Mineralogical, geochemical and isotopic (C, O, Sr) features of the unique high-grade REE-Nb ores from the Tomtor deposit (Arctic Siberia, Russia)

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Abstract. The mineralogy (SEM), geochemistry (LA-ICP-MS) and isotopic composition of C, O and Sr in carbonates from uniquely high-grade REE-Nb ores of the Tomtor massif is presented. Testing of the formation conditions for uniquely high-grade ores from the Tomtor deposit was conducted.

1 Introduction

The Tomtor carbonatite (with alkaline ultrabasic rocks) deposit occupies about 250 km² in the northern Sakha Republic (Yakutia). It exceeds 20 km in diameter and has a concentric zonal structure: a carbonatite core surrounded by microcline-mica, microcline-apatite-mica rocks, an incomplete ring of basic and ultrabasic rocks, foidolites, and alkaline and nepheline syenites on the periphery. All rocks are weathered, with the thickest eluvium derived from REE carbonatites and consisting of kaolinite-crandallite, siderite, goethite, and francolite layers. Ores with the highest Nb-REE enrichment occur as sheets in eluvium depressions within the Tomtor core (Buranniy, Severny and Yuzhny sites) [1, 2]. The formation of the rich Tomtor ores, especially, those of the Buranniy site, are still a subject of controversy with the range of possibilities including igneous, sedimentary, hydrothermal-sedimentary, volcanic-sedimentary, or biogenic-sedimentary mechanisms. The conditions of superposed alteration of rocks and ores likewise remain debatable: it is unclear whether they experienced oxidation or reduction by waters percolated from the overlying coal-bearing deposits. Previous hypotheses have interpreted the ores as (1) altered alkaline carbonatitic-peridotitic tuffaceous lavas [3]; (2) epigenetically altered topmost eluvium [4]; (3) lacustrine deposits comprising talus and chemogenic sediments [5]; (4) littoral-sublittoral deposits with cyanobacterial communities [6]; or (5) products of

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the joint action of hydrothermal activity, low-temperature sideritization, and weathering during the Tomtor history [7, 8].

2 Samples and method

This paper presents a study of the Tomtor rocks recovered from exploratory boreholes and a bulk sample for in-process testing. The sample was taken from a 2×2 m pit in the Buranniy site. The Tomtor high-grade ores were recovered from core storages of Ebelyakh and Amakinskii areas in 2013 and from airtight containers with technological samples at the Krasnoyarsk mining and chemical factory. The Nb-REE ore was taken from the northern part of the Buranniy area.

Elements from K to U were determined by LA-ICP-MS using a high resolution ICP-MS spectrometer ELEMENT Finnigan MAT in IGM SB RAS (Novosibirsk) [9].

The composition and micro- (nano)morphology of the ore minerals were studied using a MIRA 3 LMU (Tescan Ltd.) SEM and an INCA Energy 450+ XMax 80 (Oxford Instruments Ltd.) (IGM SB RAS, analyst N.S. Karmanov). The accelerating voltage was 20 kV, and the beam current was 1600 pA (1.6 nA). Under those measurement conditions, the probe end diameter was ~12 nm, but the locality of the analysis was determined by the size of the focal spot diameter, which reached 5 micron or more depending on the effective atomic number of the sample and the wavelength of characteristic X-radiation. The count time was 30 s. The detection limit for most of the elements was 0.2–0.3%, but it could sometimes reach 0.5–0.8% or more if spectral overlaps were observed. The random error of determination of the main components ($C > 10$ –15%) was usually no more than 1%. The error of determination of the components whose contents were 1–10% ranged from 2 to 6%, being usually no more than 10%. For contents near the detection limit, the error could reach 20–30%. During a more detailed study of the content of impurities, the count time was 150 s, which made it possible to reduce the detection limits of the impurities and the random error of the analysis by approximately a factor of two.

5 Discussions and conclusion

The research presented in this paper led to the inference that the rich Tomtor ores were deposited in a shallow thermal lake as a result of hydrothermal-sedimentation and/or volcanic-hydrothermal-sedimentation processes, with mediation of thermophilic microbial communities (Lazareva et al., 2015). The lake formed by a hydrothermal geological event that postdated the emplacement and exposure of magma and its weathering [3, 10, 11]. The results that confirm this inference are specifically as follows.

1. The Nb, REE, Sc, Th, P, and Ti rich- ores (natural concentrates) formed in surface conditions, under the effect of thermal waters, in a relatively shallow outflowing lake (in a limnic-paludal setting).

2. The rich-ores are composed of authigenic ultrafine-grain mineral particles and aggregates (90% <10 μm particles) of REE and trace element phosphates (monazite and crandallite group minerals), free from traces of mechanical wear, and notably less abundant detrital minerals (pyrochlore, Ti oxides, etc.).

3. The rich-ores have a layered structure and a micro-layered texture produced by alternation of crandallite group minerals, monazite (and locally rhabdophane), Ti-Fe-Nb oxides, clay minerals (kaolinite, smectite, etc.), and goethite; they include angular and undeformed grains of detrital pyrochlore.

4. The relatively rich ores (including the Buranyi site) preserve bacteriomorphic nano- and microstructure, with remnants of microbial communities and plants showing close relationships on the micro- and nano-level (fig. 1 a, b, c, d).

5. Goethite-siderite ores contain microscopic layers with framboidal pyrite (fig. 1 e, f) known to be formed with microbial mediation [12].

