
SHORT COMMUNICATIONS

Behavior of Lanthanides during the Formation of the Iul'tin Deposit, Chukchi Peninsula

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The determination of the factors of ore formation and sources and evolution of hydrothermal solutions is an important geochemical problem. Recent studies of tin and tungsten deposits have employed new methods and approaches to elucidate, on the one hand, the reasons for the formation of large and very large deposits and, on the other hand, the physicochemical parameters of formation of these deposits. These studies resulted in the extension or even revision of existing genetic models.

The rare earth elements (REEs), which include La and lanthanides, are traditionally used as indicators of fractionation in magmatic systems and exogenic processes. The elements whose contents are specific for solutions of particular compositions and that preserve the respective signatures during solution–rock exchange reactions and infiltration toward mineralized zones can be used as geochemical tracers of the nature of hydrothermal fluids. The contents and ratios of REE in minerals can be used as indicators of the nature and evolution of hydrothermal solutions, because mixing of waters from different sources and an increase in the fraction of exogenic waters in ore-bearing fluid are distinctly reflected in the REE distribution patterns of minerals [1–3].

The reconstruction of REE behavior in the hydrothermal process requires the estimation of their concentrations in fluid. The composition of fluid is usually determined by the analysis of water extracts of quartz. However, it should be kept in mind that this technique provides information on all types of inclusions, both primary and secondary.

A more reliable approach to the reconstruction of the REE composition of ore-bearing solutions in high-temperature tungsten deposits is the use of REE partition coefficients between minerals (wolframite, fluorite, and scheelite) and fluid. The coefficients were calculated for chloride–fluoride solutions at 350–500°C, which corresponds to the conditions of greisen formation [4] (table).

The Iul'tin tin–tungsten deposit in the Chukchi Peninsula (Russia) is a typical example of ore-bearing

high-temperature hydrothermal systems related to granites [5, 6].

Based on the oxygen and hydrogen isotope compositions of minerals, it was concluded that the Iul'tin deposit was formed by hydrothermal solutions of mixed origin, magmatic and meteoric, which interacted with the country rocks before arriving at the system (Fig. 1). Thermodynamic calculations showed that mixing was the main factor of ore deposition in the Iul'tin deposit [7, 8]. The most vigorous convective motion of meteoric waters occurred after the formation of the ore mineral assemblage.

In this study, we estimated the distribution of REEs in concentrating minerals (wolframite, fluorite, and scheelite) and in the wall-rocks at the ore body.

Cross-sections at two horizons, VII and III, were selected for the analysis of wall-rocks (Fig. 1). Samples were taken across the strike of ore body 62/50 at an interval of 10–200 cm. The rocks of horizon VII are greisenized leucogranites, and those of horizon III are hydrothermally altered sedimentary and metamorphic rocks. Minerals were collected from horizons VII–III, and the vertical extent of the cross-section is 300 m.

The contents of REE were determined by the ICP–MS technique using an Element-2 mass spectrometer at the Laboratory of experimental geochemistry of the Faculty of Geology, Moscow State University, and Laboratory of isotope geochemistry and geochronology of the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences.

For rock analysis, samples were digested using a standard procedure in a hot mixture of concentrated acids (HF : HNO₃ : HCl in the proportion 5 : 1 : 1) in a Volta microwave oven. A rock sample 0.1 g in weight was loaded into a 7-cm³ Savillex™ vial with 3.5 mL of the acid mixture. After microwave heating, the sample with HCl was evaporated three times for the elimination of fluorides under a lamp with vapor withdrawal using a water-jet pump. The residue was quantitatively transferred into 50 mL of 3% HNO₃ solution. Before mea-

[†] Deceased.

