and the first postore mineral complexes is exhibited also in the concentration of trace elements in sulfides. According to the microprobe results, the As, Hg, Cu, and Zn contents in pre- and postore pyrites are virtually identical. The same may be said about Fe, Co, Ni, Sb, Hg, Cu, and Se in cleiophane and Fe, As, Sb, Cu, and Hg in jordisite.

The second postore stage was the time when the youngest veins of polychrome fluorite with quartz, chlorite, calcite, and pyrite were formed. These veins were accompanied by kaolinization and zeolite–smectite alterations. Jordisite and cleiophane were identified in insignificant amounts. This mineral complex is not so abundant in the SOF as older complexes. A chronological gap between the first and the second postore stages was confirmed by dating of fluorite mineralization with adularia and kaolinite (123 ± 5 Ma) at the Urtui and Garsonui deposits near the SOF (Kotov et al., 1995).

Thus, the studies performed allowed us to substantiate the fluorite–pitchblende assemblage; to reveal more extensive and intense development of postore hydrothermal alteration; to demonstrate similar features of pre- and postore mineral complexes; and to find a new mineral phase, a U–Si metagel, which was previously regarded as coffinite.

PHYSICOCHEMICAL FORMATION CONDITIONS OF MINERAL COMPLEXES AS DEDUCED FROM FLUID INCLUSION STUDY AND RESULTS OF MINERALOGICAL INVESTIGATIONS

According to data reported by G.B. Naumov, M.V. Mironenko, A.A. Nikitin, M.N. Kandinov, I.V. Mel'nikov, V.Yu. Gorbunov, and other researchers, the primary brannerite–pitchblende ores in the SOF were formed from hydrothermal solutions at 200–150°C as a result of pressure release, degassing of carbon dioxide, breakdown of complex uranyl–carbonate compounds, and reducing of uranium (Naumov et al., 1985; Mironenko, 1985; Mel'nikov, 1985).

The results of recent detailed studies of FIs in quartz of the preore, uranium ore, and first postore stages in combination with paragenetic analysis of mineral assemblages allowed us to refine and partly modify the ideas regarding the physicochemical conditions that existed in the ore-forming and postore hydrothermal systems (Krylova et al., 2003, 2006).

The study of individual inclusions in quartz of the preore stage showed that the mineral formation proceeded from relatively concentrated solutions (8.3–9.5 wt % NaCl equiv) of sodium chloride composition at 210–190°C.

Fine-grained quartz 1 of the uranium ore stage, which is limited in abundance, was formed after albite and is characterized by an anomalously high homogenization temperature (T_{hom}) of 540–510°C and a low salinity of solution (2–8 wt % NaCl equiv).

Quartz 2 was formed before brannerite and pitchblende at 460–290°C. As follows from FI study, the salinity of solution varied from 0.4 to 26.5 wt % NaCl equiv or higher. No correlation was established between T_{hom} of inclusions and the concentration of salt therein (Fig. 7).

The homogenization temperature of inclusions in quartz 2 from the Antei deposit (385°C, on average) is

higher than at the Strel'tsovka deposit (349°C, on average). This difference may be explained by the fact that the Antei deposit is a root portion of the ore-bearing hydrothermal system, where high-temperature fluid circulated in a large fluid conduit (ore-bearing suture no. 160). At the Strel'tsovka deposit, located higher, the ore-bearing solutions spread along bedding-plane detachments and cooled while interacting with host rocks.

The FIs in quartz of the uranium ore stage are sodium chloride and less frequently sodium bicarbonate–chloride in composition (Fig. 7). Free oxygen is sharply predominant in the gas phase (88.0–99.7 mol %), hydrogen occurs in a subordinate amount (<0.2–9 mol %), and carbon dioxide (10 mol %) was detected in one inclusion.

Taking into account the almost complete absence of carbon dioxide, methane, and hydrogen sulfide in FIs, the calculation of the critical temperature and an approximate estimate of the density and pressure were performed using the Flincor program for the NaCl–H₂O system. The computations have shown that T_{hom} of inclusions in quartz 1 exceeds the critical temperature for the respective concentrations by 100–140°C; i.e., the fluid responsible for precipitation of quartz 1 was supercritical. The density and pressure of such a fluid cannot be estimated.

The homogenization temperature of some low-concentration inclusions in quartz 2 (400–415°C) is somewhat lower than the critical value or exceeds it by 5–20°C. The calculation of the systems under conditions close to critical showed that the solution density was low (~0.48 g/cm³). Under subcritical conditions, inclusions are denser (0.51–0.87 g/cm³). The pressure varies from 480 to 140 bar.

Fluorine occurred in the ore-forming hydrothermal system in significant amounts, as follows from the high abundance of fluorite in ore mineral assemblages. At the postore stage, fluorite was replaced by quartz, carbonate, hydromica, and chlorite pseudomorphs.

As follows from the occurrence of albite and almost coeval brannerite, the mineral-forming fluid at the beginning of the uranium ore stage was characterized by elevated alkalinity. Further, the solution likely was neutralized, with formation of pitchblende.

The high temperature of the ore-forming hydrothermal system, appreciably exceeding the previous estimates, comes into conflict with the uranyl–carbonate model of transport and deposition of uranium (Naumov, 1978) because uranyl–carbonate complexes are not stable at temperatures above 300–200°C (Romberger, 1988). In addition, carbon dioxide and hydrocarbonate ion are detected in FIs only in rare cases; indications of boiling and degassing of carbon dioxide were not established.

