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GEOCHEMISTRY

REE Behavior in Tin-Bearing Hydrothermal-Magmatic Systems (An Example of Deposits of the Far East)*

Corresponding Member of the RAS **N. S. Bortnikov**[a],
N. V. Gorelikova[a], **and P. G. Korostelev**[b]

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REE behavior in hydrothermal-magmatic systems has been imperfectly understood [1–9], although these data could play a crucial role in understanding mineralizing processes. The study of the REE fractionation processes in hydrothermal media holds the great interest in the comprehension of a fluid evolution during the mineral formation and could give important information to reveal fluid sources and its physicochemical parameters. The research of factors controlling REE distribution in the fluid/mineral system is one of the prime problems in estimating the media parameters. An investigation of REE in minerals of tin-bearing hydrothermal-magmatic systems of the Far East has been conducted to compensate for this gap.

We examined minerals of tin-bearing assemblages (tourmaline, chlorite, fluorite, apatite, feldspar, biotite, and carbonate) from cassiterite–silicate–sulfide deposits of the Amur and Primorye regions, as well as from tourmaline granites, pegmatites, greisens, and skarns. Tin deposits of the Far East associate with multiphase series of granitoids of higher basicity from gabbros to leucocratic granites. They are located at a considerable distance from these plutonic bodies. Cassiterite–silicate–sulfide ore-magmatic systems studied are placed within the Sikhote-Alin accretionary fold system and are confined to the structures of active continental paleomargins. They evolved from the Cretaceous to the Paleocene through repeated alternation of settings of suprasubduction (Andean) and transform (Californian) continental margins [10]. The isotope and geochemical data attest that the sources of tin-bearing magmatism and mineralizing fluids within this region have a heterogenic origin and are connected, on one hand, with the injection of asthenosphere diapirs into fractures of subducted lithosphere and, on the other hand, with the subduction processes. The ore bodies are stockworks, metasomatic mineralized zones, and open-space filling veins. Silicate minerals tourmaline and chlorite are dominant in these deposits. They are associated with cassiterite, quartz, sericite, and sulfides of Fe, Cu, Pb, Zn, Mo, As, and other elements. The cassiterite–tourmaline ores are typical of tin veins of the Komsomol'sk ore region (Priamurye), while chlorite is a principal mineral in most commercial tin deposits of the Primorye region.

To investigate REE geochemistry, we selected minerals formed at various stages of mineralization characterized by distinct physicochemical parameters. In these tin hydrothermal-magmatic systems, tourmaline and chlorite have a long-term history of crystallization fixing in its composition the evolution of the fluid regime. Besides tourmaline and chlorite, associated minerals (feldspar, biotite, apatite, fluorite, and carbonates) are analyzed. The work presents various tin-bearing assemblages with tourmaline and chlorite, such as granites, pegmatites, greisens, tin-bearing skarns, quartz–feldspar and cassiterite–quartz veins from deposits of the Komsomol'sk (Solnechnoe, Pereval'noe, Festival'noe, Chalbinskoe) and Badzhal (Pravo-Urmi) areas of the Priamurye. A series of deposits of the Primorye region (Vysokogorskoe, Nizhnee, Luchistoe, Dubrovskoe, Arsen'evskoe, Khrustal'noe, Silinskoe, Verkhnee Tsinkovoe, and Levistskoe) are also examined. To elucidate the role of the crystallochemical factor over REE distribution in the mineral structure, tourmalins of various compositions (elbaite, dravite, Ca-bearing dravite, and schorlite) were analyzed. Tourmaline from pegmatite schlieren of Choldamy tuffs, aplites of Araratsky massif, and greisens of the Mo-bearing stage from the Solnechnoe deposit were found to be Fe-rich shorl, whereas Fe–Mg shorl-dravite and dravite are typical of the productive stage of tin deposits.

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[a] *Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences (IGEM), Staromonetnyi per. 35, Moscow, 119017 Russia; e-mail: ngor@igem.ru*

[b] *Far East Geological Institute, Far East Division, Russian Academy of Sciences, pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia*