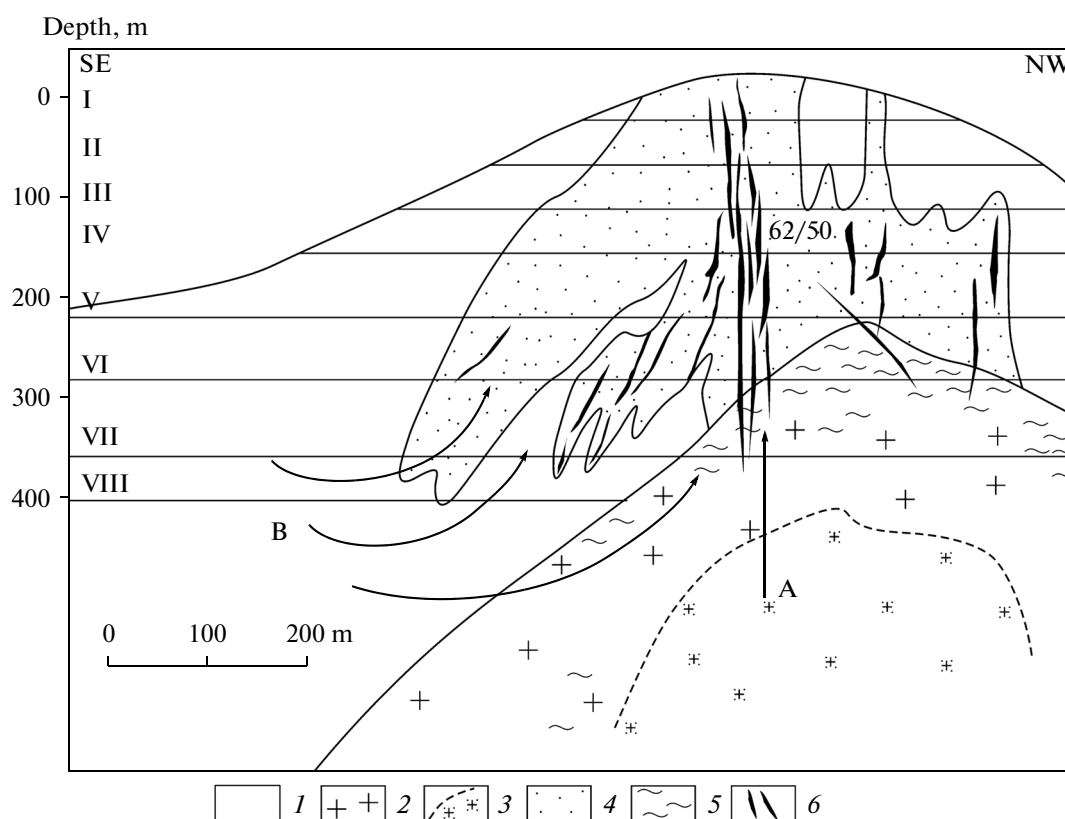


Fig. 1. Schematic geological cross-section of the Iul'tin deposit (Sushchevskaya, 2005) and reconstructed pathways of magmatic (A) and exogenous (B) fluids. (1) Metamorphosed sedimentary rocks (P_2), (2) muscovite leucogranite of the Iul'tin stock (K_2), (3) porphyritic biotite leucogranite of the Iul'tin stock (K_2), (4) metasomatized wallrock, (5) greisenized leucogranite, and (6) ore bodies. I–VIII are the numbers of horizons.

surements, the solution was diluted by a factor of 100, and indium was introduced as an internal standard. The accuracy of analysis was checked by measuring the STM-1 standard prepared using the same procedure. The deviation from the certified values was no higher than 5%.

The classical method of fluorite digestion is boiling in concentrated sulfuric or perchloric acid. Hydrogen fluoride is evaporated and calcium and admixtures are transferred into the solution [9]. This technique was not used, because acids of necessary purity were not available, and, moreover, the presence of excess perchloric or sulfuric acid would have resulted in the need to account for a new matrix in measurements.