The absence of appreciable amounts of carbon dioxide in ore-bearing solutions is supported by the absence of carbonates in the uranium ore mineral complex even in basalts rich in Ca²⁺, Fe²⁺, and Mg²⁺. In the presence

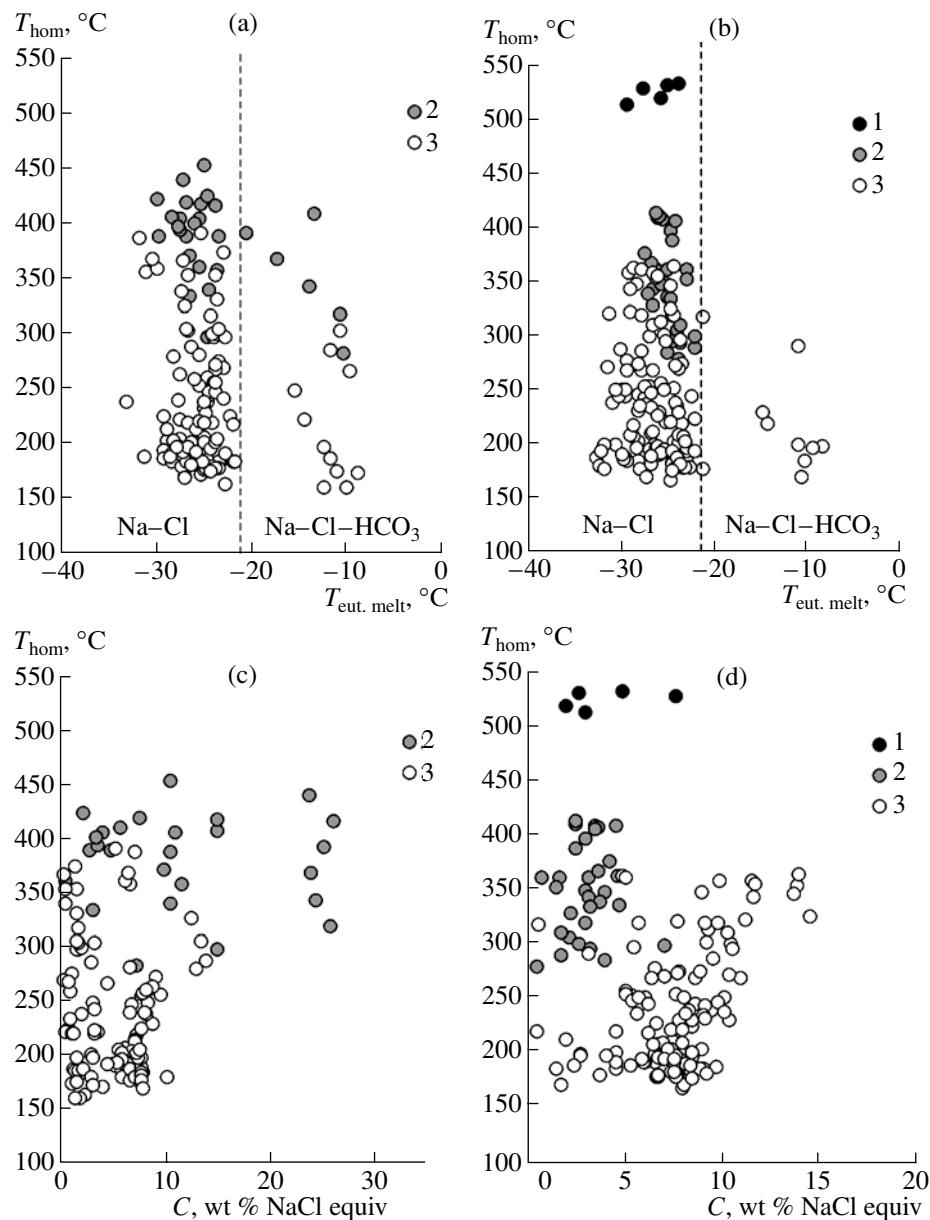


Fig. 7. (a, b) T_{hom} vs. $T_{\text{eut. melt}}$ and (c, d) T_{hom} vs. C for FIs for the (a, c) Antei and (b, d) Strel'tsovka deposits. (1) Quartz 1 and (2) quartz 2 of the uranium ore stage; (3) quartz of the first postore stage. The dashed line separates the fields of sodium chloride and sodium bicarbonate–chloride solutions.

of CO_2 or HCO_3^- in ore-bearing fluid, the above cations should be fixed in the form of carbonates.

Inadmissibility of the uranyl–carbonate model of U^{6+} transfer in the fluid phase at the SOF deposits is also supported by the absence of evidence for existence of U^{6+} in solution. Pitchblende and brannerite do not show spatial relations to minerals–reductants (pyrite and other sulfides) or organic matter that is contained in tuffaceous and sedimentary interlayers of the host sequence. The results of sampling of host rocks at the Tulukui deposit for organic carbon (data of I.V. Mel'nikov et al., IGM RAS) show that, on the scale of the deposit, ore-

bodies are spatially separated from halos of elevated C_{org} contents (0.01–0.04%) or show crosscutting relations in areas of. The basement rocks and volcanics within the caldera contain carbonaceous matter in concentrations no higher than tenths of a percent, which cannot provide reduction of the great mass of uranium in local high-grade orebodies. The absence of an effect of carbonaceous matter on the formation of hypogene uranium minerals in ore of the SOF has been confirmed by special investigations carried out by Uspensky et al. (1986). No indications of potential reductants (H_2S , CH_4 , etc.) in ore-bearing solution itself were revealed either.

Thus, taking into account new data on the high temperature of hydrothermal ore-forming fluid, high fluorine activity in the process of uranium ore formation inferred from mineralogical data, and the absence of signs that would support the existence of U^{6+} in solution, complex fluoride compounds of U^{4+} should be regarded as the most probable species of ore matter transport. Since uranium ore is localized in virtually all varieties of intrusive, volcanic, sedimentary, and metamorphic rocks (Ishchukova et al., 1998), their chemical composition hardly exerted a substantial effect on the stability of complex uranium compounds. Under these conditions, a drop in temperature to 350–300°C should be the crucial factor of ore deposition, which is consistent with computations carried out by Ryzenko (2006).

