

Main minerals of abnormally high-grade ores of the Tomtor deposit (Arctic Siberia)

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Abstract

The Tomtor massif of Paleozoic ultramafic alkaline rocks and carbonatites is located in the northern part of the Sakha Republic (Yakutia). The massif (its total area is ~250 km²) is ~20 km in diameter, with a rounded shape and a concentrically zoned structure. The core of the massif consists of carbonatites surrounded by a discontinuous ring of ultramafic rocks and foidolites. The outer part is composed of alkali and nepheline syenites. All rocks are weathered and covered with eluvium, which is the thickest after carbonatites enriched in phosphates and REE. The weathering profile consists of four layers, from the top: kaolinite–crandallite, siderite, goethite, and francolite. The highest-grade ores are observed in the bedded deposit which fills depressions in “sagging” eluvium. The ores are laminated and cryptogranular, with high Nb, Y, Sc, and REE contents (on average, 4.5% Nb₂O₅, 7–10% REE₂O₃, 0.75% Y₂O₃, and 0.06% Sc₂O₃). The highest-grade ores are natural Nb and REE concentrates. The total REE content in some layers is >10%. The morphologic features of the highest-grade phosphate ores from the northern part of the Buranniy site were studied. The ore-forming minerals belong to the pyrochlore group, crandallite group (goyazite), and monazite-Ce. The pyrochlore group minerals occur mainly as crystals that were completely replaced by barium–strontium pyrochlore and/or plumbopyrochlore but retained the original faces; also, they occur as numerous conchoidal fragments. The grains of the pyrochlore group minerals sometimes have a zonal structure, with an unaltered pyrochlore core and a reaction rim. Goyazite occurs predominantly as colloform grains. According to SEM and TEM data, monazite occurs in the ores as ~50 nm particles, which cover the outer part of halloysite tubes (800–3000 nm long and 300 nm in diameter) as a dense layer and make up peculiar biomorphic aggregates. The mineralogical data, the occurrence of biomorphic aggregates, and the close association of organic remains with ore minerals suggest that the high-grade ores of the Tomtor deposit, including the Buranniy site, resulted from a hydrothermal–sedimentary process with a presumably important role of bioaccumulation of REE phosphates.

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Keywords: pyrochlore; minerals of the crandallite group; monazite; halloysite; REE deposit; carbonatites

Introduction

In the early 1990s, a unique Nb–REE deposit related to the Tomtor massif of ultramafic alkaline rocks and carbonatites was explored in the northern Sakha Republic (Yakutia). The content of Nb₂O₅ in the highest-grade ores is more than three

times higher than that in the ores of the well-known Araxá deposit, Brazil (Cordeiro et al., 2011); it is estimated at 4.5%, the maximum content being 24% (Lapin, 2011; Tolstov, 2006). The total contents of rare-earth oxides are similar to world analogs of REE deposits; the average content of these oxides in the ores is 7–10% (in some zones up to 40%). The ores have high Y₂O₃ (on average, 0.75%) and Sc₂O₃ (on average, 0.06; maximum value, 0.1–0.3%) contents (Lapin, 2011; Tolstov, 2006). The highest-grade ores of the Tomtor deposit (Buranniy site) are acknowledged as a natural Nb and

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REE concentrate (Dobretsov and Pokhilenko, 2010; Epshtein et al., 1994; Tolstov et al., 2011). The genesis of such high-grade ores was discussed before, but it remains a disputable issue of great interest because of the high economic significance of these ores in the contemporary world.

Geologic summary. The Tomtor deposit is related to the Tomtor massif, which is located east of the Anabar Shield, in the northern Siberian Platform. It is a concentric ring intrusion and one of the world's largest carbonatite massif both in total area (~250 km²) and in the size of the core (40 km²) (Bagdasarov, 1997, 2009; Dobretsov and Pokhilenko, 2010; Egorov et al., 1985; Epshtein et al., 1994; Erlikh, 2004; Kravchenko and Pokrovsky, 1995; Kravchenko et al., 1992; Parfenov and Kuz'min, 2001; Porshnev and Stepanov, 1980, 1981; Tolstov, 2006; Tolstov and Tyan, 1999; Vladykin, 2009; Vladykin and Torbeeva, 2005; Vladykin et al., 2014). The Tomtor massif lies in the axis of the Udzha uplift, which is 30 km wide and stretches for 200 km from north to south (Parfenov and Kuz'min, 2001). The Tomtor and Bogdo massifs and two massifs unstripped within the uplift are assigned to the Udzha alkaline province.