A new method was proposed for fluorite digestion. It is based on calcium fluoride dissolution in 5 M nitric acid. For decomposition, 30 mg of fluorite were loaded into a 7-cm³ SavillexTM vial together with 3 mL 5 M HNO₃ and 0.5 mL of concentrated HCl. The subsequent operations were the same as those for rock digestion. Fluorite sample FI-01 from the Kalangui deposit of Transbaikalia was used as an in-house standard. This monomineralic fluorite sample was crushed and digested using the procedure described above.

A special method of acid digestion at 200°C was developed for the dissolution of wolframite and scheelite, because the reaction rate at room tempera-

ture was found to be too low. A mineral sample 20-mg in weight was loaded into a 3-mL SavillexTM vial with 2.5 mL HCl and 0.3 mL HNO₃. Then, the vial was placed in a Ti alloy container with a 50-mL Teflon insert; pressure was imposed by introducing the desired amount of distilled water into the insert. Then, the containers were hermetically sealed, placed into a tubular furnace with a temperature controller, and kept at 200°C for 24 h. Then, the containers were cooled with

Partition coefficients of REEs between hydrothermal minerals and solution (Raimbault, 1985)

Element	Mineral–solution partition coefficient		
	fluorite	wolframite	scheelite
La	280	85	20000
Ce	280	80	30000
Sm	300	65	6000
Eu	350	100	6000
Tb	550	150	5000
Yb	3000	7500	4500
Lu	4000	7000	4000