The physicochemical parameters of hydrothermal solutions at the first postore stage were determined on the basis of FI study in comb quartz. Homogenization temperatures range from 396 to 168°C, largely being within 250–200°C; the highest temperature is characteristic of postore quartz from high-grade orebodies localized in large fault zones. The pressure of postore solutions approximately estimated with the Flincor program is 25–49 bar.

FIs in quartz of the first postore stage are filled with sodium chloride and less frequently sodium hydrocarbonate–chloride solutions (Fig. 7). The mineralization of the solutions varies from 0.4 to 15 wt % NaCl equiv. In the gas phase of FIs captured by quartz localized in high-grade orebodies, oxygen is sharply predominant (89.0–99.8 mol %). The hydrogen content is 0.2–9.5 mol %. In FIs entrapped in quartz that occurs in ordinary and low-grade ore, the oxygen concentration falls and the leading role belongs to H_2 and CO_2 . In barren rocks, carbon dioxide is the main component; oxygen is absent, and hydrogen is noted rarely.

The radiolysis of water is the most probable cause of production of free oxygen and hydrogen in uranium-bearing fluids (Dubessy et al., 1988). The preferential accumulation of O_2 in comparison with H_2 in solutions circulating within orebodies at both the uranium ore and postore stages is most likely explained by a higher diffusion coefficient of hydrogen (Vovk, 1979). The depletion of oxygen beyond orebodies may be caused by its consumption for oxidation of Fe^{2+} -bearing silicates in the course of percolation of oxygen-bearing solutions through rocks (Perez et al., 2005). The accumulation of oxygen in orebodies explains the hypogene replacement of pitchblende contained in high-grade ore by becquerelite $[Ca(UO_2)_6O_4(OH)_6 \cdot 8(H_2O)]$ and the prevalence of U^{6+} over U^{4+} in the U–Si metagel under unlikely conditions for development of supergene alteration.

The initial portions of postore solutions most likely were characterized by elevated acidity, as is evidenced by the occurrence of hydromica and the increase in porosity at the expense of leached plagioclase. By the end of the postore stage, the solutions were neutralized and inverted toward an increase in alkalinity, which provided for crystallization of carbonate and formation of coffinite instead of the U–Si metagel.

REE IN PITCHBLENDE AND IGNEOUS ROCKS

The behavior of REE in geochemical processes has attracted the attention of researchers for many years. Both products of magmatic activity, including that in the eastern Transbaikal region (Badanina et al., 2004, 2006), and hydrothermal mineralization, including uranium mineralization (Fryer and Taylor, 1987; Hidaka and Gauthier-Lafaye, 2001; Aleshin et al., 2006) have been studied in this respect. New data on the REE distribution in rocks and minerals have been obtained recently from experiments on magmatic and hydrothermal systems (Veksler et al., 2005; Veksler, 2004; Shmulovich et al., 2002). Some specific features of REE behavior were interpreted in terms of quantum mechanics (Mioduski, 1997; Dzburinsky, 1980; Fidelis and Siekierski, 1971). Taking into account the new data, we, together with M. Cuney (CREGU, France), have studied the REE distribution in pitchblende and igneous rocks of the SOF to obtain additional genetic information.

The REE contents in pitchblende hosted in granite at the Antei deposit, in trachybasalt at the Strel'tsovka deposit, and in trachydacite from the Strel'tsovka and Oktyabrsky deposits were determined with a Cameca IMS-3f ion microprobe (analyst J. Bonhoure, CRPG, France). The REE contents in host rocks were measured with ICP-MS (CRPG, IEM RAS). It has been established that sharp depletion in LREE (La, Ce, Pr, and Nd) and enrichment in Sm, Eu, and Gd relative to other REEs is a characteristic feature of pitchblende hosted in any rock (Aleshin et al., 2006). As a result, a pronounced Sm–Nd discontinuity is observed in the chondrite-normalized REE patterns (Fig. 8).

The REE patterns in the most abundant host rocks of the SOF (granite, rhyolite, dacite, and basalt) are generally typical of such kinds of rocks. The slight fractionation of REE in basalt is expressed in a low-angle pattern (Fig. 9a). Dacite is characterized by a poorly expressed negative Eu anomaly and somewhat elevated HREE (Er, Tm, Yb, and Lu) contents in comparison with basalt (Fig. 9b). The Hercynian granite in the basement of the Strel'tsovka caldera reveals a more distinct Eu minimum and enrichment in HREE and depletion in LREE relative to dacite (Fig. 9c). Rhyolite is distinguished by the deepest Eu minimum and the highest HREE contents (Fig. 9d). The REE distribution was analyzed in rocks affected by metasomatic alteration of various intensity, from slightly altered “background” rocks to rocks intensely replaced by hydromica, carbonate, and chlorite. As can be seen from Fig. 9, the alteration practically does not change the REE patterns.

The comparison of the REE patterns of pitchblende hosted in basalt, dacite, and granite with the REE patterns of host rocks reveals a positive correlation of the LREE/HREE ratio. This ratio progressively increases in the series granite–dacite–basalt, and this increase is expressed in a steeper slope of chondrite-normalized REE patterns (Fig. 9). A similar trend is traced for REE patterns of pitchblende hosted in the respective rocks