The Tomtor massif intrudes Neoproterozoic dolomites, schists, and siltstones and Vendian metamorphic terrigenous rocks (Fig. 1). Despite the extensive geological survey and research, the structure and conditions of formation of the massif are not completely known, because most of it was studied with a sparse network of drillholes. For the same reason the description of the rocks is often based on their position in the massif rather than on chronology as it was rightfully suggested in (Vladykin and Torbeeva, 2005). With regard to the high diversity of the rocks, different stages of their formation, the lack of dating, and the abundance of secondary processes which changed the original appearance and geochemical characteristics of the rocks, such a “structural description” might be justified for the present moment.

The outer ring of the Tomtor massif consists of alkali and nepheline syenites (predominant) and ultramafic rocks–foi-dolites (nepheline–pyroxene rocks of the jacupirangite–melteigite and ijolite–melteigite series) (Bagdasarov, 1997; Parfenov and Kuz'min, 2001; Tolstov, 2006; Tolstov and Tyan, 1999) (Fig. 2). The ultramafic rocks and foidolites make up an incomplete ring (1.5–2.0 km wide) in the central part, fringing the carbonatite core of the massif (6 km in diameter); between the core and ultramafics, there are microcline–micaceous (±apatite and calcite) rocks, in the east and west. The carbonatite core consists of two groups of rocks based on Nb and REE content: barren (western part) and ore-bearing (eastern part, Fig. 2). Picrite and alnoite dikes and pipes cut different rocks. Their formation might be temporally separated from the main intrusive phases. Along with the core, the rocks of the carbonatite complex make up a series of veins and crescent-shaped lenses in nepheline–pyroxene rocks in the northeastern part of the massif, which are of calcite–phlogopite–magnetite composition (Tolstov, 1994, 2006).

Thick (up to 300 m) laterite, after ore-bearing phosphate–REE carbonatites, is observed on all rocks of the massif. The weathering profile consists of four layers (from the top):

kaolinite–crandallite, siderite, goethite, and francolite (Tolstov, 2006; Tolstov et al., 2011).

Very high-grade ores make up three sheet deposits filling depressions in the “sagged” weathering profile after carbonatites (Fig. 3) (Konoplev et al., 1995; Lapin, 2011; Tolstov, 2006). The high-grade ores are partly overlain by Permian coal-bearing clastics (Figs. 1, 3). The rocks of the massif and preserved fragments of Permian sediments are mostly overlain by Jurassic marine sediments and Quaternary sediments (Fig. 1).

Age. The age of the Tomtor rocks was first determined by the K–Ar and Rb–Sr methods more than 20 years ago (Entin et al., 1990), at 810 to 240 Ma. According to (Entin et al., 1990, p. 50), the Tomtor massif evolved as a pluton in 800–670 Ma and as a subvolcanic and volcanic structure with numerous volcanic centers in 670–240 Ma. The data presented by the authors testify to the existence of more than ten stages. When interpreting the results of Entin et al. (1990), Kravchenko and Pokrovsky (1995) presumed that the dates obtained indicate two important events: at ~800 and 400 Ma. The latest U–Pb (two samples) and ⁴⁰Ar/³⁹Ar (four samples) dating of the Tomtor rocks testify to two formation stages (Vladykin et al., 2014). Dating was carried out for zircon grains from alkali syenite and ore-bearing phosphate–carbonate tuff. The zircon grains from alkali syenite yield the age of 689 ± 5 Ma, whereas those from ore-bearing phosphate–carbonate tuff yield the age of 394 ± 7 Ma. The ⁴⁰Ar/³⁹Ar ages of Mg–biotite confirm that the barren carbonatites are assigned to the first time interval, 693 ± 8 and 681 ± 6 Ma, whereas the lamproites and ore-bearing carbonatites are assigned to the second one (412 ± 2 and 400 ± 4 Ma, respectively). At 700 ± 30 Ma, ore-bearing carbonatite and mafic–ultramafic igneous complexes, which are regarded as derivatives of the mantle superplume that split the supercontinent Rodinia (Kuzmin and Yarmolyuk, 2014), formed along the edge of the Siberian continent.

