
SHORT COMMUNICATIONS

Behavior of Lanthanides during the Origin of Mineralized Domes: an Example of the Spokoininskoe Deposit, Transbaikalia

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Abstract—The paper reports data on concentrations of lanthanides in rocks, fluorite, and wolframite from the Spokoininskoe greisen deposit in eastern Transbaikalia. Lanthanide concentrations in the ore-forming fluid are calculated using mineral/fluid distribution coefficients. The data on REE are consistent under the assumption of a single, but evolving, genetic source. The REE concentrations are similar for rocks variably affected by greisenization and are controlled by the solubility of monazite contained in the granite. The younger quartz–albite–muscovite veins and segregations contain elevated concentrations of LREE, which is explained by an increase in the monazite solubility in alkaline solutions during the late evolution of the fluid.

Keywords: ore-forming (W) fluid, rare-earth elements, composition of minerals, ore-forming processes, wolframite deposits, greisens

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INTRODUCTION

This publication is the final one in a series presenting the results of our studies of the possibility of using indicator properties of lanthanides to gain an insight into specifics of the origin of high-temperature hydrothermal W and Sn–W deposits genetically related to granites. Our earlier studies were focused at the Mo–W veined Akchatau deposit in Kazakhstan and at the W–Sn Iul'tin and Svetloe deposits in Chukotka, which differ in certain traits of mineral-forming processes (Matveeva, 1997; Popova et al., 2014, 2016).

The Spokoininskoe greisen deposit in eastern Transbaikalia is of the stockwork type, and its reserves amount to 35.5 thousand tones of WO₃ (as of 2013). The deposit is actively developed by the CJSC Novoorlovskii Mining and Processing Company (*On the State...*, 2014). Structurally, the deposit is a mineralized dome and is spatially constrained to one of the apical domes of the Khangilai–Shilka granite pluton of Late Jurassic age (Rundkvist et al., 1971). The granite is overlain by poorly permeable hornfelsized rocks of the Onon Formation of Late Proterozoic age (Beus et al., 1962, Potap'ev, 1971). The deposit was produced by magmatic fluid and shows no evidence of its mixing with waters of any other genesis, which also follows from isotopic data (Matveeva et al., 2002). The greisenization process took place at temperatures of 450–300°C. The pressure at the transition from the magmatic to hydrothermal process decreased

from 5 to 0.5 kbar, and this resulted in hydrodynamic focusing of the ascending fluid flows at the apical portion of the massif. The ore mineralization was produced at a pressure of about 0.5 kbar. The fluid flow was shielded by the roof rocks, and this defined the upper boundary of the orebody, which coincides with the contact of the intrusion.

Greisenizing solutions at this deposit were typically oversaturated with carbon dioxide and heterogeneous. The heterogeneity of the fluid was caused by its degassing (onset of immiscibility) during the evolution of the hydrothermal system. The Spokoininskoe deposit was formed in a relatively stable tectonic environment. The originally homogeneous fluid ascending from deep zones of the magmatic chamber unmixed into an H₂O- and CO₂-rich phases as a result of decreasing temperature. The filtration of the two-phase fluid through highly permeable rocks was associated with the hydrodynamic separation of phases and the enrichment of the frontal portions of the fluid flows in the gas phase. The two-phase filtration of fluids at the Spokoininskoe deposit was characterized by the simultaneous segregation of the gas and liquid and condensation of the aqueous solution from the CO₂-rich phase, as is typical of immiscibility in the H₂O–CO₂ system (Matveeva et al., 2002).

Geochemical criteria of the filtration dynamics of two-phase fluids at greisen deposits (carbon isotopic

