

REE in fluid inclusions of quartz from gold deposits of north-eastern Russia

Research Article

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Abstract: Inductively coupled plasma-mass spectrometry (ICP-MS) has been used to determine rare earth element concentrations in aqueous solutions extracted from fluid inclusions. Quartz has been sampled from ores of three major types of polygenic gold hydrothermal systems of North-Eastern Russia: (1) gold-quartz-sulphide (Au-Q, Nezhdaninsk); (2) gold-antimony (Au-Sb, Sarylakh) and (3) intrusion-related gold-bismuth-siderite-polysulphide (Au-Bi-Sid, Arkachan) large deposits located in terrigenous rocks of the Verkhoyansk fold belt. The total concentration of REE in the fluid inclusions is not high (up to 52 ppm). The contribution of LREE dominates in REE balance ($\Sigma\text{LREE}/\Sigma\text{HREE}=7.4-112.1$). The chondrite-normalized REE patterns of inclusion fluids for the Au-Q and Au-Bi-Sid deposits are characterized by LREE enrichment with a positive or negative Eu anomaly. REE patterns for the regenerated quartz from Au-Sb deposits are characterized by pronounced differentiation between light and heavy lanthanides in fluid inclusions. Significant total REE concentration decreasing (on 1-2 order) from early to late stages of Nezhdaninsk and Arkachan deposits is revealed. The positive correlations of total REE concentrations with Rb, Cs, Li and B contents in fluid inclusions are shown. The REE distribution in fluid inclusions can be used as indicators of the contribution of magmatic fluid in the hydrothermal system.

Keywords: Fluid inclusion • rare earth elements • ICP-MS • gold deposits

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1. Introduction

The rare earth elements (REE) have similar chemical properties and behave coherently during geochemical processes. It is assumed that the REE distribution in rocks and minerals reflects the REE distribution in the ore-forming fluid. The REE characteristics of hydrothermal minerals are controlled by the composition of the fluid and physicochemical conditions during precipitation. Consequently, the REE patterns of hydrothermal minerals can

be used to estimate the sources and the physical-chemical properties of fluids. The REE composition of the fluid depends on the degree of fluid-rock interaction and abundance of complex species, such as HCO_3^- , CO_3^{2-} , Cl^- , and OH^- . Sorption processes and chemical complexation may largely influence the mobility of REE in hydrothermal fluids during fluid evolution.

The REE distribution in fluid inclusions in a mineral should characterize a fluid at the moment of formation of this mineral. Quartz is a widespread mineral on gold deposits; consequently, the REE distribution in fluid inclusions in the quartz can be used as an indicator of the ore-forming process.

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Some investigations have appeared in the last decades, but several factors made the REE analysis of fluid inclusions difficult. This is due to the inclusions being very small: inclusion matter is difficult to extract and the concentrations of REEs are usually low. Few methods are capable of REE analysis of fluid inclusions. Norman et al. [1] combined the crush-leach technique with instrumental neutron activation analysis to determine REE content in fluid inclusions. Salvi and Williams-Jones [2] and Kwak and Abeysinghe [3] used scanning electron microscopy with an energy dispersive x-ray system to determine REE content in the solid phases within fluid inclusions. The results are qualitative and fail to characterize the bulk REE pattern of the inclusion contents. Ghazi et al. [4] had demonstrated that the crush-leach method, followed by ICP-MS analysis of leachates, is effective for REE determination. Su et al. [5] proposed a new technique for extracting fluid from inclusions by a modified decrepitation-leach procedure, and then analyzing REE contents of inclusion fluids by ICP-MS. The modern method of LA-ICP-MS also has a number of restrictions.

Over the last decade, REE distribution in fluid inclusions has been studied for different types of deposits: greisen [6, 7], porphyry [1, 4, 8], gold orogenic [9–12], Karlin type [5], SEDEX [13] and others.

The purpose of the present paper is to study the REE distribution in fluid inclusions in quartz from the largest polygenic gold deposits of North-Eastern Russia. It is demonstrated that the REE distribution in fluid inclusions by ICP-MS analysis can be used as a geochemical indicator for these ore-forming systems.

2. Material and Methods

The objects of this study were three major types of polygenic gold hydrothermal systems of North-Eastern Russia: (1) gold-quartz-sulphide (Au-Q, Nezhdaninsk); (2) gold-antimony (Au-Sb, Sarylakh); and (3) gold-bismuth-siderite-polysulphide (Au-Bi-Sid, Arkachan). These large deposits are in terrigenous rocks of the Verkhoyansk fold belt (Fig. 1). Tectonic, igneous activity, geodynamic evolution and metallogeny of North-Eastern Russia are described in detail in [14, 15].

The Nezhdaninsk is a world-class mesothermal low-grade disseminated and lode deposit (470 t of Au) located in the zone of Minoro-Kiderik fault of the South-Verkhoyansk Fold Belt [17]. The ore field is composed of rocks belonging to the Verkhoyansk Complex, comprised of the Lower and Upper Permian sand-shale sequence that forms Dyba Anticline. The Kurum granite-granodiorite pluton (98 ± 2 Ma, zircon Pb-Pb, SHRIMP) is situated near the

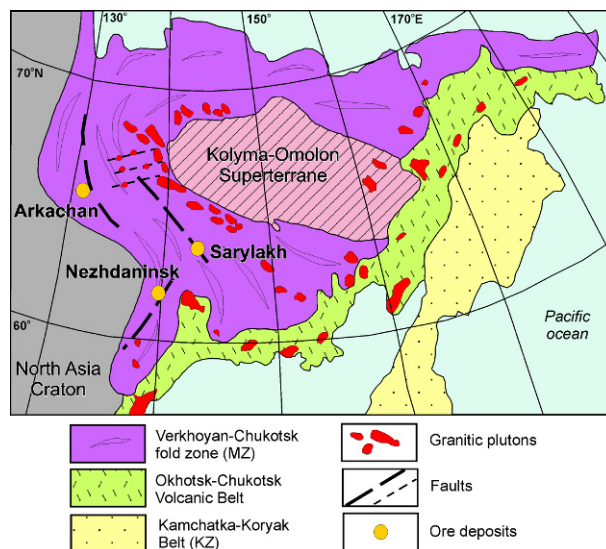


Figure 1. This is the location of the studied deposit on the tectonic map of North-Eastern Russia.

NNE periphery of the ore field. Dykes and veins of aplite-like granite, aplite, and pegmatite cross the contact zones of the pluton. Veinlets of semi-transparent quartz with Au-Mo-W-Bi mineralization are observed in the contact zones of the pluton. The Au-Mo-W-Bi veinlets are composed of the following mineral assemblages: molybdenite-(wolframite)-muscovite, quartz-pyrrhotite-loellingite-arsenopyrite, galena-sphalerite-chalcopryrite-scheelite, and gold-bismuthine-sulfotelluride-bismuth. Native gold (750–980) occurs as thin inclusions in loellingite together with pyrrhotite and native bismuth.