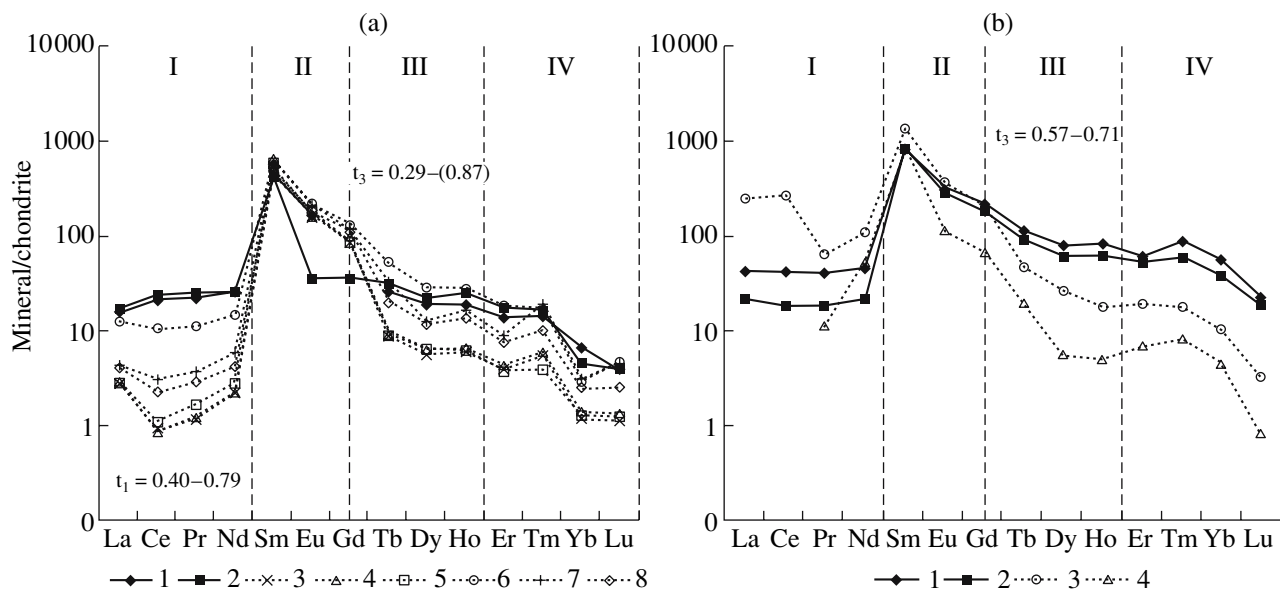


Fig. 8. Chondrite-normalized REE patterns of pitchblende. (a) Hosted in dacite, (1, 2) sample St-220h, (3–8) sample 85-67a from the collection of I.V. Mel'nikov; (b) hosted in granite, (1, 2) sample St-602, and basalt, (3, 4) sample St-391. (I–IV) Tetrads; t_1 and t_3 are the values of the tetrad effect in tetrads I and III, respectively.

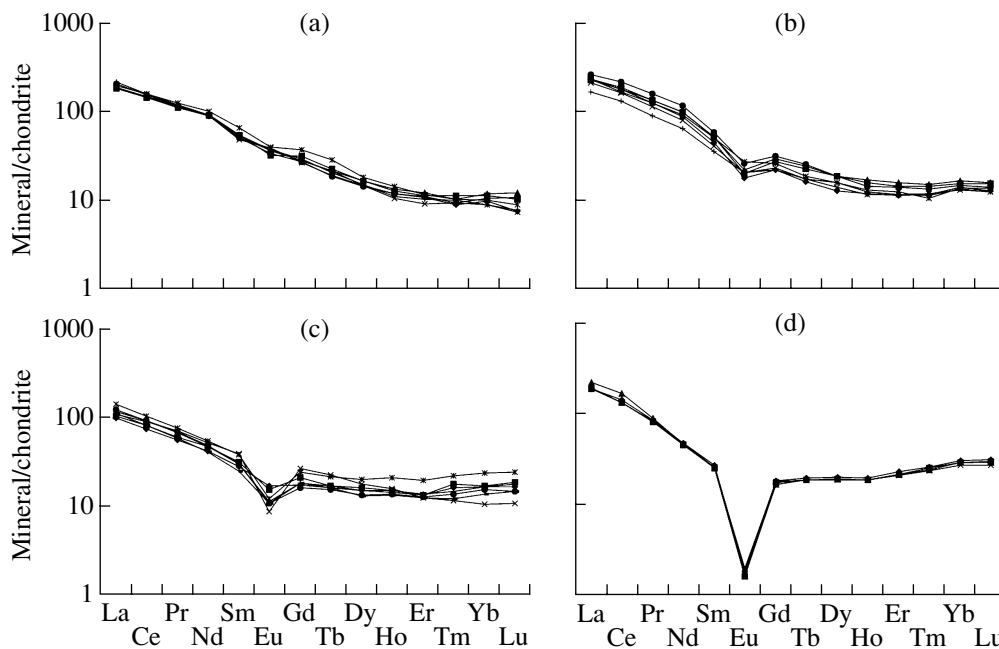


Fig. 9. Chondrite-normalized REE patterns of (a) basalt, (b) dacite, (c) Variscan granite, and (d) rhyolite in the Strel'tsovka ore field.

(Fig. 10). Thus, the host medium exerts some effect on LREE and HREE contents in pitchblende, but high Sm, Eu, and Gd contents are retained in uranium oxide from all host rocks.

The tetrad effect is another characteristic feature of the REE pattern of pitchblende. This effect is of great importance with regard to suggestions on the source of REE and U. This phenomenon of anomalous REE frac-

tation was established for the first time experimentally in immiscible liquids (Fidelis and Siekierski, 1966), and subsequently it was revealed in various natural systems, including seawater and marine sediments, meteoric hydrocarbonate water (Takahashi et al., 2002), F-bearing carbonatite (Bunh et al., 2003; Veksler et al., 2005), and silicic Li–F melts, whose evolution is controlled by separation into immiscible melts and flu-

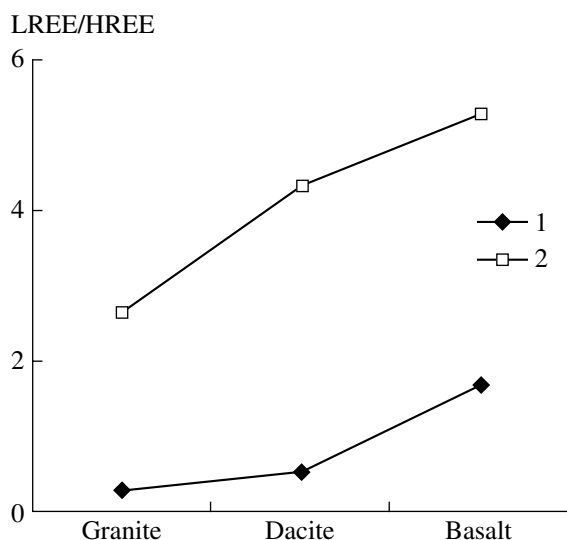


Fig. 10. LREE/HREE ratio of pitchblende hosted in granite, dacite, and basalt and of host rocks. (1) Pitchblende, (2) rocks.

ids to a greater extent than by crystal fractionation (Badanina et al., 2006; Monecke et al., 2002; Irber, 1999; Bau, 1996).