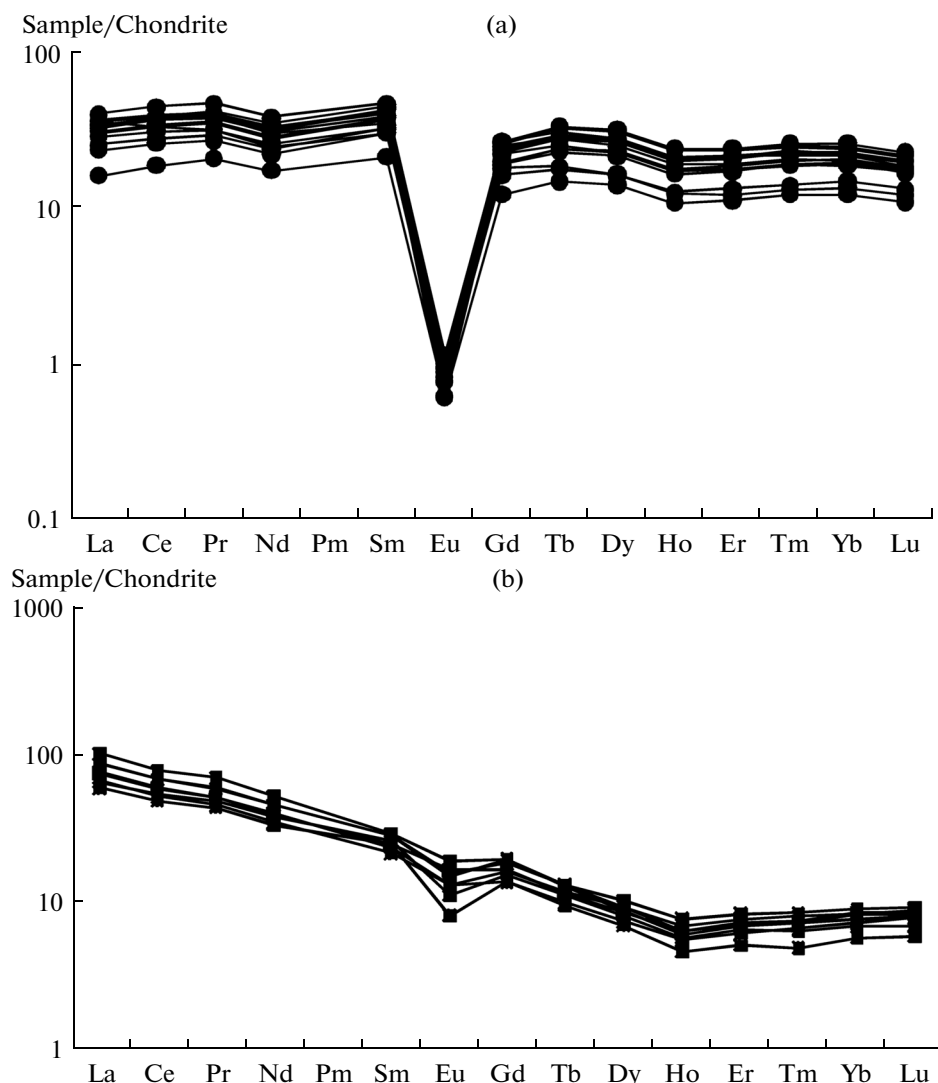


Fig. 2. Chondrite-normalized REE patterns of wall-rocks from ore zone 62/50: (a) greisenized muscovite leucogranites of horizon VII and (b) hydrothermally altered metamorphosed sedimentary rocks of horizon III.

flowing water and opened, and the vials were recovered. The treatment of wolframite with hydrochloric acid resulted in the formation of a yellow tungsten oxide precipitate. The solution with precipitate was transferred into a polypropylene ampoule, and the volume was brought to 50 mL using 3% HNO_3 . In order to check the efficiency of cation dissolution, several wolframite samples were dissolved by the method used for rocks. In such a case, the material was completely dissolved. However, such solutions are unstable in time and have high tungsten contents. A comparison of the results of measurements showed that the REE concentrations are identical, and only Th was significantly entrained by the tungsten oxide precipitate.

The contents of REEs in fluid inclusions were determined by the water extract technique. A 0.5-g quartz sample (monomineralic fraction with a mean grain size of 0.05 mm) was ground in a dry agate mortar. The powdered sample was loaded into a quartz ampoule with

0.5 mL 0.01 M HCl. The solution was filtered to produce the first extract. The quartz powder was then twice treated with 5 mL of 0.01 M HCl, and the solution was filtered. The REEs were measured in the first and third extracts; and the concentrations of REEs in fluid inclusions were estimated from the difference between the two analyses (third extract was used as a background accounting for the possible contribution of the dissolution of possible mineral contaminants in quartz samples). The recalculation to the concentrations of components in fluids was performed using the abundance of water in quartz determined by the PMR method by Suschkevskaya et al. [10].

The REE contents shown in all diagrams were normalized to the CI chondrite composition [11].

The results of REE analysis in the rocks showed that metasomatic imprints did not obliterate the characteristic features of the REE distribution patterns of the host rocks of the ore body (Fig. 2). The REE patterns of the