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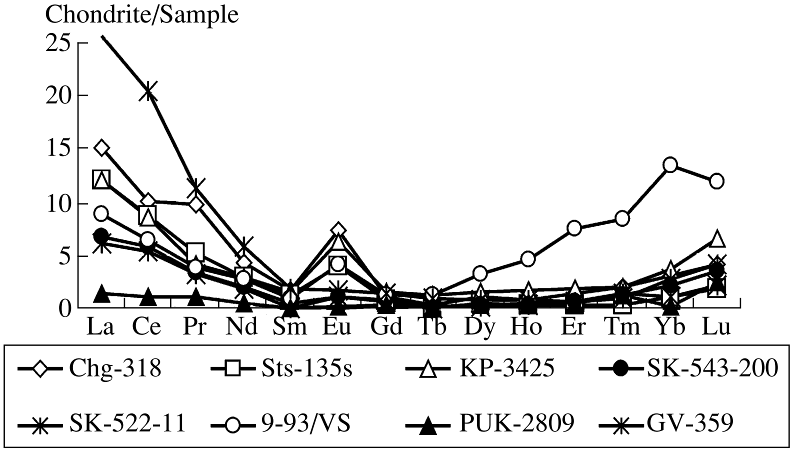

Fig. 1. Chondrite-normalized REE_n patterns in tourmalines from tin-bearing associations of the Far East. (Chg-318) Schlieren with mica in tuffs; (Sts-135s) schlieren in diorites; (KP-3425) Mo-bearing greisens; (SK-543-200) Solnechnoe deposit; (9-93/VS) Vysokogorskoe deposit; (PUK-2809) greisens of the Pravo-Urmi deposit; (GV-33) aplites from the Ararat massif.

Tourmaline, a mineral-chameleon, is found to be a widespread polygenetic mineral forming at endogenic deposits of Sn, W, Mo, Au, and other rare metal ores. At tin-bearing deposits, it represents a "through" mineral and forms over a wide range of physicochemical conditions including magmatic, greisen, and more late hydrothermal stages, which conditioned a marked typomorphism of the mineral reflected in the composition of the main components and in the trace element associations. The REE composition is among typochemical signs of the mineral of vital importance. REE distribution in minerals gives important information for understanding the geological processes and fluid sources that produced the ore deposits.

Thirty samples of tourmalines, 40 samples of chlorites, and about 15 associated minerals have been analyzed (IGEM). Feldspar, fluorite, biotite, and chlorite were decomposed using a standard procedure. A special procedure was used to analyze tourmaline. Fifty mg of mineral powders were decomposed by a mixture of H_2SO_4 + HF acids in a Milestone microwave using four-stage program "Turmalin." The solution after decomposition was evaporated to remove HF and H_2SO_4. A dry remnant was twice evaporated by H_2O to remove F ion. Then 10 ml 26% HNO_3 was filled into measured retorts, an inner standard was added, and the measurement of REE abundances was conducted by an ICP mass spectrometer (PQ2 Instruments, England).

Analysis of REE data obtained in tourmalines from granites, pegmatites, greisens, tin-bearing skarns, and quartz–feldspar and cassiterite–quartz veins was found to be different in terms of both the total REE abundances and the chondrite-normalizing REE_n pattern. The total REE abundances in this mineral vary from 267.14 to 0.28 ppm. LREEs dominate in tourmaline (La / Yb = 37.86–3.21), and most of the REE distribution patterns display a positive Eu anomaly (Figs. 1, 2). The basic part of samples has hump-shaped REE distribution patterns, and only a few of them (as a rule, with a low REE content) show a flat REE_n pattern. Some REE_n patterns for tourmaline show the noncoherent (non-CHARAC) REE behavior within tetrads La–Nd, Sm–Gd, Gd–Ho, and Er–Lu [11], which testifies to complexion processes of volatile components with some lanthanoids.

The study of REE distribution patterns in minerals of the greisen stage from the Solnechnoe deposit demonstrates the role of the crystallochemical factor for REE partitioning among minerals. It is clearly displayed in Ca-bearing minerals, such as apatite, feldspar, fluorite, and carbonate. Thus, apatite, plagioclase, and fluorite have a high REE content compared to coexisting biotite and orthoclase. However, in low-temperature Ca-bearing minerals, such as carbonate, the Ca ion does not positively influence entrance of REE into their structure and the total REE content is low.

Chlorites from cassiterite–chlorite veins are characterized by a high Fe content and a low oxidation degree of Fe based on the Mossbauer spectroscopy data. They are represented by prochlorite, ripidolite, and thuringite, while chlorites from the metasomatites differ considerably in a high Mg content and form pennine, clinochlore, and diabantite. The REE concentrations in the total REE abundances and in the chondrite-normalized patterns range widely in chlorites from various mineral assemblages (from 55.03 to 1.73 ppm). All samples are rich in LREE (La / Yb = 48.28 – 1.1). Most of the REE distribution patterns display positive Eu anomalies, but some show negative Eu anomalies (Figs. 3, 4). The chlorites can be divided into three different subgroups according to their REE patterns. The first two groups have a hump-shaped REE pattern. The third one is characterized by a flat type. As a rule, the large positive and negative Eu anomalies are common to chlorites with high REE abundances, while samples having a low REE content are accompanied by a flat shape type. To understand the factors affecting the