An anomalous character of REE fractionation is expressed in the division of gentle chondrite-normalized patterns into four segments consisting of convex (M-type) or concave (W-type) arcs named tetrads: the first tetrad (La, Ce, Pr, Nd), the second tetrad ((Pm), Sm, Eu, Gd), the third tetrad (Gd, Tb, Dy, Ho), and the fourth tetrad (Er, Tm, Yb, Lu), as can be seen from Fig. 8. Promethium, which does not occur in nature, is not shown in this figure. The different behavior of geochemically cognate elements with the same charge $3+$ (except $\text{Ce}^{3+, 4+}$, $\text{Eu}^{3+, 2+}$, and some others) and systematically decreasing ionic radius is caused by different stability of their organic, carbonate, and halogen compounds owing to a different degree of occupancy of the $4f$ orbital by electrons. REE with the $4f$ shell occupied multiply to $1/4$ (La, 0; Nd, (Pm), $1/4$; Gd, $1/2$; Ho, Er, $3/4$; Lu, 1) differ in the force of bonding with ligands in complex compounds from REE with the $4f$ orbital occupied nonmultiply (Fidelis and Siekierski, 1971). The enrichment of one part of the melt–fluid or fluid–fluid system in REE with a multiply occupied $4f$ orbital gives rise to the depletion of another part of the system in these REE and, thus, to the existence of complementary mirror M- and W-types of the tetrad effect in the normalized REE patterns.

The value of the tetrad effect was calculated according to Monecke et al. (2002). Tetrad effects with a value of >1.2 for the M type and <0.8 for the W type are thought to be statistically significant. Irber (1999) proposed less strict criteria of significance: >1.1 and <0.9 , respectively. The second tetrad is not considered because of the absence of Pm in nature and the anomalous behavior of Eu. The first tetrad is also less significant due to the anomalous behavior of Ce, while the fourth tetrad is commonly less expressed owing to the higher degree of occupancy of the $4f$ orbital and its closeness to the core (Irber, 1999). Thus, the third tetrad is the most stable and clearly expressed.

A significant effect of W type in the third tetrad ($t_3 = 0.29$ – 0.87) is displayed everywhere in pitchblende from the SOF (Fig. 8). In some segregations of pitchblende hosted in dacite (sample 85-67a), this effect is also displayed in the first tetrad ($t_1 = 0.40$ – 0.79). The composition of the host rock does not exert any effect on the intensity and type of the tetrad effect. For example, pitchblende hosted in dacite demonstrates an intense effect in the third tetrad and a clearly expressed effect in the first tetrad along with a poorly expressed effect in the third tetrad and the absence of an effect in the first tetrad (Fig. 8a). At the same time, pitchblende hosted in such contrasting rocks as basalt and granite shows a similar effect in the third tetrad (Fig. 8b).

The REE patterns in uranium oxide from deposits of different genesis and age (69–2000 Ma) vary widely (Fryer and Taylor, 1987; Hidaka and Gauthier-Lafaye, 2001) in total REE content, fractionation of LREE and HREE, sense and intensity of the Eu anomaly, and other attributes. It is supposed that the REE pattern is controlled to a greater extent by properties of the hydrothermal fluid (its Eh and type of complex anion) and by the source of U and REE rather than by the crystal chemistry of this mineral.

The REE pattern of pitchblende bears additional information on the possible source of uranium at the SOF deposits. The sharp Sm–Nd discontinuity caused by depletion in LREE might be explained by their fixation in an LREE-containing mineral, but such a mineral is unknown in ore. However, the same effect may be achieved by fractionation of monazite in the silicic magma as a potential source of uranium. Numerous analytical data on granites and modeling calculations corroborate such a possibility (Yurimoto et al., 1990; Sevigny, 1993).

The W-type tetrad effect is another specific feature of the REE pattern of pitchblende. Of all the aforementioned natural settings where this effect was established, only the evolved Li–F silicic melt is suitable for the SOF. This suggestion is confirmed by the abundance of rare-metal Li–F granites, ongonites, and rhyolites in the eastern Transbaikalian region. The ages of these rocks are close to the age of uranium ore mineralization in the SOF (144 – 138 and 135 ± 2 Ma, respectively).

The upper crustal magma chamber at a depth of ~ 5 km, the emptying of which during eruption of rhyolitic melt led to the subsidence of the Strel'tsovka caldera, is the most obvious candidate for such a source. However, rhyolites derived from this magma chamber do not reveal either a Sm–Nd discontinuity in the REE pattern or a tetrad effect typical of the REE pattern of pitchblende (Figs. 8, 9d). Moreover, the Y/Ho

and Zr/Hf ratios of rhyolites (36.4–36.9 and 25.0–26.4, respectively) indicate that these rocks are not highly evolved because their geochemical signature is close to the CHARAC field, which corresponds to the normal behavior of CHARGE-and-RADIUS-Controlled elements. This field is characterized by $Y/Ho = 24–34$ and $Zr/Hf = 26–46$, whereas anomalous ratios typical of evolved melts may differ from the normal ratios by many times toward either greater or lesser values (Bau, 1996).

Thus, the REE pattern and other geochemical attributes of rhyolites do not testify to the advanced fractionation of the silicic melt, development of the tetrad effect, and fractionation of monazite. This reasoning does not allow us to regard the U- and F-rich silicic melt derived from the upper crustal magma chamber as a source of uranium for deposits of the SOF.