The Nezhdaninsky deposit is located in a tectono-magmatic zone up to 15 km long and 4 km wide. The deposit is composed of more than 50 ore bodies: mineralized brecciated zones, veins and vein zones. The mineralized brecciated zones are of sub-meridional orientation; the large thickness (up to 40 m), extent on trending (10 m), and on depth (2 km) are of major industrial importance. Three stages (Table 1) in the mineralization have been revealed [17, 18]. Numerous barren veins and veinlets of massive gray quartz with rather rare pyrite, chalcopryrite and galena were formed during an early hydrothermal-metamorphic stage. Coarse-grained milky-white quartz with ore mineral assemblages was formed during the main product Au-Q stage. Ore bodies of this stage are accompanied by a halo of beresitization with metasomatic gold-bearing pyrite (2–50 ppm Au) and arsenopyrite (20–710 ppm Au) [19]. The Ar-Ar age of the metasomatic mica was estimated as 119 Ma. Ore bodies are usually cross-cut by veinlets (up to 5 cm) of late quartz of Ag-Pb stage. Regenerated quartz often cements the fragments of early

milky-white quartz (Fig. 2a). The veinlets are combined by transparent quartz with numerous vugs with quartz crystals and a Ag-mineral assemblage. These mineral assemblages are similar to mineralization of Ag-Pb deposits of this area and age that was estimated as 95 ± 4 Ma.

The Sarylakh is the largest Au-Sb deposit in Russia. The reserves are estimated at 180 kt Sb and 40 t Au. The ore grades are 8 ppm Au and 20% Sb. The Sarylakh deposit is situated in the Taryn metallogenic zone of the East Yakutian post-accretionary metallogenic belt. The Upper Triassic sand-shale rocks deformed into an asymmetric anticline about 2 km wide which hosts the deposit. The SW limb of the anticline is complicated by the Adycha-Taryn regional fault consisting of two or three nearly parallel branches, the Ore Fault being the major one [20]. The plane of this fault dips to the NE (40° – 75°) at angles of 55° – 85° . Seven ore bodies are mineralized brecciated zones accompanied by quartz-pyrite-sericite metasomatic rocks (up to 100 m wide) and later dickite-pyrophyllite alteration near stibnite veins. Mineralized brecciated zones are 2 km along the strike; their thickness varies from 0.8 m to 17 m in bulges. Two stages of low-sulphide gold-quartz and stibnite mineralization are distinguished. Milky-white quartz is the main vein mineral. Ankerite is localized at vein selvages. Pyrite and arsenopyrite occur in quartz as non-uniformly distributed pockets of coarse-grained aggregates. Chalcopyrite-sphalerite-galena and fahlore-sulphoantimonite aggregates fill interstices between quartz grains. The sequence of formation of mineral assemblages is shown in Table 1. The stibnite veins intersect productive milky-white quartz veins, which are often brecciated (Fig. 2b). The recrystallization of the early massive milky-white quartz is accompanied by quartz redeposition as small (3–5 mm) druses in cavities of dissolution. Numerous small fragments of early quartz in fine-grained recrystallized stibnite are transformed into dipyratidal-prismatic crystals 1–2 mm in size. These transparent quartz crystals contain inclusions of stibnite, pyrite and arsenopyrite with Ni admixture, gold oxides, and hydroxides (Fig. 2d). The temporal interruption between two stages of mineral formation is of 30–40 Ma. Low-sulphide gold-quartz stage developed 115–120 Ma and stibnite mineralization occurred not older than 70–80 Ma. The shallow-seated stibnite mineralization was superposed by moderately deep gold-quartz mineralization in Sarylakh deposit.

The Arkachan gold deposit (100 t of Au) is located in the tin-bearing metallogenic zone of the Western part of the Mesozoic Verkhoysansk fold-thrust belt. The ore field consists of sandstones and siltstones of the Middle and Upper Carboniferous and Lower Permian. The deposit is situated in the core of the Kygyltas anticline fold. Granite-

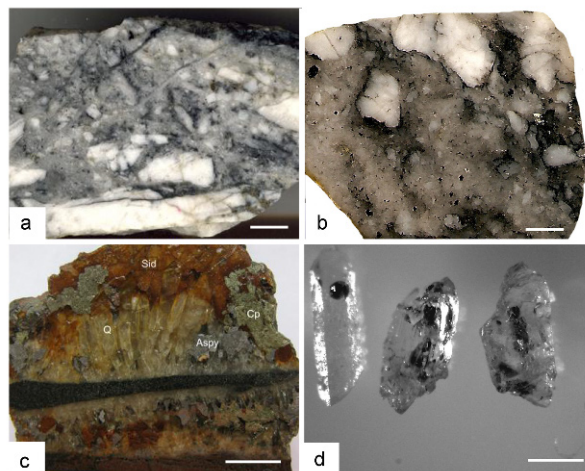


Figure 2. Relationships of minerals from auriferous quartz veins. a, b – fragments of milky-white quartz cemented by regenerated quartz (a – Nezhdaninsk, b – Sarylakh); c – quartz-siderite-polysulphide vein, Arkachan; d – crystals of regenerated quartz with inclusions of stibnite, pyrite, arsenopyrite (Sarylakh). Scale bar is 1 cm.

porphyry dykes (K_1) have been injected into the sedimentary sequence. An aeromagnetic anomaly shows that the non-exposed granite intrusion occurs beneath the deposit at 2 km depth. Few sub-parallel mineralization zones are controlled by NE-trending faults, dominating in this area. The similar fault zones control the localization of small magmatic intrusion and associated tin deposits [16, 21].

The gold mineralization zones consist of series of veinlets (“a linear ore stockwork”). Thickness of veinlets is commonly <5 cm (rarely 20–40 cm). Gold ore bodies are accompanied by halo of beresitization. Siderite is a major gangue mineral (10–30 vol. %). The sulphide minerals comprise 5 to 70 % of total vein volume (averages ~ 10 vol. %). Pyrite and arsenopyrite are the predominant sulphides (Fig 2c). Several mineral paragenetic assemblages have been recognized from the cross-cutting relations between mineral aggregates (see Table 1). The mineral fabrics suggest that usually minerals were crystallized in open spaces. Everywhere vein selvages are combined with the quartz-forming brush of small transparent crystals and druses. Inclusions of chalcopyrite and pyrrhotite are often observed in large transparent crystals of such quartz. Muscovite spherulites overgrow quartz crystals and then arsenopyrite-pyrrhotite aggregates overgrow on them. Later siderite often forms druses crystallized. The pyrrhotite precedes siderite or co-precipitates it. Pyrrhotite continues to deposit after siderite together with chalcopyrite and Bi-minerals. Bi-minerals are later minerals of ore vein: they crystallize in vugs and micro-fissures among earlier minerals. The

Table 1. Geological, mineralogical and geochemical characteristics of studied deposits.