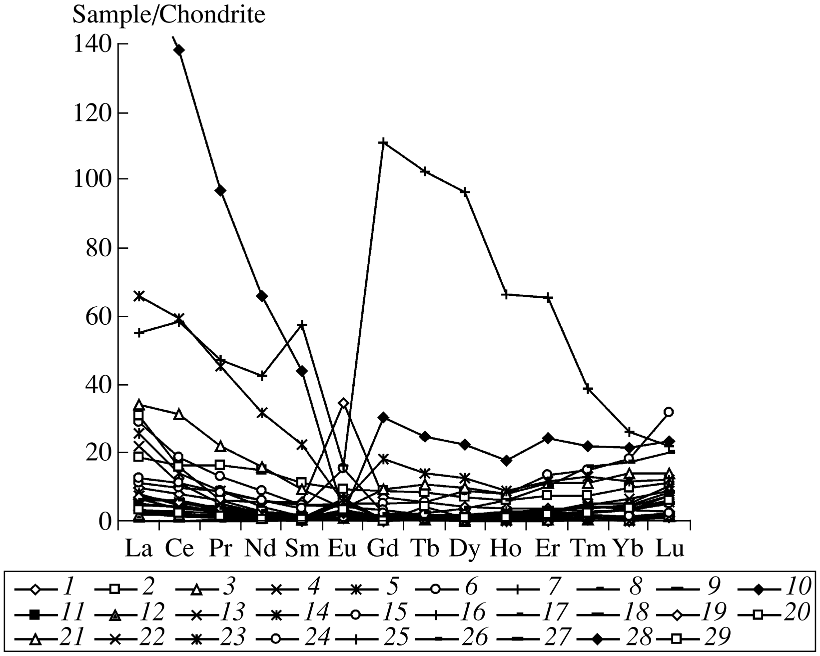

Fig. 2. Chondrite-normalized REE_n patterns in tourmalines from various tin-bearing assemblages. (*1*) Quartz–cassiterite–tourmaline vein; (*2*) fluorite–quartz–carbonate vein; (*3*) albite–tourmaline zone in granites; (*4*) quartz–tourmaline–muscovite greisen; (*5*) quartz–feldspar vein; (*6*) schlieren in granite; (*7*) quartz–tourmaline metasomatite; (*8*) rare metal pegmatite; (*9*) quartz-cassiterite ore; (*10*) quartz–feldspar–muscovite pegmatite; (*11*) quartz–tourmaline vein; (*12*) quartz–muscovite greisen; (*13*) quartz–sulfide ore; (*14*) quartz–feldspar greisen; (*15*) quartz-siderophylite greisen; (*16*) quartz–tourmaline vein; (*17*) Ca-dravite veinlet; (*18*) rare metal pegmatite; (*19*) tourmaline metasomatite; (*20*) monzodiorite; (*21*) schlieren in granite; (*22*) plagioclase–tremolite rock; (*23*) granite; (*24*) metamorphic rock; (*25*) tourmalinite after granite; (*26*) quartz–cassiterite vein; (*27*) quartz–tourmaline association; (*28*) tourmaline granite; (*29*) greisen.

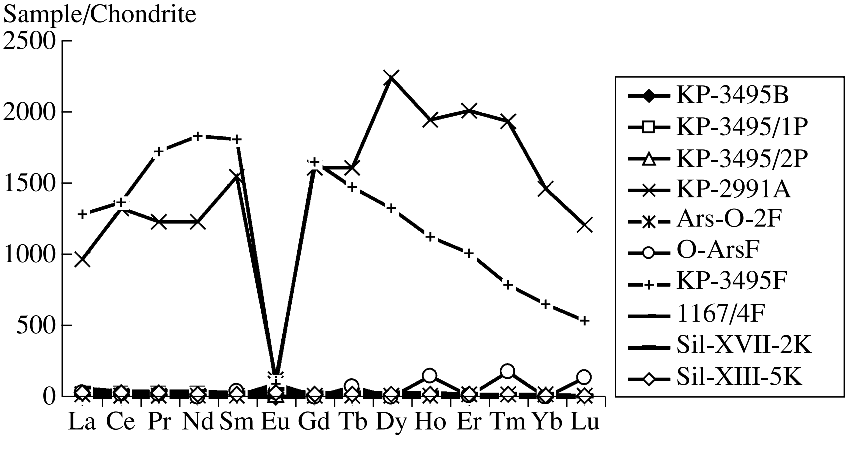

Fig. 3. Chondrite-normalized REE_n pattern in biotite (KP-3595B), apatite (KP-2991A), phlogopite (KP-3495F, Ars-O-2F, O-ArsF, 1167/4F), feldspar (KP-3495P), and carbonate (Sil-XVII-2K, Sil-XIII-5K) from tin deposits of the Far East.