Rhyolites of the Strel'tsovka caldera are close in geochemistry and age to the rare-metal Li–F granites and ongonites of the eastern Transbaikalian region enriched in uranium. The REE patterns in different phases of the Khangilay granitic complex (Badanina et al., 2004, 2006) turned out to be helpful for interpretation of the REE pattern of pitchblende from the SOF. The Khangilay pluton is situated in the Aginsky Block 250 km northwest of the SOF and is composed of granitic rocks varying from the least evolved biotite granite to highly evolved amazonite–microcline–albite–lepidolite leucogranite with accessory topaz and fluorite. The late phases are accompanied by Ta mineralization (the Orlovka deposit) and W ore (the Spokoiny deposit).

The early biotite and two-mica granites are characterized by chondrite-normalized REE patterns without a Sm–Nd discontinuity or tetrad effect and are similar in this respect to rhyolites from the Strel'tsovka caldera. In the younger four phases, these attributes appear with progressively increasing intensity up to a distinct M-type effect in several tetrads ($t_1 = 1.9$, $t_3 = 1.5$, $t_4 = 1.3$) and a pronounced Sm–Nd discontinuity.

The comparison of the chondrite-normalized REE patterns of the most evolved granites of the Khangilay pluton and of pitchblende from the SOF demonstrates their similarity in the occurrence of the Sm–Nd discontinuity and a mirror tetrad effect of M type in granite and W type in pitchblende. The first attribute is interpreted as a result of fractionation of monazite that retains LREE and depletes residual melt enriched in H_2O , F, and U in these elements.

The mirror tetrad effect is caused by release of fluid from the U- and F-bearing melt at the late stage of its evolution with enrichment of fluid in U, F, and complex REE compounds with a multiply occupied 4f orbital; the melt becomes enriched in REE with the 4f shell occupied nonmultiply, which causes development of an M-type tetrad effect.

The real possibility of derivation of Na–Al–F fluid from the melt with formation of complementary pairs of M- and W-type tetrad effects has been demonstrated

by experiments carried out by Veksler et al. (2005). The tetrad effect of W type was observed in cryolite (Na_3AlF_6), whereas in magmatic fluorite (CaF_2) this tetrad effect was not detected. It was concluded that the tetrad effect is caused by fractionation of aluminium fluoride rather than fluoride REE complexes. A similar conclusion on two types of fluids derived from melt—diluted aqueous fluid that causes greisenization of host rocks and Na- and F-bearing brine that gives rise to albitization of rocks—has been drawn as a result of comprehensive study of the granitic Khangilay pluton (Badanina et al., 2004, 2006).

Thus the REE patterns of pitchblende may be explained by the formation of uranium mineralization from postmagmatic fluids derived from the evolved U- and F-bearing silicic magma. If the magmatic source of uranium and REE is accepted as the most probable, then the discovery of the W-type tetrad effect in pitchblende as a natural postmagmatic mineral is the first case in world practice and a missing link in the system of evidence for magmatic fractionation of REE with formation of the tetrad effect.

DISCUSSION

The comprehensive studies of the SOF deposits allow us to consider critically the existing genetic models of uranium ore formation and argue for a refined model of postmagmatic ore generation, which, in our view, explains the available data more consistently.

The rocks that host the uranium mineralization in the caldera and the underlying basement cannot be regarded as the main source of economic uranium reserves. The following facts come into conflict with such an interpretation.

As has been shown by Andreeva et al. (1990) and supported by our observations, the background low-intensity metasomatic alteration, although it converts a part of syngenetic uranium into a mobile state, does not lead eventually to its removal. In this regard, the argument for leaching of a considerable amount of uranium from rocks at the preore stage and its redeposition in orebodies seems to be unconvincing.

As has been established from mineralogical study of the ore field, postore metasomatism led to the replacement of an appreciable portion of the primary uranium mineralization (pitchblende and brannerite) with a U–Si metagel and intense alteration of host rocks expressed in their replacement by hydromica, chlorite, quartz, and carbonate. The intensity of this alteration was higher than that of similar alteration at the preore stage. The removal of uranium from host rocks at the middle and upper levels of the deposits was most likely caused by postore alteration (Ishchukova et al., 1998, p. 500).

The high temperature (530–300°C) of uranium-bearing solutions, markedly exceeding the temperature of preore solutions (250–200°C), also contradicts hypothesis of uranium leaching from host rocks.

According to this model, the temperature of postmagmatic solutions must progressively fall from early to late portions.

According to another model of uranium leaching from the upper flows of U-bearing rhyolites, the uranium ore was formed as a result of convective circulation driven by a thermal anomaly related to the upper crustal magma chamber. It is suggested that this process gave rise to the leaching of uranium from rhyolites, its transfer to a depth of a few kilometers, heating of solutions, and their subsequent ascent with formation of deposits (Chabiron et al., 2003). However, as follows from calculations performed by Malkovsky et al. (1994) and Malkovsky and Pek (1993), fluid flows in convective cells, having approached to within a few hundred meters of the surface, should reach it as an ideal fluid conduit and escape into the hydrosphere.

The 3D model of the upper crust constructed with the GeoSpline GIS module shows that the spatial disposition of the main fluid conduits makes unlikely the formation of large convective cells, breaking them into a number of local cells. The master fluid conduits comprise the steeply dipping Meridional and Central fault zones and the boundary caldera faults that reached the upper crustal magma chamber, as well as the NE-trending Argun and East Urulyungui fault zones, inclined to the northwest (Fig. 1). The latter fault zones do not open the magma chamber and partly screen the ascending flows.

In terms of the model under consideration, it is difficult to explain the transfer of uranium from the upper level of oxygen-rich subsurface water, where uranium should largely occur in the form of U^{6+} , to deeper levels that are characterized by reducing conditions. In this case, U^{6+} must be reduced to U^{4+} with formation of a secondary enrichment zone, which is not actually observed.