Ores at the Burannyi site. The ores at the Burannyi site are the best explored (Fig. 2). Despite the long history of research, there is no consensus on the genesis of the highest-grade pyrochlore–crandallite–monazite ores in the Tomtor massif. According to different authors, they were presumed to be altered alkali carbonatite–ultramafic tuff lavas (Entin et al., 1990), hydrothermal ores (Kravchenko et al., 1992), epigenetically altered upper layers of the weathering profile (Lapin and Tolstov, 1991, 1993), or lacustrine sediments including clastic and chemogenic sedimentary material (Konoplev et al., 1992, 1995). Finally, it was presumed that the Tomtor high-grade ores were generated by the activity of cyanobacterial communities in the littoral/sublittoral marine zones (Zhmur et al., 1994).

Through the history of research, there has been no chance of reliable age determination for the ores. It is presumed that an ancient weathering profile overlain by the high-grade ores formed in the late Devonian–Early Carboniferous. However, no faunal remnants suitable for dating were defined in the latter. Despite the high monazite contents, the form and structure of the mineral syngenetic with the ores are unsuitable for reliable dating. Only the coal-bearing sediments above

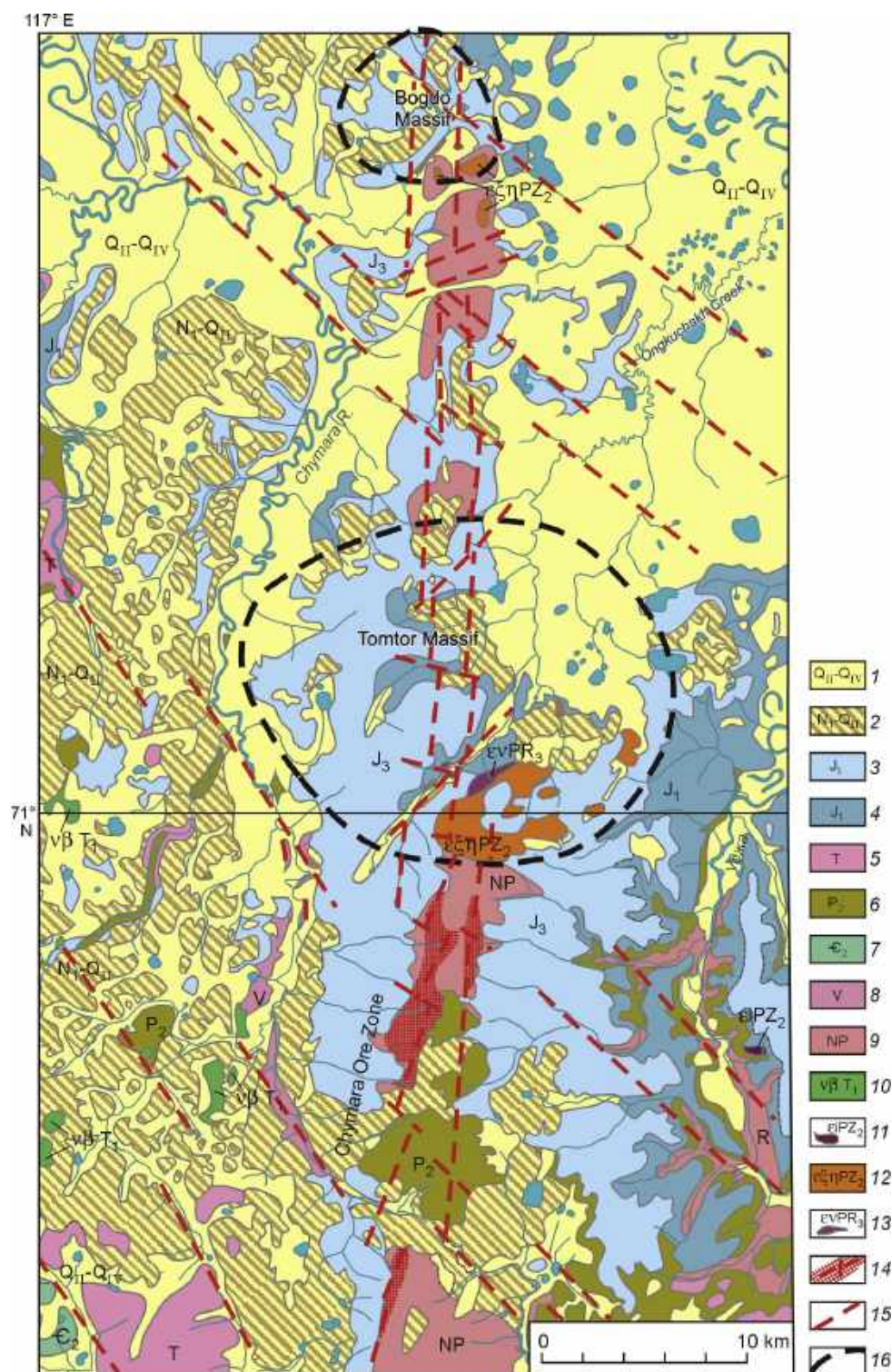


Fig. 1. Geological sketch map of the Tomtor massif, based on the results of work of the Amakinskaya and Ebelyakhskaya geological surveys (Kaban'kov, 1965; Tolstov and Tsybul'skaya, 1998). 1, Quaternary sediments; 2, Pliocene–Middle Quaternary sediments: alluvial sandy loam, sand, and pebble gravel; 3, 4, Jurassic System: marine sediments: siltstone, sandstone, limestone, conglomerate, and clay; 5, Triassic System: mafic tuffs and basalts; 6, Permian System, upper series: sandstone, siltstone, coal, and clay; 7, Cambrian sediments: predominantly limestone; 8, Vendian: predominantly dolomite; 9, Neoproterozoic: predominantly dolomites; 10, dolerite intrusions, stocks, and dikes; 11–13, Molodo–Udzhia intrusive complex: 11, alkaline ultramafic rocks (alnoite, alkali picrite, etc.); 12, alkali nepheline syenite; 13, foidolites (nepheline–pyroxenite rocks); 14, hydrothermally altered rocks; 15, large faults; 16, boundaries of alkaline massifs.