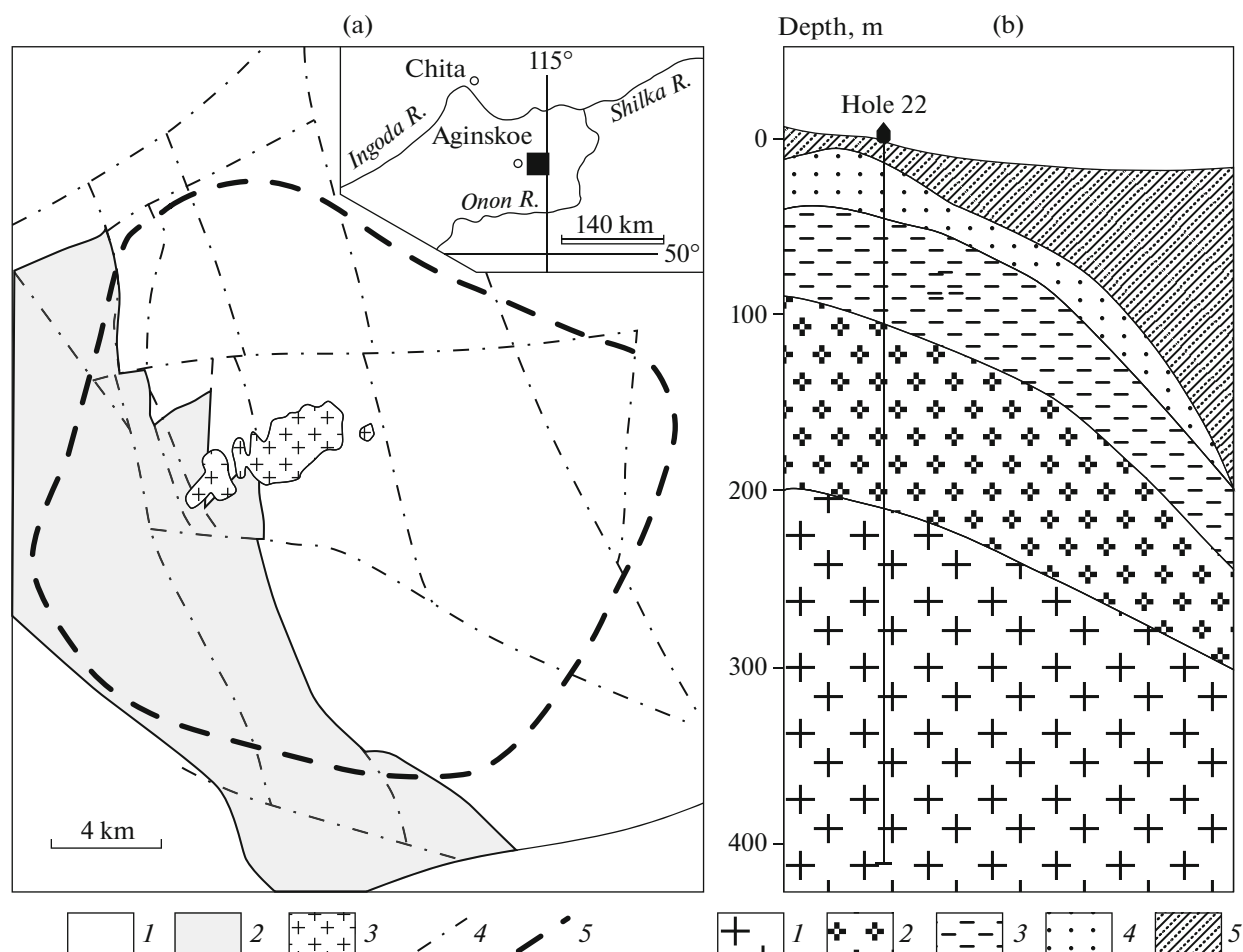


Fig. 1. Schematic geological map of the Spokoininskoe deposit. (a) Overview map of the Khangilai pluton (Matveeva et al., 2002). (1) Late Proterozoic metamorphosed sandstone, shale, and volcanic rocks; (2) Triassic sandy-clayey rocks; (3) granite; (4) faults; (5) contour of the unexposed granite pluton, based on gravimetric data. The solid square in the inset shows our study area. (b) Vertical zoning of the Spokoininskoe deposit. (1) Granite without traces of alterations discernible by the naked eye; (2) albitized and greisenized granite with lean ore dissemination; (3) intensely greisenized granite with disseminated wolframite mineralization; (4) muscovite-quartz greisen; (5) hornfels.