The mantle-derived basaltic melts can hardly be the most probable source of uranium as suggested by Ishchukova et al., (1998) for the following reasons.

The Sm–Nd discontinuity in chondrite-normalized REE patterns of pitchblende may be explained only by fractionation of monazite in silicic melt.

Although the level of U content in basalts is elevated by three to four times relative to the global average, it remains not very high and insufficient for the formation of ore-bearing solutions.

The highest U and F contents have been detected in the lower basaltic flows, dated at 170–160 Ma, whereas the younger basalts are distinguished by lower concentrations of these elements, testifying to the depletion of basaltic magma in uranium long before the ore formation.

The results of our comprehensive investigations agree best with the magmatic model of uranium ore formation developed by Wolfson and his team. According to this model, the upper crustal chamber of silicic magma was a source of uranium, which was separated into the fluid phase, transported by hydrothermal solu-

tions in the form of uranyl–carbonate complexes, and deposited as ore at a reducing barrier. The data obtained have allowed us to refine some aspects of this model.

It is suggested that another silicic magma rather than rhyolite derived from the upper crustal magma chamber served as a source of uranium. According to experimental results (Peiffert et al., 1996; Zharikov et al., 1987), the coefficient of uranium partitioning between haplogranitic melt and fluid indicates that the melt should be enriched in uranium and the fluid, depleted in this element.

The Sm–Nd discontinuity in the REE patterns of pitchblende is explained by monazite fractionation in the inferred parental silicic melt, and the tetrad effect of W type, as a result of separation of the evolved melt into immiscible phases. None of these features are detected in rhyolites that fill the Strel'tsovka caldera.

The chronological gap of ~5 Ma that separates the last injections of granosyenite porphyry dikes along the faults bounding the caldera (140 Ma) and uranium ore deposition (135 Ma) is too long for the existence of a melt completed by derivation of ore-bearing solutions. According to numerical modeling of conductive heat transfer taking into account the latent heat of crystallization carried out by Malkovsky and colleagues at IGEM RAS with the finite difference method, an upper crustal magma chamber should crystallize within 26–60 ka after cessation of volcanic activity. All these data argue against the hypothesis that regards the upper crustal magma chamber as a potential source of uranium.

In the light of the available evidence, a crustal source of silicic magma enriched in F and U is the most probable source of uranium for the SOF deposits. The source melt is close in composition to the parental magma of the highly evolved Li–F granites of the Khangilai pluton and other rare-metal granites and ongonites of the eastern Transbaikalian region. This suggestion is supported by the Sm–Nd discontinuity and the tetrad effect of W type in pitchblende, which find a convincing explanation in separation of U-, F-, and REE-bearing fluid from the evolved Li–F silicic magma.

The magmatic source of uranium is indirectly supported by the fluorite–pitchblende mineral assemblage in ore and the U–F geochemical association in igneous rocks of the ore field. This parallelism allows us to suggest the progressive concentration of these elements in magmatic melts from older basic to younger silicic magmas with the subsequent separation of U-bearing fluid and deposition of U and F minerals in ore. This hypothesis is supported by the supercritical state of the first portions of ore-bearing fluid, established from the study of FIs in quartz.

The high temperature of U-bearing solutions rules out the existence of uranyl–carbonate complexes. The absence of evidence for migration of U^{6+} and the close relations between U and F allow us to suggest that uranium migrated as complex fluoride compounds of U^{4+} . Rare earth elements also might fractionate into fluid in