Deposit	Nezhdaninsk	Sarylakh	Arkachan
Metallogenic zone	South-Verkhoyansk	Taryn (East-Yakutia)	West-Verkhoyansk
Ore controlled structure	Regional submeridional deep-seated fault (Minoro-Kiderik)	Regional north-west deep-seated fault (Adycha-Taryn)	Fault zone of north-east direction (Nyektominsk)
Host rocks	Sandstones, siltstones, shales (P)	Sandstones, siltstones, shales (T ₃)	Sandstones, siltstones, shales (C ₂₋₃ -P ₁)
Igneous complexes	Granitoid massif (κ 1-2); lamprophyre, gabbro-diorite dykes (J ₂ -K ₁) and stocks (K)	Dacite dykes and stocks (T ₃ - κ 1), andesite-basalt (K ₂ -P)	Intraplate granitoides dykes and stocks (K)
Geochemical type	Gold-silver-polymetallic	Gold-antimonic polygenic	Gold-bismuth-siderite-polysulphidic
Structure-mineral type	Mineralized brecciated zones, veins and vein zones	Mineralized brecciated zones, veins	Linear stockwork zones
Wallrock alteration	Berezitization	Berezitization	Berezitization
Main ore minerals	Py, Apy, Gn, Sp	Stb, Apy, Py	Apy, Py, Po
Minor ore minerals	Frb, Bng	Brt, Cst, Ast	Ccp, Bsm
Main vein minerals	Q, Dol, Ank, Ab	Q, Ank, Dol, Cal	Q, Sid, Ms
Average C _{Au} (Au reserves)	5 g/t (470 t)	8 g/t (40 t)	6 g/t (100 t)
Mineral stage (mineral assemblages)	1st. <i>Hydrothermal-metamorphic stage</i> (Q-Ank) 2st. <i>Au-Q stage</i> (Py-Apy-Q, Au-Ccp-Gn-Sp, Au-Tnt-Ttr-Sst, Brt-Stb-Ank) 3st. <i>Ag-Pb stage</i> (Gn-Sp-Frb-Prt, assemblages of regenerated minerals – Q, Au, Ag-Gn, As-Bng, Sid)	1st. <i>Hydrothermal-metamorphic stage</i> (Q-Ank) 2st. <i>Au-Q stage</i> (Py-Apy-Q, Au-Ccp-Gn-Sp, Au-Tnt-Ttr-Sst-Ank) 3st. <i>Sb stage</i> (Dck-Brt-Stb, assemblages of regenerated minerals – Q, Sid, Ni-Apy, Au, Aan).	1st. <i>Hydrothermal-metamorphic stage</i> (Q-Ank) 2st. <i>Au-Bi-Sid stage</i> (Q-Ms-Sch-Co-Apy-Py, Po-Sid-Ccp-Au-Bsm, Ank-Cal) 3st. <i>Ag-Pb stage</i> (Q-Gn-Sp-Frb-Prt)
Elements-impurity in Au	Fe, As, Pb, Sb, Cu, Hg	Sb, Fe, As, Cu	Sn, Cu, Bi, As
Fineness of native gold	2st. 750-900 3st. 560-720	2st. 885-950 3st. 965-1000	2st. 780-920
Oxygen isotope composition of vein quartz ($\delta^{18}\text{O}$, ‰)	1st. +15.4...+16.1 2st. +13.8...+16.5 3st. +13.5...+16.9	1st. no data 2st. +14.8...+17.0 3st. +16.5	1st. +15.6±0.2 2st. +13.6...+16.3 3st. +8.9...+9.4
Oxygen isotope composition of fluid co-existing with quartz ($\delta^{18}\text{O}$, ‰)	1st. +8.5...+9.2 (300°) 2st. +7.6...+10.4 (320°) 3st. +5.1...+8.5 (260°)	1st. no data 2st. +7.9...+10.1 (300°) 3st. +4.9 (200°)	1st. +8.5...+8.9 (300°) 2st. +6.7...+9.4 3st. +2.0...+2.5
PT conditions (°C, kbar)	2st. 368-267; 2.0-0.7 3st. 387-129; 1.9-0.8	2st. 318-253; 3.4-1.2 3st. 244-189; 2.0-0.3	2st. 385-279; 1.8-1.1 3st. 324-261

Ab – albite, Ank – ankerite, Apy – arsenopyrite, Aan – auroantimonates, Ast – aurostibite, Brt – berthierite, Bsm – bismuthine, Bng – boulangerite, Cal – calcite, Ccp – chalcopryrite, Cst – chalcostibite, Dck – dickite, Dol – dolomite, Frb – freibergite, Gn – galena, Ms – muscovite, Au – native gold, Prt – pyrargyrite, Py – pyrite, Po – pyrrhotite, Q – quartz, Sch – scheelite, Sid – siderite, Sp – sphalerite, Stb – stibnite, Sst – sulfostibnite, Tnt-Ttr – tennantite-tetrahedrite.

ankerite and minor calcite finish the process of mineral formation. The last mineralization is presented by Ag-Pb veins and veinlets (see Table 1).

Samples for REE analyses in this study include: quartz from productive Au-Q and Au-Bi-Sid stages; regenerated quartz from Ag-Pb and Sb stages; and quartz from Au-Mo-W-Bi mineralization of Kurum massif. 20 samples have been studied (Table 2).

The unified technique of the bulk analysis of chemical composition [22] was developed in the isotope laboratory of the Central Institute of Geological Exploration for Base and Precious Metals of Moscow, Russia (TsNIGRI). The technique includes a complex of high-sensitivity methods: gas and ionic chromatography and ICP-MS. This complex of methods allows determination of a wide spectrum of components in the fluid phase included in small quantity

Table 2. Vein petrography and mineralization of studied samples.

Sample	Description	Location
	Nezdaninsk deposit <i>Au-Q stage</i>	
N1	Quartz vein with large pockets of arsenopyrite, scheelite, sphalerite	Ore zone 3, +700 m
N2	Quartz vein	Ore zone 1, +50 m
N3	Lens (0.05×1 m) of macrocrystalline semi-transparent quartz in stockwork zone	Ore zone 1
	<i>Ag-Pb stage</i>	
N4	Vein zone (2.5 m) of glassy quartz	Ore zone 1, +1200 m
N5	Veinlets and pockets of transparent quartz crystal in vein (1 m) of milky- white quartz	Ore zone 1, +700 m
	<i>Au-Mo-W-Bi mineralization</i>	
N6	Macrocrystalline transparent quartz in aplite among hornfels	Kurum massif
N7	Quartz-pyrrhotite vein (30 cm) with chalcopyrite. Pockets of sulfides (5×2 cm) occur in the central part of the vein.	Kurum massif
	Sarylakh deposit <i>Au-Q stage</i>	
S1	Milky-white drusy quartz	Ore zone 4
S2	Milky-white drusy quartz	Ore zone 1, + 840 m
S3	Milky-white drusy quartz	Ore zone 1, +730 m
S4	Milky-white quartz sometimes semi-transparent	Ore zone 1, +680 m
S5	Milky-white quartz	Ore zone 1, +530 m
S6	Milky-white drusy quartz with needles of stibnite and carbonates in vughs	Ore zone 1, +200 m
	<i>Sb stage</i>	
S7	Crystals of transparent quartz in medium-crystalline stibnite	Ore zone 1, surface
S8	Crystals of transparent quartz in medium-crystalline stibnite	Ore zone 1, +730 m
	Arkachan deposit <i>Au-Bi-Sid stage</i>	
A1	Quartz-siderite veinlet with pockets of sulphides	Ore zone 3, +1150 m
A2	Quartz veinlet (2 cm) with rare pockets of carbonates	Ore zone 4, +1050 m
A3	Drusy quartz veinlet with chalcopyrite, arsenopyrite	Ore zone 4+ 1250 m
A4	Veinlet of semi-transparent quartz	Ore zone 4, +1050 m
	<i>Ag-Pb stage</i>	
A5	Quartz-siderite veinlet with quartz druses	Ore zone 2

of quartz (0.5–1.0 g). The small weight of the probe allows for selection for the analysis of the quartz grains of one generation, containing mainly one type of fluid inclusions. Such an approach pulls together the bulk analysis of contents of fluid inclusions with the analysis of individual fluid inclusions. It provides reliability of genetic interpretation of the obtained data and gives a possibility of data securing, independent of the sizes of fluid inclusions.