shape of the chlorite REE distribution pattern, their crystallization temperatures were estimated using the homogenization temperature of fluid inclusions in associated quartz and the chlorite geothermometer [13] based on the Al_{IV}/Al_{VI} relation in the mineral structure. The crystallization temperatures of chlorites from tin deposits of the Priamurye and Primorye range from 220 up to 410°C. A clear dependence of the total REE abundance on the crystallization temperature was found. Thus, the high-temperature chlorites (370–390°C) from the contact zone of diorite of the deep horizons of the Solnechnoe, Arsen'evskoe, and Khrustal'noe deposits and chlorite formed after porphyrite dike from the Arsen'evskoe deposit have a high REE abundance. Chlorites from middle- and low-temperature ores are characterized by a lower REE content.

A comparative analysis of REE distribution in tourmalines and chlorites studied demonstrate a clear rela-

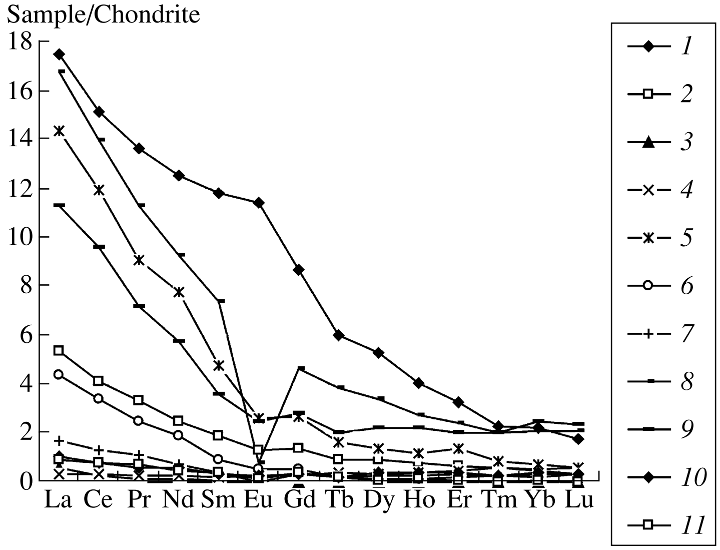

Fig. 4. Chondrite-normalized REE_n patterns in chlorites from tin deposits Arsen'evskoe (*1–4*), Nizhnee (*5*), Verkhne-Zinkovoe (*6*), Silinskoe (*7*), Solnechnoe (*8, 10*), Pereval'noe (*9*), and the Olimpiskaya zone of the Komsomol'sk region (*11*).

tionship between lanthanides abundances and the temperature, Eh, and pH of mineralizing fluids. Thus, high-temperature minerals from magmatic associations, pegmatites, skarns, and greisens of Mo-bearing stage formed at 700–550°C are quite rich in lanthanides, while REE abundances in minerals of the hydrothermal stage of tin deposits (the crystallization temperature is 380–320°C) are considerably reduced. This fact indicates that the temperature of mineral formation has the strongest influence on REE fractionation processes. Eu and Ce anomalies in REE_n patterns reflect the influence of Eh and pH of mineralizing medium on the REE fractionation processes [8]. The effect of medium alkalinity is observed in associations formed at various pH parameters of solutions. Thus, tourmalines from quartz–feldspar veins have considerably higher lanthanide abundances compared to tourmalines from quartz–muscovite greisens formed at low pH of the medium. The presence of positive and negative anomalies in REE_n patterns in tourmaline, chlorite, and other minerals from various mineralization stages of tin deposits testifies to an alteration of medium parameters over the ore process. Minerals of an early stage characterized by reduced conditions usually have a positive anomaly, which shows the presence of Eu^{2+} in solutions. Minerals of late stages formed at oxidizing conditions are characterized by Eu^{3+} predominance. The fractionation of Eu could be influenced by mixing of magmatic deep fluids with meteoric oxidizing waters [12], which is reflected on late assemblages of minerals and the break in the primary zonality of deposits. Fluid inclusion studies and mineral compositions of ores infer that the REE were transported either as fluoride, chloride, or boron complexes, or as a combination of three of them. A marked LREE enrichment of minerals implies that LREEs predominate in the coexisting fluid. The chemical bond of Cl-bearing LREE complexes is stronger than that of HREE complexes. Therefore, one can infer that REEs are predominantly migrating in the fluid as C1-bearing complexes.

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