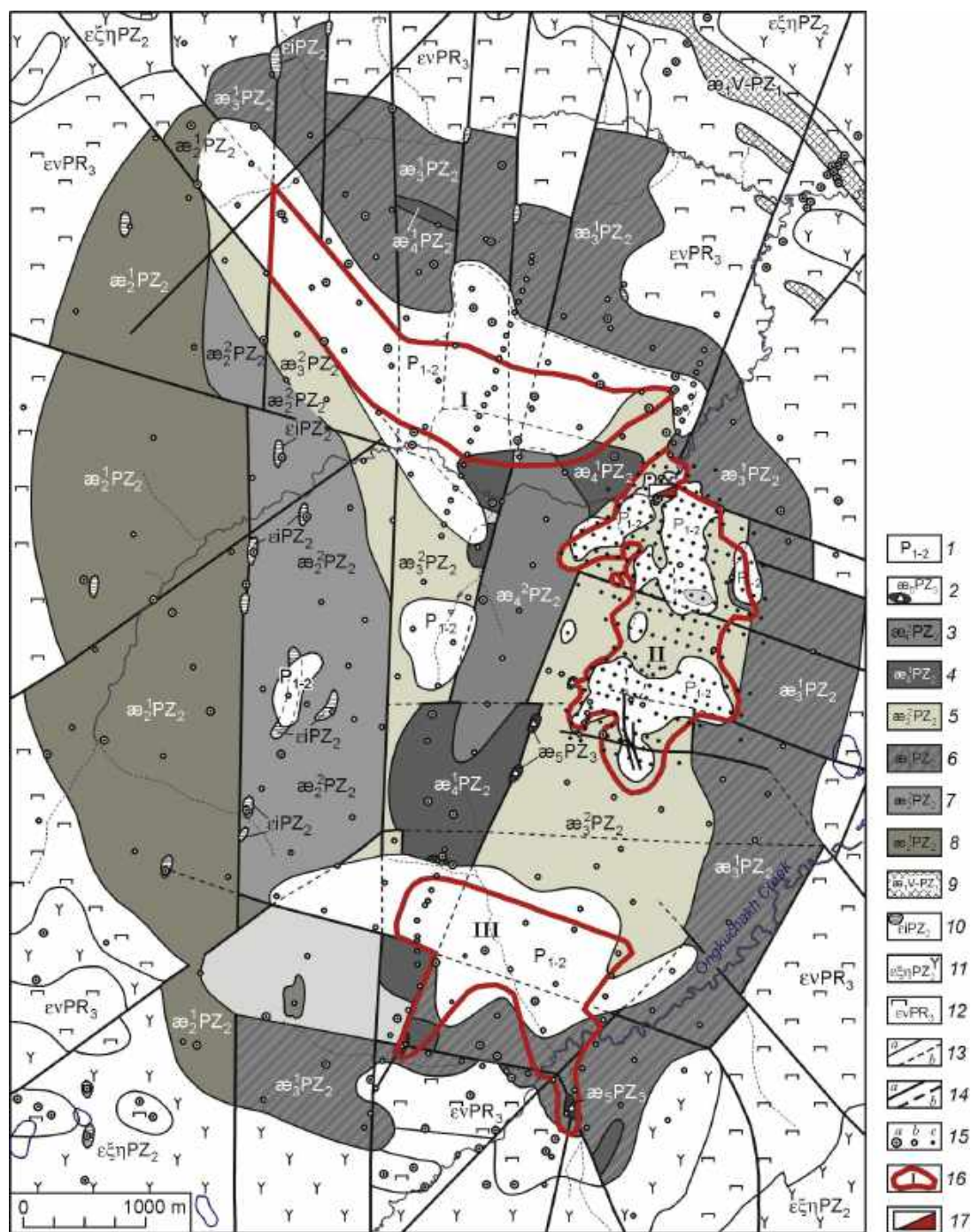


Fig. 2. Geological sketch map of pre-Jurassic rocks in the central Tomtor massif, after (Tolstov and Tsybul'skaya, 1998). 1, sediments: Paleozoic group, Permian System, undifferentiated lower-upper series, igneous rocks of the Tomtor massif; 2–9, carbonatite complex: 2, carbonatite breccias; 3, 4, rare-metal group: 3, rare-metal carbonatites; 4, ankerite–chamosite rocks; 5–9, phosphorus–rare-metal group; 5, phosphorus–rare-metal carbonatites (polyminal); 6, apatite–microcline–micaceous rocks; 7, barren carbonatites (calcite and dolomite–calcite); 8, calcite–microcline–micaceous rocks; 9, kamaphorites; 10–12, silicate rocks: 10, alkaline ultramafic rocks of the alnoite–tinguaite series (alnoites, alkali picrites, tinguaite, etc.); 11, alkali and nepheline syenites; 12, foidolites (nepheline–pyroxenite rocks of the jacupirangite–urtite series); 13, geologic boundaries: *a*, observed; *b*, inferred and buried; 14, faults: *a*, observed; *b*, inferred and buried; 15, boreholes: *a*, drilled before 1985; *b*, drilled by the Ebelyakh geological survey in 1985–1990; *c*, exploratory boreholes, drilled at the Burannyi site in 1991–1994; 16, outlines of the Severnyi (I), Burannyi (II), and Yuzhnyi (III) sites; 17, exploratory borehole from which the technological sample was taken.