Quartz samples with one prevailing type of fluid inclusions have been used for the ICP-MS analyses. Petrographic and micro-thermometric studies have been carried out for this purpose in IGEM RAS by V.Yu. Prokofiev. Fluid inclusion micro-thermometry was performed on a Linkam THMSG-600 heating-freezing stage attached to an Amplival microscope (Germany) and a monitoring video apparatus. Samples were rapidly cooled to about -180°C to de-

tect the possible occurrence of clathrate, ice, salt hydrates and carbonic solid phase. Upon progressive heating, up to seven phase transitions were observed in the inclusions, namely eutectic melting (T_e), melting of the carbonic phase ($T_{m(CO_2)}$), melting of the ice ($T_{m(ice)}$), clathrate melting ($T_{m(clathrate)}$), homogenization of the carbonic phase ($T_{h(CO_2)}$), melting of the solid phase ($T_{m(solid)}$), mainly halite, and total homogenization (T_h). The bulk salinity of the fluid was calculated from the $T_{m(ice)}$ or $T_{m(solid)}$ [23], or from the combination of $T_{h(CO_2)}$ and $T_{m(clathrate)}$ [24]. The identification of the anion and cation species in solution was determined from eutectic temperatures [25]. The pressure of the heterogeneous fluid was estimated from petrographically associated vapor- and liquid-rich inclusions as the sum of the partial pressures of water vapor and CO_2 [26].

Quantitative chemical analyses of the inclusion fluid composition were carried out at the TsNIGRI (analyst Y.V. Vasyuta), using the technique reported by Kryazhev et al. [22]. This is a standard technique that includes three operations: cleaning of the sample, opening of the fluid inclusions, and element determination. The analyzed samples were 0.5– to 1.0-g aliquots of milled quartz (0.25– to 0.5-mm sieved fraction), which were cleaned using a concentrated (50 vol. %) HNO_3 solution and electrolytic streaming of H_2O . Additional cleaning was achieved with ultrasonic cleaners. Before analysis, samples were dried and then placed in a single-shot reactor that was filled with helium and preheated at 110°C . Subsequent heating to 400°C and milling with corundum beads (at temperatures of about 120°C) allowed the complete opening of the inclusions. The extracted gas phase was analyzed using a Tsvet-100 gas chromatograph to determine the concentration of water, CO_2 , methane, and other gases possibly present. The residual liquid phase was analyzed by ion chromatography (Tsvet-3006, for determination of Cl^- , F^- , SO_4^{2-} , and NO_3^- , sensitivity 0.01 mg/l) and ICP-MS (Elan-6100) after centrifugation and addition of 7 ml of ultrapure deionized water. Concentration of HCO_3^- has been calculated based on the balance of cations and anion in the solution. Thus, gases, salts, and the aqueous solvent were extracted simultaneously from a fluid inclusion during analysis, enabling the reliable calculation of component concentrations in solutions. Minimization of the number of analytical procedures diminished the probability of sample contamination in the course of analysis. Standardization of the process ensured the maximum compensation of errors and increased the reliability of determination of the specific composition of each sample. The data on blank extracts were subtracted from the results obtained. The remaining useful signal is related to the contents of fluid inclusions with a high probability. Therefore, it may be assumed that the results of bulk analyses reflect the total concentrations of elements in the solutions that fill fluid inclusions. Measurements by ion chromatography are accurate to within about 5 percent, whereas those carried out by ICP-MS show an accuracy that varies from 0.5 to 2 percent. Our study is devoted to the distribution of REE identified in aqueous solutions extracted from fluid inclusions. Detection limits range from 0.00n to 0.000n microgram per liter ($\mu\text{g/l}$).

Additionally the bulk REE content in quartz from the Arkachan deposit was determined by ICP-MS (Elan DRC II PerkinElmer, USA) after acid decomposition in a microwave field. The analysis has been carried out at the Laboratory of physical and chemical methods of investigation, Institute of Tectonics and Geophysics, Far Eastern

Branch of Russian Academy of Sciences, Khabarovsk (analyst N.V. Berdnikov).

3. Results

3.1. Fluid inclusion petrography and microthermometry

Doubly polished sections were prepared for the fluid inclusion study, including petrography and microthermometry. Fluid inclusion observations were made for quartz of different types in each deposit. Fluid inclusions can be divided into three types: (I) mixed $\text{CO}_2\text{--H}_2\text{O}$ inclusions ($\text{CO}_{2\text{L}} + \text{H}_2\text{O}_\text{L} \pm \text{CO}_{2\text{V}}$); (II) CO_2 -rich or pure CO_2 inclusions ($\text{CO}_{2\text{L}} \pm \text{CO}_{2\text{V}}$, $\text{H}_2\text{O}_\text{L}$, CH_4 , N_2), and (III) aqueous inclusions ($\text{H}_2\text{O}_\text{L} + \text{H}_2\text{O}_\text{V}$). Three-phase inclusions with a liquid aqueous solution, a gas bubble, and an isotropic cubic crystal ($\text{H}_2\text{O}_\text{V} + \text{H}_2\text{O}_\text{L} + \text{NaCl}$), identified as halite, are abundant in quartz from Au–Mo–W veins. The results of thermo- and cryometric measurements of fluid inclusions in quartz are presented in detail in [17, 20, 21] and are summarized in Table 3. The primary inclusions are predominant both in number and in volume over the secondary inclusions, so the leachate is proposed to be dominated by the primary fluid. Quartz samples with prevailing type I fluid inclusions have been chosen for the ICP-MS analysis. The fluid inclusions in these samples have been very slightly disturbed by post-depositional events. The samples investigated originate from geologically distinct positions within the deposits (see Table 3).

3.2. REE distribution in fluid inclusions

The contents of the rare-earth elements in quartz fluid inclusions of the studied deposits are summarized in Table 4. The concentrations of the light REE (LREE) and middle REE (MREE), in general, are above the detection limits. However, the concentrations of the heavy REE (HREE), especially Tm, are close to the detection limit.

The total concentration of REE in the fluid inclusions is not high (0.7–52 ppm), however it is different for studied deposits and for different stages of each deposit (Fig. 3). Lower concentrations occur in samples from the Arkachan deposit. The REEs are below the detection limit in early milky-white quartz from the Sarylakh deposit.

The contribution of LREE dominates in REE balance. HREE are below detection limits in quartz fluid inclusions from the Arkachan deposit, from Au–Mo–W–Bi mineralization of the Nezhdaninsk deposit and from the early stage of the Sarylakh deposit. The contributions of LREE and HREE are slightly decreased and the contribution of

Table 3. Summary of fluid inclusion data after [17, 20, 21].