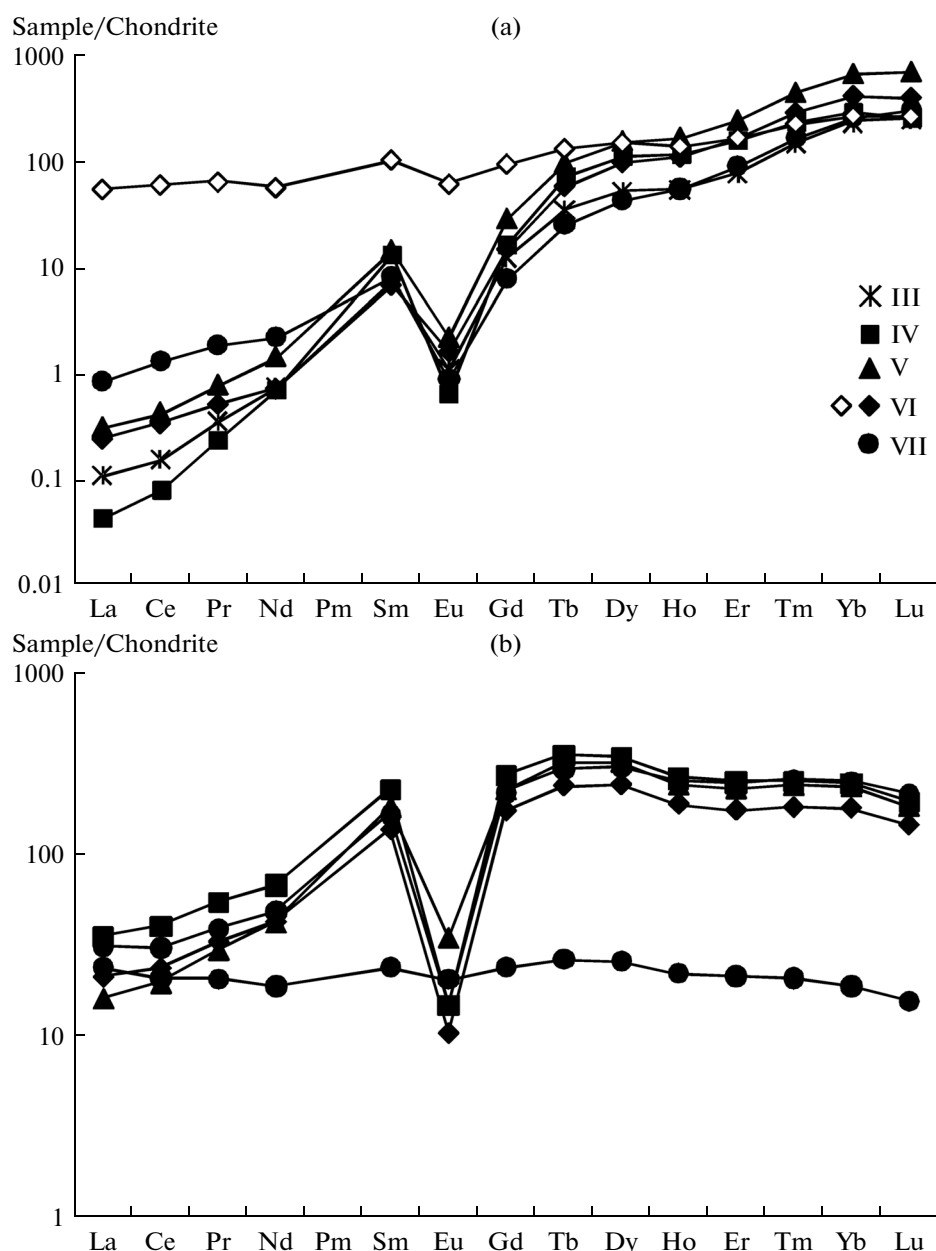


Fig. 3. Chondrite-normalized REE patterns of minerals from different horizons (III–VII): (a) wolframite (filled symbols) and scheelite (unfilled symbols) and (b) fluorite.

greisenized granites show a pronounced negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.03\text{--}0.04$), whereas only small or negligible Eu anomalies were observed in the metamorphosed sediments ($\text{Eu}/\text{Eu}^* = 0.45\text{--}0.82$). The rocks show different proportions of the light and heavy REEs. The same features were inherited by the fluids in equilibrium with the rocks and recorded in the composition of hydrothermal minerals.

The REE patterns of wolframites form a compact group and show a pronounced negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.03\text{--}0.05$, Fig. 3a). Their total REE content ranges from 122 to 356 ppm. The relative enrichment in the heavy REEs is explained by the higher par-

tition coefficients of these elements between wolframite and solutions compared with the light REEs (table).

Scheelite is a secondary mineral deposited from solutions strongly diluted by meteoric water. This is indicated by the REE patterns of scheelite, which show only a minor negative Eu anomaly (Fig. 3a). The high contents of REEs, especially light REEs, in scheelite (REE total is 380 ppm) is related to the high REE partition coefficients between scheelite and solution (table).

The REE patterns of fluorites indicate the presence of two fluorite generations in the mineralized zone (Fig. 3b).