composition and the Ca/Al ratio of the metasomatic rocks) led us to gain an insight into the flow of the heterogeneous fluids when the Spokoininskoe deposit was produced (Matveeva and Bychkov, 2001; Bychkov et al., 2012). The decrease in the $\delta^{13}\text{C}$ of the 8CO_2 -rich solutions traces the filtration pathways of the liquid phase of the two-phase fluid and characterizes the intensity of phase separation, which reached a maximum at the top of the stock. The elevated Ga/Al ratios of the metasomatites allowed us to outline the condensation region and to follow the migration pathways of the condensation-generated waters. The maximum Ga/Al ratio in the muscovite-albite-quartz veinlets cutting the contact hornfels suggests that the condensate came into the host rocks. The fact that quartz in these veinlets hosts CO_2 -rich inclusions analogous to those in minerals of the deposit itself means that the contact zone was penetrated by the gas phase (Matveeva et al., 1991).

Phase separation when the heterogeneous fluid percolated through rocks shifted chemical equilibria in the solution-rock system and consequently resulted in metasomatic transformations of the granite. The intensity of the metasomatic transformations increases toward the top of the stock, where the heterogeneity of the fluid was at a maximum. The vertical zoning produced thereby is seen as a gradual transition from fresh (as seen by the naked eye) muscovite granite to albitized granite, weakly greisenized granite with lean wolframite dissemination, and eventually to intensely greisenized granite with disseminated wolframite ore mineralization. These rocks, which were referred to as “apogranite” by A.A. Beus, consist of albite, quartz, and muscovite of apple-green color (greisen muscovite). In the most intensely greisenized domains, which occur beneath the roof of the host rocks, albite is replaced by quartz-muscovite aggregates, and the rock approaches quartz-muscovite greisen in composition (Fig. 1).

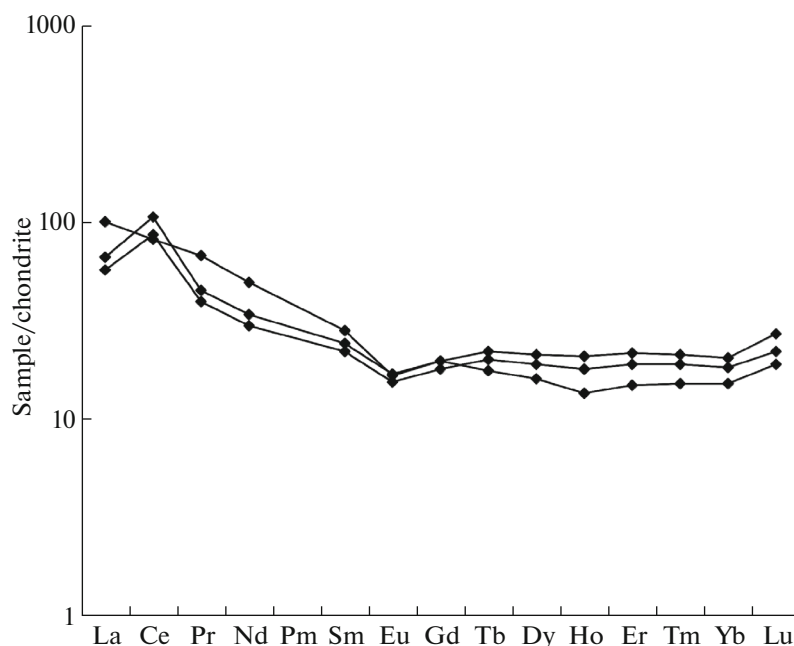


Fig. 2. Chondrite-normalized REE patterns of contact hornfels.

The metasomatic transformation of the granite was associated with a progressive increase in the acidity of the solutions, with its maximum reached when the rocks suffered high-temperature silification. The final evolution of the deposit occurred at increasing alkalinity of the solutions because of their enrichment in strong bases borrowed from the granitoids when they were metasomatized and also because volatile acidic components escaped from the fluid (Beus et al., 1962). These solutions were responsible for local albitization. The albitization process was constrained to fractured zones in the modified granite and was not associated with the deposition of any ore mineralization. The metasomatic zones are 4–5 m thick and consist of newly formed fine-grained sugar-like albite. The greisenized granite hosts segregations and veinlets up to 2 m that are made up of coarse-grained *Ms–Ab* and *Qz–Ms–Ab* rock rich in wolframite and fluorite and sometimes containing beryl. These domains are thought to have been formed by the precipitation of components leached during metasomatism (Distler, 1967).