Stage	Inclusion type(1)	n ⁽²⁾	T _h , °C	T _e , °C	T _{m(lce)} , °C	T _{m(CO₂)} , °C	T _{h(CO₂)} , °C ⁽³⁾	T _{m(clathrate)} , °C	C _{salt} , wt % NaCl equiv	CCO ₂ mol/kg solution	C _{CH₄} mol/kg solution	ρ, g/cm ³	p, bar
Nezhdaninsk													
Au-Q	I, P	171	344–280	–39...–22	–8.9...–2.9	–58.2...–57.1	24.6...30.6 L 24.7...28.1 V	7.2–9.6	0.8–8.3	5.3–2.8	0.5–1.0	0.86–1.08	1870–670
	II, P	256				–64.8...–57.2	–97.6...30.6 L					0.40–0.97	
	III, P	16	283–267	–34	–2.8				4.7			0.79–0.82	850–810
Ag-Pb	I, P	35	387–249	–36...–31	–6.2...–3.1	–59.2...–57.7	23.6...30.7 L 28.2 V	7.8–10.0	2.8–7.9	1.9–4.0	0.5–1.1	0.85–0.96	1680–490
	II, P	89				–60.5...–58.1	13.5...28.7 L					0.79–0.40	
	III, S		241–129	–38...–21	–5.5...–1.4				2.4–8.6			0.88–0.95	
Sarylakh													
Au-Q	I, P	70	318–253	–39...–31	–6.4...–3.0	–57.7...–56.6	–1.2...27.4 L	11.5–7.4	6.8–1.6	6.9–3.4	1.0–0.6	1.06–0.93	3420–1160
	II, P	83				–59.1...–56.8	–23.2...24.7 L					1.05–0.72	
	III, S	27	230–169	–29...–21	–4.0...–1.5				6.5–2.2			0.92–0.89	
Sb	I, P	9	244	–31	–4.4...	–60.3	6.0 V	10.9	6.3	2.3	1.3	0.80	2020–1260
	II, P	30				–61.3...–58.1	–149 V (N ₂) –21.9...17.2 L					0.19	
	III, S	10	189	–34	–1.9				3.2			0.95–0.80	
Arkachan													
Au-Bi-Sid	I, P	101	385–279	–49...–31	–25.2...–16.3	–56.6...–58.8	25.4...29.0 V	–10.2–4.2	18.8–26.3	3.6–1.3	0.5–0.1	0.84–1.07	1830–1060
	II, P	79				–56.9...–59.7	16.5...29.5 L					0.62–0.85	
	III, P	30	324–261	–46...–32	–2.2...–5.8				3.7–9.0			0.70–0.86	
	III, S	36	200–269	–53...–41	–16.4				19.8–22.6			0.97–1.03	

(1) – inclusion type: I – CO_{2L} + H₂O_L ± CO_{2V}; II – CO_{2L} ± CO_{2V}; H₂O_L, CH₄, N₂; III – H₂O_L + H₂O_V; P – primary and S – secondary inclusions.

(2) – number of inclusions.

(3) – homogeneous mode of CO₂: L – Liquid, V – Vapor.

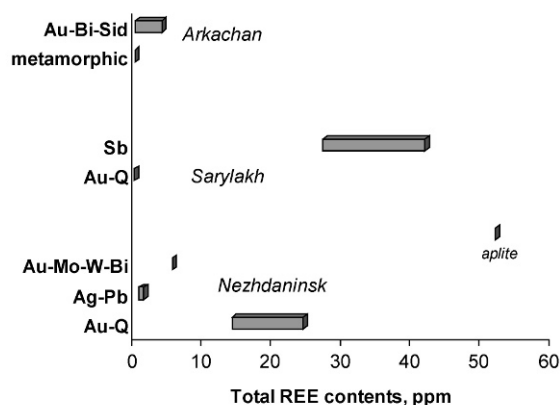


Figure 3. The total REE contents in quartz fluid inclusions for different types of deposits.

MREE is increased at the late stage of hydrothermal process on the Nezhdaninsk deposit. Cerium is the dominant LREE followed by La and Nd, except that La dominates in quartz fluid inclusions from the Au-Sb deposit. Differentiation between LREE is the most pronounced for the Au-Sb deposit.

The REE geochemistry of fluid inclusions in quartz from the early Au-Q stage of the Nezhdaninsk deposit is characterized by a relatively uniform chondrite-normalized (after [27]) REE-pattern, with variable ΣREE (14.1 to 24.3 ppm), significant LREE enrichment ($\text{La}_n/\text{Yb}_n = 11$ to 25, $\Sigma\text{LREE}/\Sigma\text{HREE} = \Sigma(\text{La}-\text{Eu})/\Sigma(\text{Gd}-\text{Lu}) = 14$ to 26), and negligible Ce-anomalies ($\text{Ce}/\text{Ce}^* = 1.1$) except for sample N3 that has a very large negative Ce anomaly ($\text{Ce}/\text{Ce}^* = 0.07$). The late regenerated quartz has low total REE contents (0.7 to 1.4 ppm). LREE enrichment remains ($\text{La}_n/\text{Yb}_n = 25.14$); no Eu anomalies were detected. An insignificant negative Ce anomaly was revealed in this quartz ($\text{Ce}/\text{Ce}^* = 0.7$ to 0.8). The highest REE contents were detected in quartz from aplite of the Kurum massif (51.9 ppm). The REE content in quartz coexisting with Au-Mo-W-Bi mineralization of the Kurum massif is much lower (5.5 ppm) (Table 4).

Fluid inclusions in quartz from the Arkachan deposit are characterized by a low REE total content (1 to 4 ppm), enriched in LREE ($\Sigma\text{LREE}/\Sigma\text{HREE} = 7.4$ to 35.5), marked by a negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.31$), and demonstrate the slightly positive Ce-anomalies ($\text{Ce}/\text{Ce}^* = 0.83$ –1.35) as shown in Table 4. Fluid inclusions from quartz coexisting with late Ag-Pb assemblage contain only $\text{La} = 0.06$ ppm and $\text{Ce} = 0.16$ ppm.

Thus, the decrease of total REE concentration in fluid inclusions from early to late quartz for the Nezhdaninsk

and Arkachan deposits is revealed. The opposite tendency is observed on the Sarylakh deposit.

Fluid inclusions in early milky-white quartz from Sarylakh deposit (6 samples) do not contain REE, whereas total REE concentrations in fluid inclusions in the late quartz coexisting with stibnite mineralization are considerable (27.1 to 41.8 ppm). The highest $\Sigma\text{LREE}/\Sigma\text{HREE} = 58$ to 112 was estimated in the late quartz. A very large negative Ce anomaly ($\text{Ce}/\text{Ce}^* = 0.14$) is revealed.

The chondrite-normalized REE patterns of inclusion fluids for the Nezhdaninsk and Arkachan deposits are characterized by LREE enrichment with a positive or negative Eu anomaly, whereas the patterns for the regenerated quartz from Sarylakh deposit are characterized by pronounced differentiation between light and heavy lanthanides in fluid inclusions (Fig. 4).

In four samples from the Arkachan deposit REE concentrations have been estimated by ICP-MS in both bulk quartz and in aqueous solutions extracted from quartz fluid inclusions. Results are shown in Fig. 5. REE concentrations in fluid inclusions are always lower than these in bulk quartz samples. In metamorphic quartz the contents of REE in fluid inclusions are close to the limit of detection whereas in productive quartz their concentrations are sometimes comparable.