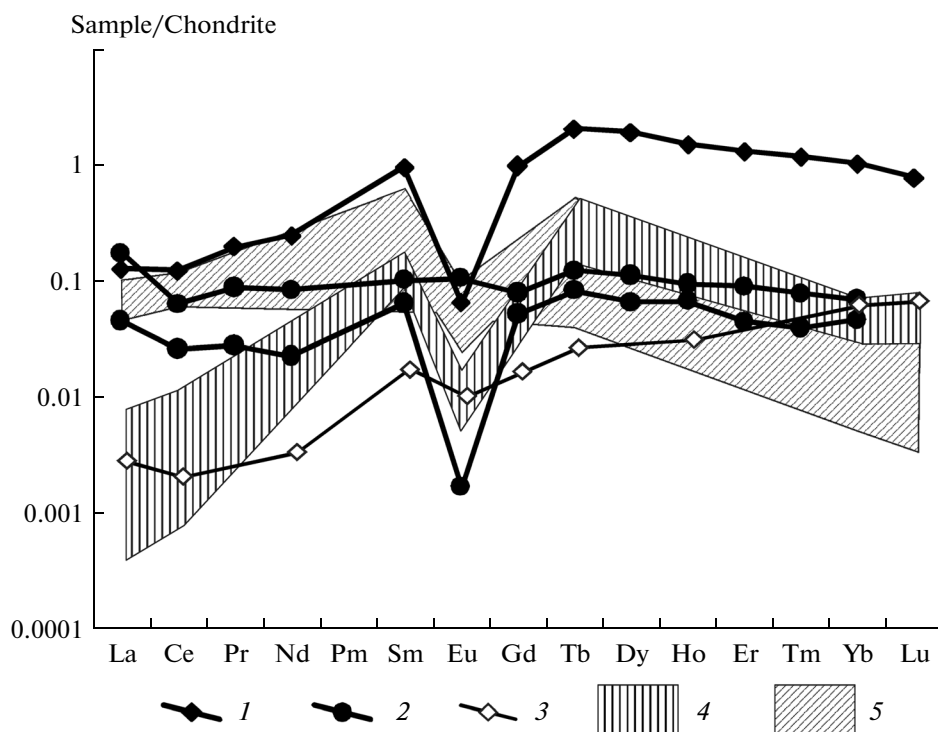


Fig. 4. Chondrite-normalized REE patterns of fluids estimated on the basis of the compositions of water extracts from quartz of (1) horizon VI and (2) horizon VII and calculated from the composition of (3) scheelite, (4) wolframite, and (5) fluorite.

An earlier generation is characterized by high REE total (371–560 ppm) and a significant negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.02\text{--}0.06$). The proportions of the light and heavy REEs are consistent with the fluorite–solution partition coefficients for REEs (table).

The late fluorite generation crystallized from solutions dominated by the exogenous component. This is indicated by low REE contents (84 ppm) and an almost negligible negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.28$).

No changes were observed in the behavior of REEs in the vertical section of the ore body. Perhaps, this is due to the fact that the main factor of ore deposition was the mixing of fluids of different origin [7], which is controlled by local hydrodynamic conditions.

The analysis of the water extracts of quartz also indicated the same two types of fluid that were established from the compositions of minerals (Fig. 4). These are magmatic fluid with a characteristic negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.03\text{--}0.07$) and enrichment in Sm, Gd, Tb, and Dy, and exogenous fluid without any significant negative Eu anomaly. The high scatter of data for the water extracts can be attributed to the uncertainty of the determination of water content in quartz.

A comparison of the REE patterns of solutions from fluid inclusions with the compositions calculated from wolframite and fluorite compositions reveals similar features: the REE contents are of the same order of magnitude, and the magnitudes of negative Eu anomaly

are also similar. The differences between fluid compositions calculated from the wolframite and fluorite compositions can be explained by the evolution of solution related to mineral crystallization.

The obtained results suggest that wolframite and fluorite were deposited during the ore-forming stage from fluids dominated by the magmatic component. At the final stage, the solutions were dominated by the exogenous component recorded in the compositions of fluorite and scheelite.

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