The ore mineralization of the deposit is classified into two types. One of them is the apogranite itself and greisen containing economic W concentrations. The other type, which is of subordinate importance, is nearly vertical wolframite–quartz veins that were formed very late in the ore-forming process.

MATERIALS AND METHODS

We have studied REE distribution in all varieties of the metasomatized granite, contact hornfels, and in the wolframite and fluorite. The samples for this study were

borrowed from a collection gathered by S.S. Matveeva in 1985–1986. Concentrations of REE were analyzed by ICP-MS on an Element-2 at the Laboratory of Experimental Geochemistry of the Geological Faculty, Moscow State University. The techniques used to prepare mineral and rock samples for their analysis are described in much detail in (Popova et al., 2014). In all plots below, the REE concentrations are normalized to CI chondrite (Palme and Jones, 2003). The composition of the wolframite, monazite, and xenotime was analyzed on a Jeol JSM-6480LV electron microscope equipped with a hybrid system of microprobe analysis at the Laboratory of Analytical Techniques of High Spatial Resolution at the Department of Petrology, Geological Faculty, Moscow State University.

RESULTS

The contact hornfels is relatively enriched in LREE ($\text{La/Lu} = 25\text{--}15$) and displays weakly pronounced Eu minima ($\text{Eu/Eu}^* = 0.7\text{--}0.8$). Two of our samples showed positive Ce anomalies, as is typical of sedimentary rocks. The total REE contents of the rocks varies from 163 to 194 ppm (Fig. 2).

The REE patterns of variably greisenized granite samples typically exhibit clearly seen Eu minima ($\text{Eu/Eu}^* = 0.2\text{--}0.3$) and the dominance of LREE over HREE ($\text{La/Lu} = 30\text{--}80$) (Fig. 3). The main REE concentrators in the granite are monazite ($\text{Ce, La, Nd...[PO}_4\text{]}$) and, to a lesser degree, xenotime YPO_4 (Distler, 1967).

Figure 4 shows the REE patterns of wolframite from the greisenized granite, quartz–wolframite veins, and quartz–muscovite–albite segregations. The patterns

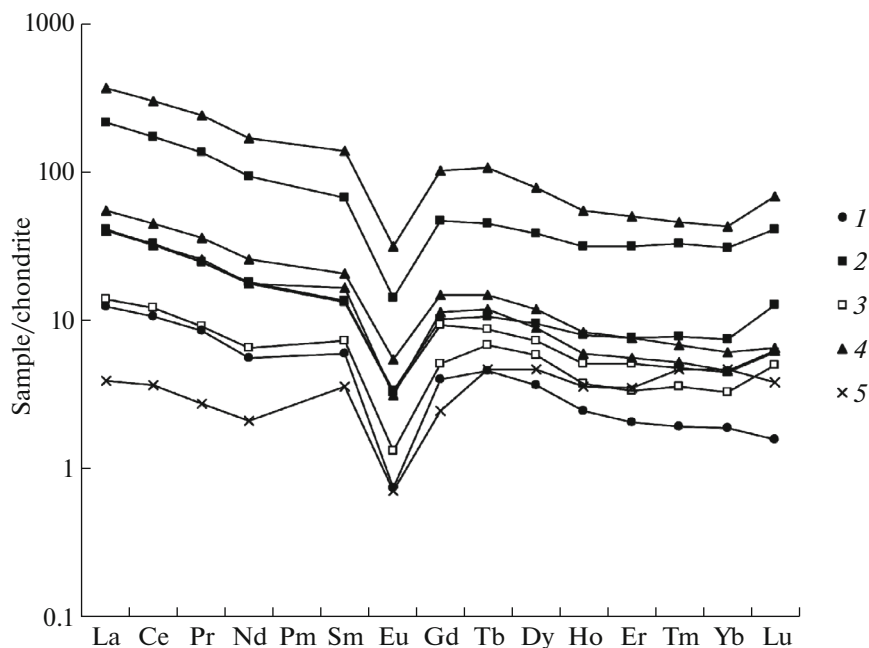


Fig. 3. Chondrite-normalized REE patterns of metasomatites at the Spokoininskoe deposit. (1) Khangilai granite; (2) weakly greisenized granite; (3) intensely greisenized granite; (4) quartz–muscovite greisen; (5) secondary albitite.