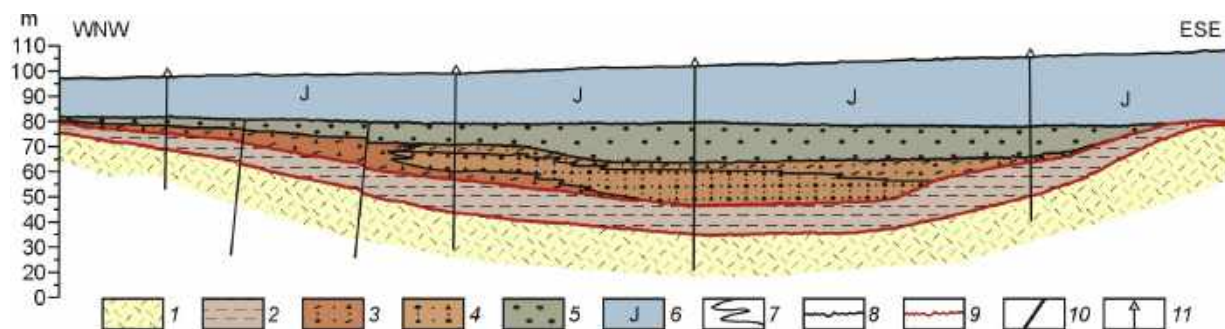


Fig. 3. Schematic geologic section of the Burannyi site (Konoplev et al., 1995). 1, weathering profile; 2, lacustrine, essentially pelite sediments with rare siltstone interbeds; 3, 4, red-colored talus and alluvial sediments, respectively; 5, coal-bearing alluvium; 6, Jurassic marine sediments; 7, facies boundaries; 8, erosional boundaries; 9, boundaries of the orebody; 10, faults; 11, boreholes.