4. Discussion

All studied polygenic gold deposits (Nezhdaninsk, Sarylakh and Arkachan) were formed as a result of a complicated fluid evolution. Long functioning of large hydrothermal systems involves fluids from different sources. Earlier complex investigations of these deposits [17, 20, 21] have shown the wide variations of ore formation parameters and heterogenic nature of ore-forming fluid. At the early stages the $\text{H}_2\text{O}-\text{CO}_2-\text{CH}_4-\text{H}_2\text{S}-\text{NaCl}$ fluid of various salinity arrived in an ore-forming system. The maximum salinity was observed for the Arkachan hydrothermal system, having the features of intrusion-related gold deposits. This fluid underwent the phase separation into substantially aqueous-carbon dioxide fluid and the gaseous fluid consisting mainly of CO_2 . In the course of the phase separation, such volatile components as CO_2 , CH_4 , H_2S , H_2 , and NH_3 escaped, leading to oxidation and pH increasing of the residual aqueous-carbon dioxide fluid. The relationship of stable oxygen, carbon and sulfur isotopes in the mineralizing fluid has shown that water, carbonic acid and sulfur in its composition had both metamorphogenic and magmatic origin. Contributions of matter from magmatic and metamorphogenic sources vary for each system. At the late stages meteoric waters were

Table 4. Concentrations of REE in the quartz fluid inclusions on the base of ICP-MS analysis of aqueous extracts (ppm).

Deposit	Nezhdaninsk						Sarylakh		Arkachan				
Stage	Au-Q			Ag-Pb		Au-Mo-W-Bi		Sb ⁽²⁾		Au-Bi-Sid ⁽³⁾			
Sample	N1	N2	N3	N4	N5	N6	N7	S7	S8	A1	A2	A3	A4
La	6.56	3.38	7.36	0.10	0.37	11.73	1.58	26.90	39.00	0.36	0.28	0.44	0.25
Ce	11.93	7.36	0.94	0.13	0.57	20.09	2.11	–	1.26	0.88	0.46	1.19	0.48
Pr	1.59	0.60	0.99	0.13	0.09	3.58	0.26	–	0.04	0.06	0.05	0.34	0.05
Nd	2.78	1.79	2.19	0.38	0.24	13.32	0.66	–	0.12	0.21	0.18	1.28	0.16
Sm	– ⁽¹⁾	0.40	0.99	–	0.06	1.19	0.26	–	0.53	0.02	0.05	0.44	0.02
Eu	0.20	0.20	0.99	–	0.02	0.20	0.26	–	0.16	–	–	0.02	0.02
Gd	0.40	0.20	0.20	–	0.03	0.80	0.13	–	–	0.04	0.05	0.22	0.02
Tb	0.20	–	–	–	0.01	0.20	–	–	–	–	–	0.02	–
Dy	0.20	0.20	0.20	–	0.02	0.40	0.26	–	0.33	0.04	0.05	0.07	–
Ho	–	–	–	–	–	0.20	–	–	0.04	–	–	–	–
Er	–	–	0.20	–	–	0.20	–	0.12	0.16	–	–	0.02	–
Tm	–	–	–	–	–	–	–	–	–	–	–	–	–
Yb	0.40	–	0.20	–	0.01	–	–	0.06	0.04	–	–	–	–
Lu	–	–	–	–	–	–	–	0.06	0.08	–	–	–	–
ΣREE	24.3	14.1	24.3	0.7	1.4	51.9	5.5	27.1	41.8	1.61	1.12	4.04	1.00
ΣLREE	22.87	13.13	11.48	0.73	1.27	48.72	4.62	26.90	40.42	1.51	0.97	3.25	0.94
ΣMREE	1.00	1.00	2.59	0	0.13	3.18	0.92	0.12	1.22	0.10	0.15	0.79	0.06
ΣHREE	0.40	0	0.20	0	0.01	0	0	0.12	0.12	0	0	0	0
La _n /Yb _n	11.14		24.99		25.14								
La _n /Sm _n		5.35	4.66		4.11	6.19	3.78		46.32	11.33	3.52	0.63	7.87
Gd _n /Yb _n	0.81		0.81		2.35								
Eu/Eu* ⁽⁴⁾					1.00	0.60						0.31	
Ce/Ce* ⁽⁵⁾	1.05	1.14	0.07	0.70	0.79	0.91	0.68	0.14		1.35	0.83	0.87	1.04

(1) – non detected;

(2) – fluid inclusions from early milky-white quartz don't contain REE;

(3) – fluid inclusions from quartz coexisting with late Ag-Pb assemblage from Arkachan deposit contain only La 0.06 and Ce 0.16 ppm;

(4) – $Eu/Eu^* = Eu_n / (Sm_n \times (Tb_n \times Eu_n)^{1/2})^{1/2}$;(5) – $Ce/Ce^* = Ce_n / ((2La_n + Sm_n)/3)$.

also involved in the hydrothermal system and mineral formation occurred at lower temperature.

In our paper we have tried to use REE distribution in the fluid inclusions as the genetic indicator. The quartz from different stages has been studied to reveal the evolution of the composition of the hydrothermal fluid.

The maximum total REE concentrations were found in fluid inclusions in quartz from aplite of the Kurum massif (51.9 ppm) and in the regenerated quartz from the Sarylakh deposit (up to 41.8 ppm). Fluids of the Sb-stage from the Sarylakh deposit are enriched by a sulfate-ion. Giere [28] shows REE enrichment of sulfate-rich acid fluids from Valles caldera. Very high REE concentrations (11.6 to 845 ppm) in fluid inclusions in quartz from the Sarekoubu orogenic gold deposit are related to CO₂-rich ore-forming fluid [11]. The high REE concentrations of the

fluids of the Woxi W-Sb-Au SEDEX deposit result from reactions with REE-rich rocks, leaching within a relatively low fluid/rock system and circulating over extremely long time periods [13]. In our investigation, significant decreasing of total REE concentration (on 1–2 order) in fluid from early to late stages of the Nezhdaninsk and Arkachan deposits is revealed. Probably, it specifies a uniform source of fluid REE-depletion with time. Decreasing of the total REE concentration in fluid inclusions in quartz from early stages to the late ones is reported for the Caijiaying (Pb-Zn-Ag) and Dajing (Sn) polymetallic ore deposits [29]; whereas late vein quartz from the greisen Kalgutinsky Mo-W deposit, Altai [6] has higher REE contents (up to 230 ppm, av. 50), and smaller fluid-saturated at higher temperatures of formation in comparison with early quartz of the Mo-stock (1.1 to 1.4 ppm). The late quartz from the