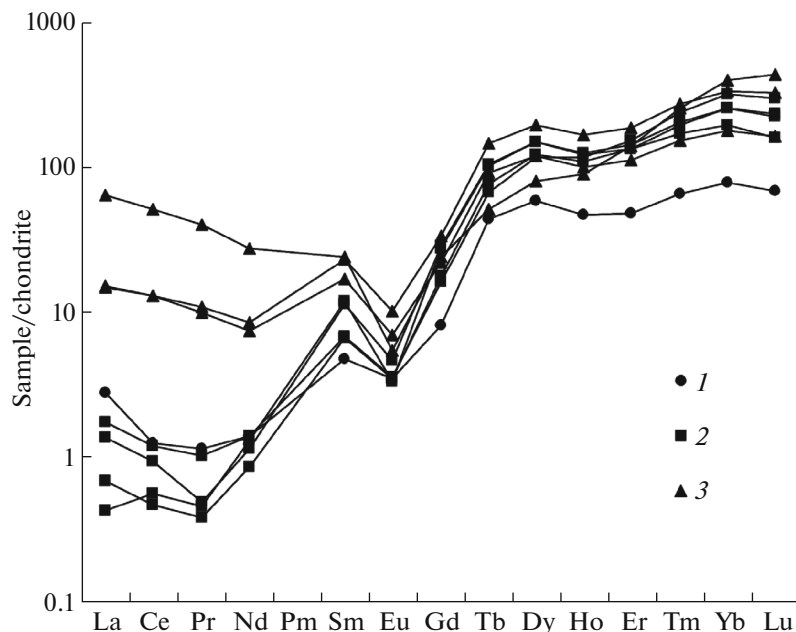


Fig. 4. Chondrite-normalized REE patterns of wolframite. Host rocks: (1) greisenized granite; (2) quartz–wolframite veins; (3) quartz–muscovite–albite segregations.

can be classified into two groups according to the REE concentrations.

One of the groups comprises REE patterns of wolframite from the greisenized granite and quartz–wolframite veins. These REE patterns compose a compact group. The total REE concentrations are 180–200 ppm. The wolframite is typically poor in LREE ($\text{La/Lu} =$

0.03–0.4), which was predetermined by the proportions of LREE and HREE in the mineralizing solution. When granite crystallizes, monazite preferably accommodates LREE, and this results in the depletion of LREE in the solutions separating from the crystallizing melt. The composition of the wolframite (microprobe data) that crystallized throughout the whole ore-forming process suggests a single REE source and con-

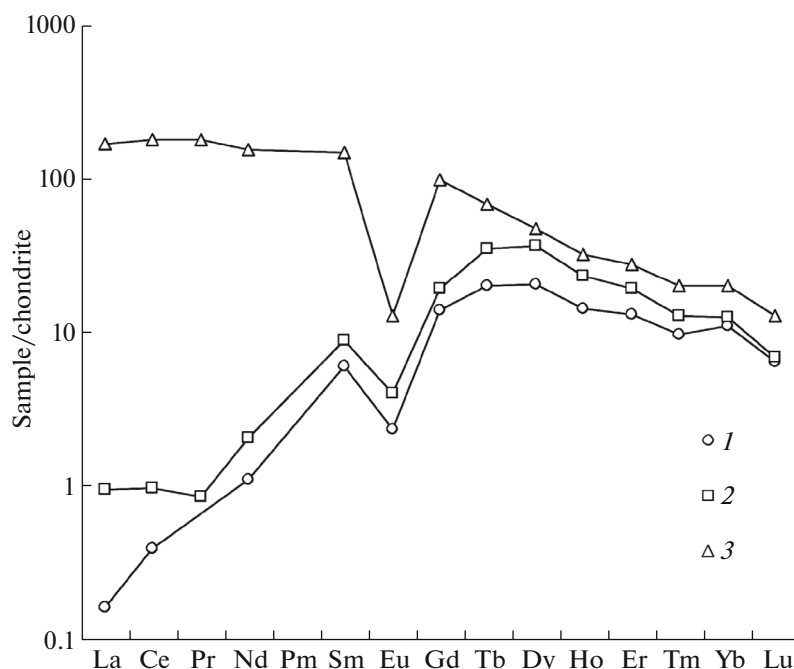


Fig. 5. Chondrite-normalized REE patterns of fluorite. Host rocks: (1) greisenized granite; (2) quartz–wolframite veins; (3) quartz–muscovite–albite segregations.

firms the conclusion that the magmatic fluid did not then mix with solutions of any other genesis.