Fig. 1. Signs of microbiological activity and organic residues in the ore deposits of Tomtor: a-c - bacteriomorphic release of monazite; d - plant residues filled with a dispersed aggregate of crandallite (ASP) minerals; e-f - pyrite framboids in ores in association with monazite (Mz). Photo - scanning electron microscope, BSE.

6. Almost all ores contain sulfide minerals (pyrite, chalcopyrite, galena, sphalerite) which indicate an anoxic setting of precipitation.

7. Carbon and oxygen isotope compositions in ores and related rocks vary in large ranges. The $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ diagram (fig. 2) shows seven fields or trends). Field I near primary igneous carbonate so-called «carbonatitic box» [13] includes carbonatites subjected to Rayleigh fractionation at the magmatic stage and autometasomatic alteration carbonatites, often with abundant sulfides, as well as rocks from the lower ore zone. Field II: mainly massive siderite (with rhodochrosite, columbite, apatite, and ASP). Field III: Nb-REE ores occurring in sheet-like deposits. Field IV: calcite-ankerite-dolomite and dolomite carbonatites and siderite (spherolite and oolite) rocks. The trends III and IV correlate well with the hydrothermal trend and with the trend that represents interaction of alkaline rocks and carbonatite with meteoric water [14]. Field V: Proterozoic and Cambrian sedimentary carbonates, including marbled carbonates of the Ulakhan-Kurung Fm. (NP – R1uk), which host the Tomtor intrusion, and fenitized rocks and ores with fluorite, Ti oxides, basnaesite, pyrochlore, and Fe, Zn, and Pb sulfides. The same field includes the isotope compositions of siderite-mica rocks with crandallite, calcite, and kaolinite. Field VI: values from -24.8 to -39.2‰ $\delta^{13}\text{C}$ is typical for biogenic organic matter. The lowest $\delta^{13}\text{C}$ values reach -54.6‰ and -56.7‰ (at $\delta^{18}\text{O}$ = +10.5‰ and 9.4‰, respectively) and correspond to fine-grained, crushed stratified rocks, composed of Fe-Mg-chlorite (shamosite), apatite, rhodochrosite, with lesser amounts of siderite, Nb-bearing Ti oxides, monazite, pyrochlore, sphalerite, and

galena. The biogenic origin of these rocks is consistent with recently published evidence of microbial mediation documenting the active role in the formation of hydrothermal-sedimentary rich ores in limnic-paludal settings, with methane inputs from seeps [15] or from bacterial activity in plant remnants [16].

Fig. 2. The isotope composition of carbon and oxygen in carbonates from rocks and ores of the Tomtor deposit. The fields (trends): I - near primary igneous carbonate; II - massive siderite; III - Nb-REE ores occurring in sheet-like deposits; IV - calcite-ankerite-dolomite and dolomite carbonatites and siderite (spherulite and oolite) rocks; V - sedimentary carbonates; VI – trend for biogenic organic matter with methane.

The origin of carbonates with low carbon isotopic composition (less than -30‰) is associated with methane. Sulfate-reducing bacteria interacts with methane and forms bicarbonate ($\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}$) with the subsequent formation of metal carbonates ($2\text{HCO}_3^- + \text{Me}^{2+} \leftrightarrow \text{MeCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$; $\text{Me} = \text{Ca, Mg, Fe, Mn}$). For the appearance of methane in the ore zone, there are two options. One of them is caused by bacterial methane (biotic methane), which is formed as a result of microbial decomposition of vegetation. The presence of vegetation is determined by the isotopic composition of organic carbon from the ore zone samples after intense acid treatment. The values of the isotopic composition range from $\delta^{13}\text{C}$ -26 to -19‰, that is, in the range characteristic for C3

plants with values of $\delta^{13}\text{C}$ -33 to -26‰. The second variant assumes the appearance of abiogenic methane with a decrease in the temperature of the carbonatite melt and the appearance of water. For example, methane is generated in the mantle under special conditions such as extremely low oxygen fugacity (for instance, at the base of continental lithosphere) and elevated water activity. These conditions may occur during crystallization differentiation in deep-level chambers of kimberlite and proto-kimberlite magmas [17].

Siderite-apatite-shamosite rocks (well 101, depth 150 m) have an isotopic composition of $(^{87}\text{Sr}/^{86}\text{Sr})_0 = \sim 0.70374$, which is in the range of 0.7032-0.7039 $(^{87}\text{Sr}/^{86}\text{Sr})_0$ characteristic of carbonatites of the Tomtor deposit. It is known that crustal magmatic formations have $(^{87}\text{Sr}/^{86}\text{Sr})_0 > 0.708$ [18]. It can be concluded that the host rocks either did not participate in the formation of rocks with an elevated content of rare elements and REE, or the isotopic composition of the strontium of the host rocks was low (about 0.7037-0.704) and they participated in the formation of ore mineralization. In addition, we cannot exclude a single source, which formed both host rocks and rare-earth mineralization.

The hydrothermal systems responsible for the formation of the rich Tomtor ores differs from their modern counterparts in island arcs (or back-arc basins, such as the Uzon-Geyser depression), but they share some similar features as well. Namely, Ca, Fe, and Mn phosphates often precipitate over bacterial cells in the microbial communities of hot springs within the Uzon-Geyser depression, at low P contents in the waters (under 160 ppm) [19], while the bottom sediments of thermal Lake Fumarol'noe consist of biogenic material (mostly diatom frustules) and framboidal pyrite.

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