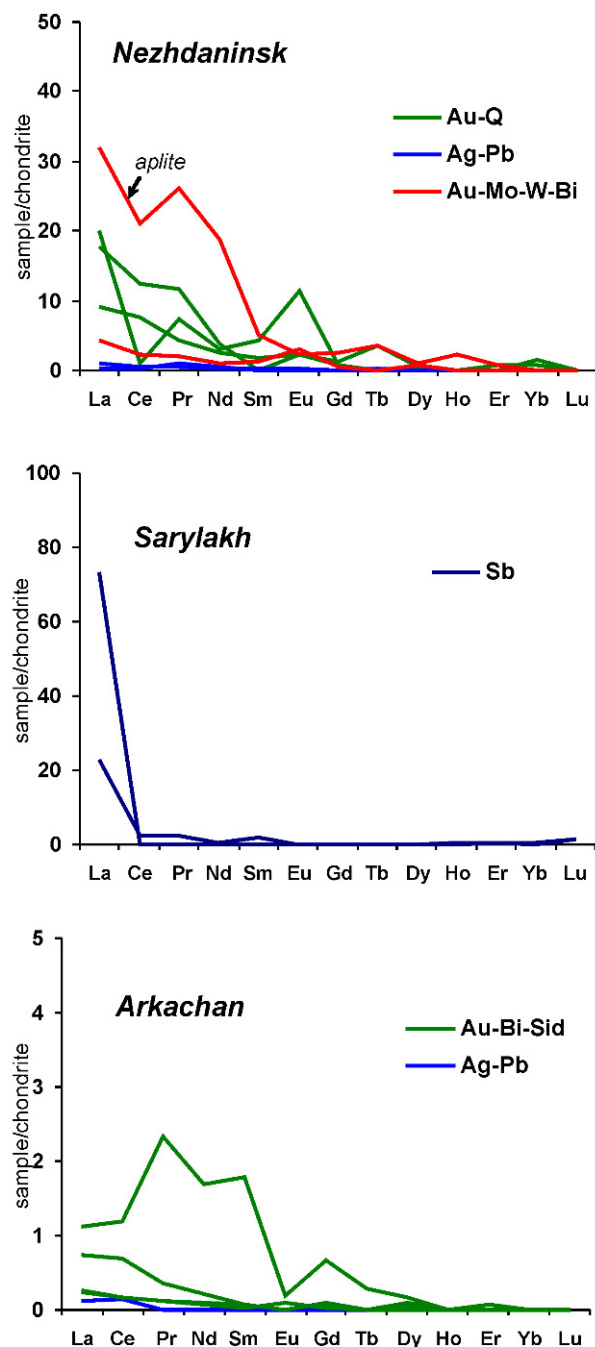


Figure 4. Chondrite-normalized rare earth element patterns for quartz fluid inclusions from Au-Sb, Au-Q and Au-Bi-Sid deposits from North-Eastern Russia. Chondrite REE values after [27].

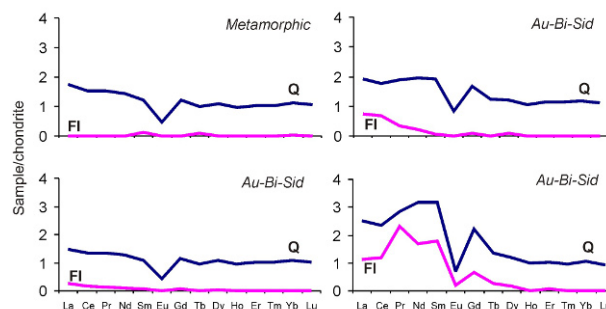


Figure 5. Chondrite-normalized REE patterns for quartz (Q) and aqueous solutions extracted from quartz fluid inclusions (FI) of Arkachan deposit. Chondrite REE values after [27].

Lannigou Carlin-type gold deposit has the highest total concentration of REE (84.17 ppm), especially LREE [5]. This implies that the LREEs may be involved in the formation of strong REE carbonate complexes.

Authors [17, 20, 21] show that the magmatic fluid prevails in some hydrothermal systems, but according to Banks et al. [30] magmatic fluids contain higher REE concentrations (200–1300 ppm) in comparison with our data. However, granite melt during its ascent to the surface at different depths can be a source of magmatic fluids with various REE patterns differing from that of corresponding melt phases [31]. Total REE concentrations in fluid phase fall sharply during the process of pressure decrease and accordingly decrease of the chlorine content in fluid. The possible reason of low REE concentration in fluids of the Arkachan hydrothermal system is abundant precipitation of carbonates together with quartz. Carbonates are enriched by lanthanides, whereas the coexisting solution is accordingly REE depleted.

The positive correlation of total REE concentrations with Rb, Cs, Li and B contents in fluid inclusions are shown on Fig. 6. Decreases in concentration of these elements correspond to the reduction of the contribution of magmatic fluid as has been mentioned above. The K/Rb ratios in fluid inclusions from productive quartz of Arkachan deposit are less than 250 that also assume a magmatic source for the ore-forming fluid.

Tomilenko with coauthors [32] studied the distribution of lanthanides in fluid inclusions and quartz from auriferous and barren quartz-vein zones of the Sovetskoe quartz-gold deposit (Yenisei Range); authors concluded that the higher REE contents and type of REE distribution in fluid inclusions can be indicators of auriferous fluid. Our data has not shown obvious dependence between total REE contents and gold contents in fluid inclusions, but we have studied only productive gold-bearing quartz. We propose that the relatively REE-rich fluids

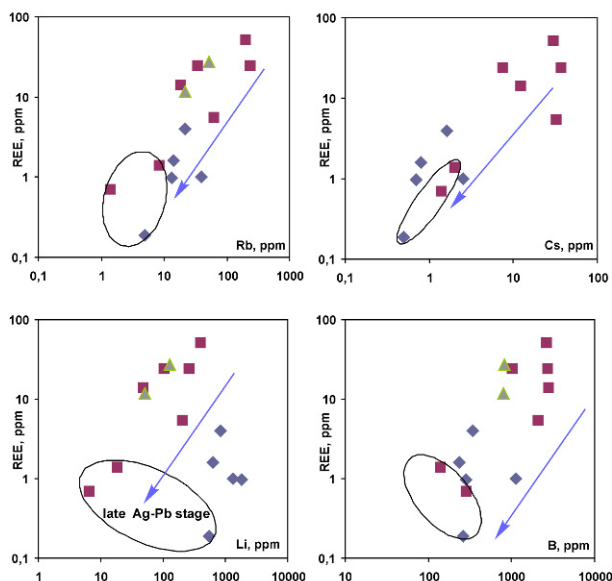


Figure 6. The total REE contents plotted against Rb, Cs, Li and B concentrations in fluid inclusions (square – Nezhdaninsk, rhombus – Arkachan, triangle – Sarylakh). The arrow shows decreasing contribution of a magmatic fluid.