The other group encompasses REE patterns of wolframite from the quartz–muscovite–albite segregations. This mineral is typically rich in REE (290–309 ppm) and richer in LREE ($\text{La/Lu} = 0.9\text{--}1.4$). The origin of the quartz–muscovite–albite segregations marked a fundamental change in the acidity of the mineralizing solutions, when the acidic solution became alkaline very late in the course of the mineralizing process.

The configurations of the REE patterns of the fluorite are similar to those of the wolframite (Fig. 5). Fluorite from the granite and quartz–wolframite veins is typically poor in REE (0.24–0.38 ppm), with HREE dominating over LREE ($\text{La/Lu} = 0.24\text{--}1.33$). Fluorite from the segregations is rich in REE (470 ppm), with LREE dominating over HREE ($\text{La/Lu} = 128$).

DISCUSSION

Analysis of the REE patterns of variably greisenized granite samples shows that the REE concentrations are not correlated with the intensity of the metasomatic transformations. For example, the maximum REE concentrations in the most intensely greisenized granite varieties varies from 714 to 76 ppm. All of our metasomate samples were found out to contain monazite and xenotime grains. Monazite is known to be little susceptible to high-temperature weakly acidic solutions and can be preserved in rocks in the course of their greiseni-

zation (Tropper et al., 2011). The REE concentrations in the variably altered granite could be controlled by their monazite contents, and the variations in the REE contents are likely explained by that monazite was unevenly distributed in the pristine rocks.

Wolframite is the main REE concentrator in greisenized granites. The ratio of REE contained in wolframite to the total REE content of the rock can be calculated from the W content: the wolframite contains no more than 0.1% of the Ce-group REE, and this percentage is higher for the Y-group REE but is also no higher than 1% in the weakly altered granite and quartz–muscovite greisen. The maximum percentage of REE accommodated in wolframite was found in a sample of greisenized granite that contained the lowest total REE concentration and a high W content.

The solubility of monazite is higher in alkaline solutions and increases at high NaCl concentrations (Hetherington et al., 2010; Williams et al., 2011; Tropper et al., 2011; Kolonin and Shironosova, 2012). This explains the low REE concentrations (13 ppm) in the younger albite metasomatites. The residual solution, which was enriched, first of all, in LREE, came into fracture zones in the greisenized granite and produced quartz–muscovite–albite segregations and veinlets, whose wolframite and fluorite are rich in LREE. Analogous relations are also known to be typical of the xenotime solubility, but the content of this mineral is low and did not allow us to quantify the enrichment effect of HREE.

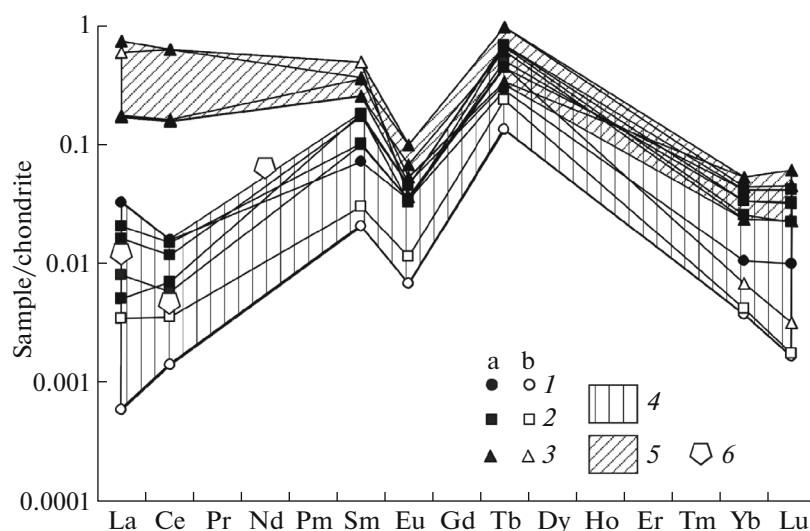


Fig. 6. Chondrite-normalized REE patterns of fluid calculated from the composition of (a) wolframite and (b) fluorite. (1) Greisenized granite; (2) quartz–wolframite veins; (3) quartz–muscovite–albite segregations; (4) fluid in equilibrium with the material of quartz–wolframite veins and granite; (6) REE concentrations calculated from the monazite solubility.