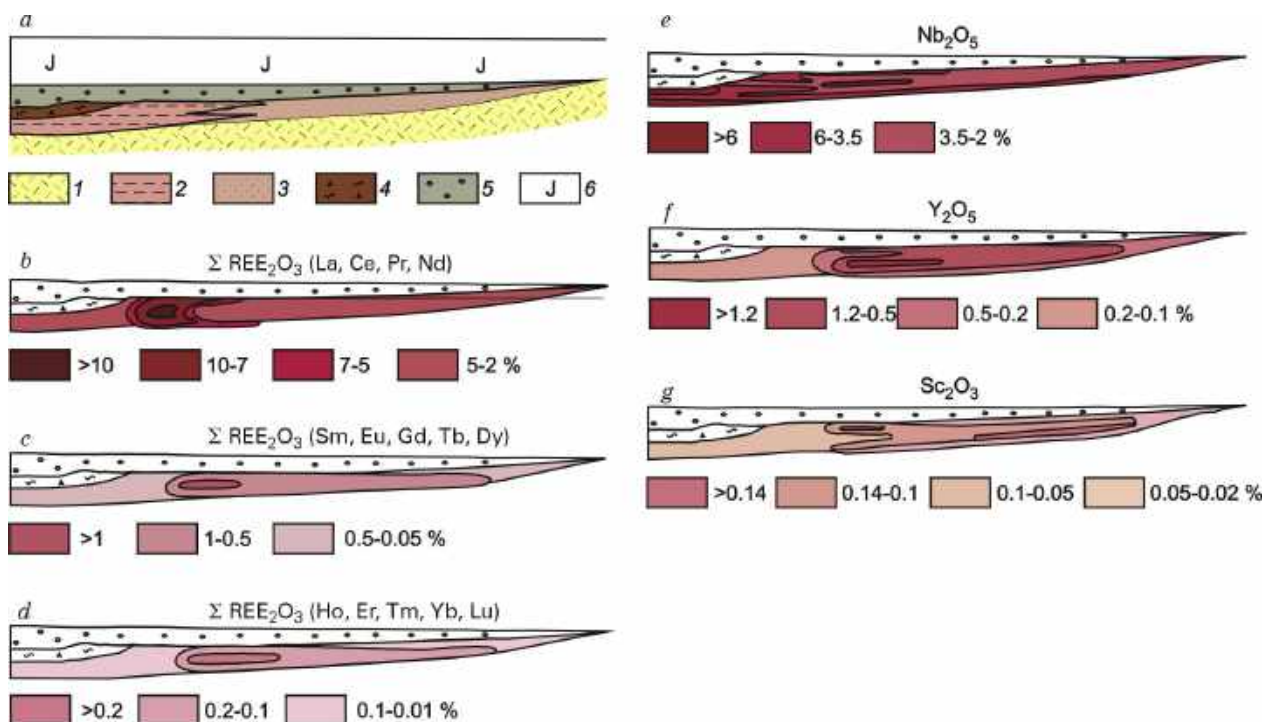


Fig. 4. Fragment of the geologic section (a) and the distribution of rare-metal mineralization in the rocks of the ore bed (b–g) (Epshtein et al., 1994). 1, weathering profile; 2, 3, lacustrine sediments: 2, silt and pelite; 3, sand; 4, 5, Permian sediments: 4, red clastics—alluvial sediments; 5, coal-bearing alluvium; 6, Jurassic marine sediments.

(Permian) are dated based on faunal remnants. Thus, the high-grade ores may have formed between 400 (412–394) and 250 Ma.

The ores, which overlie the weathering profile, make up a sheet deposit pinching out toward the edges (Dodin, 2008; Epshtein et al., 1994) (Figs. 3, 4). The upper and, partly, lower boundaries show traces of erosion (Fig. 3). The highest contents of ore components are observed at the transition from the central part to the edges of the orebody (Fig. 4).

Thus, two issues remain debatable: the genesis of the highest-grade ores at the Tomtor deposit (Burannyi site) (magmatic, sedimentary, hydrothermal–sedimentary, volcanosedimentary, or biogenic–sedimentary) and secondary alteration (oxidation or alteration under the effect of reduced

bog waters percolating from the coal-bearing sediments above in the section). In our view, the first step toward the solution of these problems should be detailed description and analysis (by the newest methods) of the composition of the ores. Using the Tomtor high-grade ore material, the authors defined new features of their composition and structure. The aim of the paper is to describe the morphology and composition of the main minerals of the Tomtor high-grade ores.

Methods