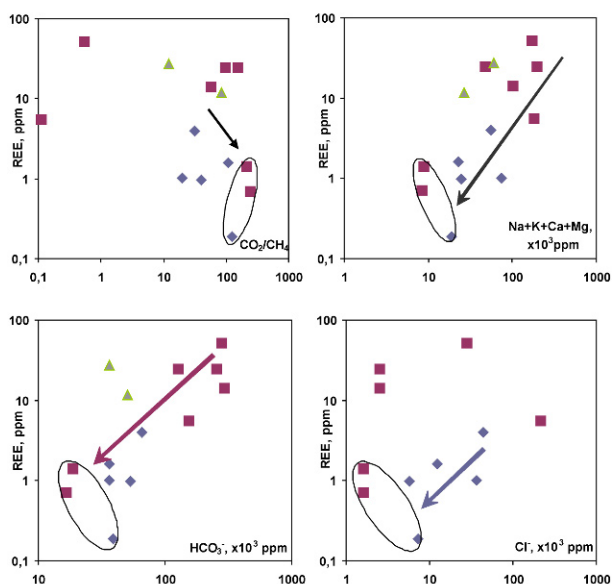


Figure 7. The total REE contents plotted against anion and cation concentrations and CO_2/CH_4 in fluid inclusions (square – Nezhdaninsk, rhombus – Arkachan, triangle – Sarylakh). The arrows show decreasing of f_{O_2} and salinity of fluid; and also the correlation between total REE concentration and HCO_3^- (Nezhdaninsk) and Cl^- (Arkachan) contents.

were responsible for deposition of gold with high fineness within one hydrothermal system. For the Nezhdaninsk and Arkachan deposits it was early fluid, and for Sarylakh – late antimony-bearing fluid.

Europium and cerium anomalies characterize the redox state of the hydrothermal system. Low REE concentrations in fluid inclusions have allowed us to calculate the Eu anomaly only for several samples. Negative Eu anomalies occur in fluid originated from Eu-depleted felsic magmas [33]. The samples from the Cu-Mo porphyry deposits show a small negative Eu anomaly [1, 4]. For the Arkachan deposit, a negative Eu anomaly is found beside fluid inclusions also in the altered host rocks and in minerals. This suggests elevated contribution of magmatic fluid in formation of this deposit. A negative Eu anomaly is present in quartz from aplite of the Kurum massif. The Ce/Ce^* ratio generally changes from 0.7 to 1.4 for studied samples. A very large negative Ce anomaly is found for the regenerated quartz of the Sarylakh deposit. It confirms elevated oxidation of fluid (high f_{O_2}) for this stage. As follows from the occurrence of pyrophyllite and dickite, the stibnite ores were deposited at a shallow depth.

REE distribution in fluid inclusions is controlled by bulk chemical composition of hydrothermal fluid. The anion and cation concentrations in the inclusion fluid are presented in Table 5. It could be underlined that sulfate ion is found only in fluids of the Au-Sb deposit. Elevated concentrations of Cl^- were observed in quartz from Au-Mo-W-Bi mineralization from the Nezhdaninsk deposit (occurring in the contact zone of Kurum granitic massif) and in quartz from the Arkachan intrusion-related deposit. At lower temperatures and pressures sulphate complexes are responsible for a large fraction of the REEs in solution and LnSO_4^+ can be the predominant species [34], for example at the Au-Sb Sarylakh deposit. Besides, SO_4^{2-} probably formed the complexes of LREE and HREE with equal effectiveness [35]. This is demonstrated by the REE pattern for the Au-Sb deposit. In contrast, Cl^- formed the complexes of LREE more strongly than HREE and, in the fluids of the Nezhdaninsk and Arkachan hydrothermal systems, a marked LREE enrichment is shown. This fractionation trend is best explained if the REE are predominantly present in solution as Cl^- complexes.

The total REE contents are higher in the solutions having a lower CO_2/CH_4 ratio and higher $\text{Na}+\text{K}+\text{Ca}+\text{Mg}$ (Fig. 7). The former trend corresponds to decreasing f_{O_2} of fluid and the later pattern demonstrates that REE concentrations increase with higher salinity of inclusion liquids. Assuming that Cl^- content in the fluid inclusions increases together with the REE concentrations, our data also suggest that REE could be transported as chlorine complexes in the Arkachan hydrothermal system (Fig. 7).

Table 5. Chemical composition of inclusion fluids from Au-Sb, Au-Q and Au-Bi-Sid deposits from North-Eastern Russia (g/kg H₂O).

Sample	Stage	CO ₂	CH ₄	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Na	K	Ca	Mg
<i>Nezhdaninsk deposit (Au-Q)</i>										
N1	Au-Q	1546.9	9.9	2.5	— ⁽¹⁾	257.2	34.4	149.6	3.1	9.4
N2	"	1743.3	30.1	2.5	—	293.6	15.3	10	71.1	4.9
N3	"	98.2	1	2.5	—	127.4	—	14.4	21.1	12.5
N4	Ag-Pb	266.3	1.1	1.6	—	16.6	6.7	1.3	0.3	0.04
N5	"	272	1.3	1.6	—	18.7	6	2.2	0.3	0.3
N6	Au-Mo-W-Bi	29.5	54.5	27.8	—	279	27.6	131.3	13.6	1.5
N7	"	16.3	148.5	213.8	—	154.6	60.3	12.8	101.4	7.4
<i>Sarylakh deposit (Au-Sb)</i>										
S1	Au-Q	66.7	1.4	—	9.2	46.0	4.8	0.9	7.4	4.1
S2	"	207.0	1.0	—	—	2.5	0.6	0.3	0.1	—
S3	"	31.9	0.3	—	—	2.1	0.5	0.1	0.2	—
S4	"	91.9	0.3	0.2	—	2.0	0.7	0.1	0.02	—
S5	"	139.8	0.9	0.2	—	1.0	0.3	0.1	0.1	—
S6	"	187.9	2.0	0.2	—	1.8	0.6	0.2	0.02	—
S7	Sb	107.0	1.3	—	22.6	50.7	5.0	7.3	9.6	5.0
S8	" (crystals)	76.4	6.2	—	172.3	36.5	5.8	21.6	25.7	6.6
<i>Arkachan deposit (Au-Bi-Sid)</i>										
A1	Au-Bi-Sid	22.6	1.1	36.2	—	36.2	55.7	8.6	8.6	1.0
A2	"	37.4	1.2	44.4	—	65.6	48.8	4.3	1.9	0.3
A3	"	16.8	0.4	5.8	—	53.3	18.3	3.1	2.6	0.4
A4	"	26.5	0.2	12.2	—	36.6	16.8	3.5	2.0	0.5
A5	Ag-Pb	25.4	0.2	7.2	—	38.8	12.9	1.3	4.2	0.4

⁽¹⁾ – non detected.

Values of Rb and Cs in fluid inclusions also show positive correlations with Na+K. HCO₃⁻ content in the fluid inclusions increases together with the REE concentrations in the Nezhdaninsk hydrothermal system, suggesting that REE could be transported as HCO₃⁻ complexes.

5. Conclusions

1. Level of REE concentration in fluid inclusions and their differentiation depends on bulk chemical composition of hydrothermal fluid.
2. Significant depletion of total REE concentration (on 1–2 order) in fluid from early to late stages of the Nezhdaninsk and Arkachan deposits is revealed. Likely for both cases, it specifies a uniform source of fluid REE-depletion with time.
3. The positive correlation of total REE concentrations with Rb, Cs, Li and B contents in fluid inclusions are shown. This corresponds with a decreasing contribution of magmatic fluids into hydrothermal systems for studying deposits.

4. Decreasing of total REE concentration in fluid inclusions corresponds to elevated f_{O_2} and lower salinity of the hydrothermal fluid.

5. Low REE concentration in fluids of the Arkachan intrusion-related deposit suggests that fluid was separated from magma forming in a shallow-depth magmatic chamber.

6. Not only REE distribution in rocks and minerals, but also concentration of REE in fluid inclusions can be use as a genetic indicator of the hydrothermal process.

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