The distribution coefficients of REE between wolframite, fluorite, and solution determined in (Raimbault, 1985) for the parameters of the greisen process makes it possible to operate with comparable values of the REE patterns of the solutions. Figure 6 shows the REE composition of solutions that were in equilibrium with wolframite and fluorite from the Spokoininskoe deposit. The solutions can be classified into two groups.

The first, and the main, group comprises solutions that were in equilibrium with wolframite and fluorite from the greisenized granite and quartz–wolframite veins, i.e., solutions that produced the ore mineralization. These solutions are noted for low total REE concentrations (0.01–0.1 ppm) and low contents of LREE ($\text{La/Lu} = 2\text{--}30$). The calculated REE concentrations in the mineralizing fluid fall within the range reported in (Prokof'ev et al., 2008), which presents ICP-MS analyses of fluid inclusions in quartz syngenetic with wolframite in the greisen and quartz–wolframite veins at the Spokoininskoe deposit.

The solubility of monazite in H_2O and NaCl solutions was studied using both naturally occurring mineral and synthetic La, Ce, and Nd phosphates (Pourtier et al., 2010; Tropper et al., 2011). Most of the experiments were carried out at high temperatures (600–800°C) and pressures (2–10 kbar), and only the solubility of NdPO_4 was studied at parameters close to those at the Spokoininskoe deposit (Pourtier et al., 2010). At 300°C and 2 kbar, the monazite solubility is 0.3 ppm. For our monazite composition, Nd concentration in the aqueous fluid is estimated at 0.045 ppm. The La and Ce concentrations were extrapolated from the solubility values of the pure phosphates at high temperatures and were thus estimated at 0.005 and

0.0048 ppm, respectively. The calculated concentrations of La, Ce, and Nd are displayed in Fig. 6 and are reasonably good consistent with the values calculated from the wolframite and fluorite compositions for the group-1 solutions.

The other group consists of solutions that were in equilibrium with wolframite and fluorite from the segregations. Thanks to monazite dissolution, they are richer in REE (the total REE concentrations vary from 0.4 to 1.0 ppm) and LREE ($\text{La/Lu} = 118\text{--}1823$). These solutions operated late during the evolution of the hydrothermal process. The alkaline composition of these solutions and their high Na concentrations resulted in the albite–muscovite–quartz assemblage.

Comparison of the REE concentrations of wolframite and fluorite from the Spokoininskoe deposit and deposits of the Sn–W–quartz vein–stockwork type (such as Iul'tin and Svetloe) reveals their remarkable differences. The REE distribution between minerals from vein-hosted deposits is noted for a significant variability, which reflects the evolution of the fluid at a high water/rock ratio (Popova et al., 2014, 2016). In this situation, the REE patterns are geochemical indicators that shed light onto the fluid source, crystallization sequences of the minerals, and stages of the mineral-forming processes.

Metasomatites at the Spokoininskoe deposit are characterized by low water/rock ratios, with the behavior of REE controlled by accessory minerals. In this instance, the concentration ratios of REE provides no clue to the genesis of the hydrothermal solutions but reflects the evolution of the chemical composition of the fluid.

CONCLUSIONS

1. Similarities between the REE patterns of wolframite, a mineral that crystallized throughout the whole ore-forming process, suggest that REE were borrowed from a single source.

2. The REE concentrations in wolframite and fluorite during the greisen process in the mineralized dome of the Spokoininskoe deposit were controlled by the solubility of granite-hosted monazite.

3. Wolframite and fluorite from the quartz–muscovite and quartz–muscovite–albite segregations contain elevated concentrations of REE because of an increase in the monazite solubility in the alkaline solutions.

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