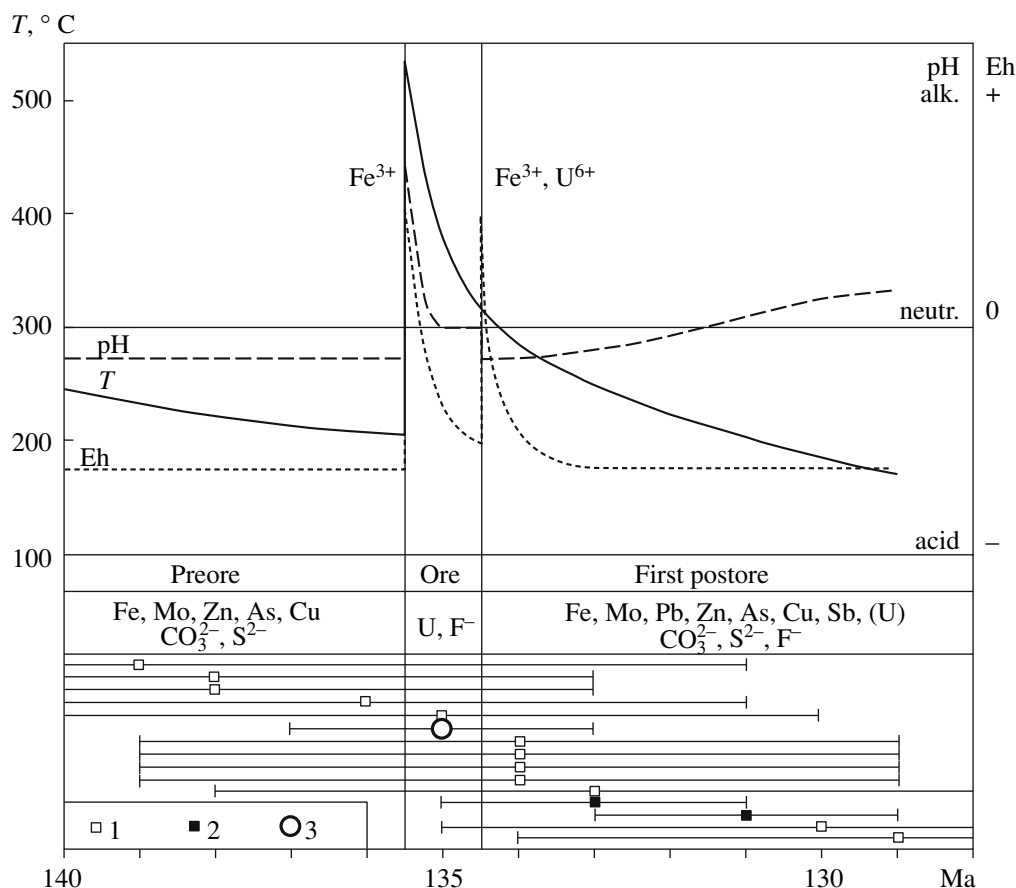


Fig. 11. Variation of the main physicochemical parameters of hydrothermal fluids at the preore, uranium ore, and first postore stages and geochemical specialization of the respective mineral complexes. (1–3) Isotopic age of hydromica (Andreeva et al., 1996) and pitchblende (Chernyshev and Golubev, 1996): (1) K–Ar age of hydromica, (2) Rb–Sr age of hydromica and ankerite, (3) U–Pb age of pitchblende.

the form of complex fluoride or aluminofluoride (Veksler et al., 2005) compounds.

The occurrence of two types of FIs—brine and low-density solution—in quartz formed at the uranium ore stage in combination with sodic wall-rock metasomatism is consistent with recent experimental data (Veksler, 2004) and natural observations (Badanina et al., 2004). It was suggested that low-density aqueous fluid and sodic brine with an anomalously high ability to transport ore components were derived from the F-bearing subalkaline silicic melt.

The rare-metal Li–F granitic plutons of the Kukulbei Complex are widespread in the eastern Transbaikalian region. The Kir-Kirin pluton of U-bearing morion leucogranite, dated at 145–138 Ma, is situated 40 km north of the Strel'tsovka caldera. The large Kibirevka–Idanga leucogranitic pluton, which likely also belongs to the Kukulbei Complex, is located 10–15 km to the northeast. Therefore, there are all grounds to infer that a similar hidden pluton that may exist beneath the SOF is a source of uranium. According to geophysical data, the most intense gravity minimum is located to the northwest of the Strel'tsovka caldera down-dip the East

Urulyungui Fault Zone. This minimum is more pronounced than the local lowering of the gravity field related to the upper crustal magma chamber beneath the caldera (Ishchukova et al., 1998). It cannot be ruled out that this minimum marks a hidden leucogranitic pluton.

To provide insights into the origin of mineral complexes pertaining to the preore and the first postore stages and their relationships with uranium ore mineralization, we considered the evolution of the main physicochemical parameters of the hydrothermal system, the geochemical specialization of mineral complexes, and the duration of their formation.

As is shown in the summary chart (Fig. 11), the hydrothermal solutions of the preore and the first postore stages are close in their physicochemical parameters. The temperature of the hydrothermal fluids that led to preore alteration and the formation of sulfide–carbonate–cryptocrystalline quartz veins ranges from 250 to 200°C. The temperature of postore solutions generally fits this range, but in high-grade uranium orebodies localized in large fault zones it rises to 300–350°C. Most likely, this was caused by thermal anomalies that arose within orebodies due to the circulation of high-

temperature ore-forming solutions. The first postore stage immediately followed the ore deposition (see below) and thus the thermal anomalies had no time to disappear by this moment.

The solutions at the preore stage and in the beginning of the first postore stage produced hydromica and were slightly acid (Andreeva and Golovin, 1998). At the end of the first postore stage, when carbonate and coffinite precipitated instead of the U–Si metagel, the solutions were neutralized and became alkaline. The reducing character of solutions of the pre- and postore stages follows from the occurrence of sulfides and chlorite. Only at the onset of the first postore stage did oxidizing conditions exist locally within high-grade orebodies, providing oxidation of U^{4+} to U^{6+} and formation of iron hydroxides. This phenomenon was caused by radiolysis of hydrothermal fluid as a result of irradiation by uranium and products of its decay.

The geochemical specialization of both the preore and the first postore mineral complexes is characterized by development of sulfides (pyrite, marcasite, jordisite, and cleiophane) and native Cu, As, and Sb. The crystallization of colloidal solutions resulted in the formation of chalcedony-like quartz, amorphous Mo sulfide, the U–Si metagel, and gels of complex and variable compositions.

The duration of the preore and the first postore stages was determined by K–Ar and Rb–Sr dating of hydromicas. According to these data (Andreeva et al., 1996), hydromica crystallized continuously from 139 to 129 Ma ago.

The ore formation is a sharp anomaly against this background in all respects. This is a high-temperature process (530–300°C against 250–200°C typical of the preore and the first postore stages) that started with alkaline metasomatism and formation of brannerite and subsequently gave way to neutralization of solutions and deposition of pitchblende. The dispersed iron hydroxides testify to oxidizing conditions at the beginning of the uranium ore stage; however, by the deposition of brannerite and pitchblende, the environment had changed to reducing one. The purely uranium specialization of the ore mineral complex contrasts with the chalcophilic and siderophile specialization of the preore and the first postore mineral complexes. These complexes also differ in anions: only fluorine is typical of the uranium ore complex, whereas, in both the preore and the first postore complexes, bicarbonate ion dominates and S^{2-} occurs as well.

The duration of the uranium ore stage was estimated by Malkovsky and colleagues at 0.5–1.0 Ma from the mathematical modeling of heat and mass transfer. The process is described in terms of forced convection and provides formation of uranium reserves at the Strel'tsovka and Antei deposits.

Thus, it may be suggested that the mineral formation at the preore and the first postore stages was a common long-term postmagmatic process likely initiated

by emplacement of an upper crustal intrusion and eruption of silicic magmas. The process was interrupted 135 Ma ago by a relatively short-term injection of high-temperature U-bearing solutions derived from another chamber of evolved Li–F silicic magma. After the deposition of ore at a temperature barrier, the ongoing circulation of hydrothermal solutions gave rise to the development of hydromica and alteration of the primary uranium ore, as well as to more local and intense alteration of host rocks.

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