The paper presents the study of the Tomtor rocks recovered from exploratory boreholes and a bulk sample for in-process testing (Tolstov, 2013). The sample was taken from a 2 × 2 m

shaft in the northern part of the Burannnyi site (Fig. 2); the thickness of the sediments above the ores was 15 m. The Tomtor high-grade ores were recovered from the core storages of Ebelyakh and Amakinskii Villages in 2013 and from airtight containers with technological samples at the Krasnoyarsk mining and chemical combine. The substance (ore which is the richest in REE) was taken from the northern part of the Burannnyi site (Fig. 2).

Elements from K to U were determined by synchrotron-radiation X-ray fluorescence at a VEPP-3 station of element analysis (accelerating mode was 2 GeV, and beam current, 100 mA) at the Siberian Synchrotron Radiation Center (analyst Yu.P. Kolmogorov). The energy-dispersive X-ray optics of synchrotron-radiation XRF was applied in two modes of primary monochromatic beam (33 keV) (Baryshev et al., 1986; Bobrov et al., 2001). The EXD spectra were processed in the AXIL software, and the contents were calculated by the external standard method. Loparite concentrate (CBT-16A, no. 350-73 in the State Register) was used as a standard ($\text{Ta}_2\text{O}_5 = 0.64$, $\text{Nb}_2\text{O}_5 = 8.4$, $\text{TiO}_2 = 38.5$, $\text{ThO} = 0.69$ wt.%, $\Sigma\text{REE} = 31.4$ wt.%: $\text{CeO}_2 = 16.2$, $\text{Dy}_2\text{O}_3 = 0.017$, $\text{Eu}_2\text{O}_3 = 0.053$, $\text{Gd}_2\text{O}_3 = 0.017$, $\text{La}_2\text{O}_3 = 8.4$, $\text{Nd}_2\text{O}_3 = 4.1$, $\text{Pr}_2\text{O}_3 = 1.59$, $\text{Sm}_2\text{O}_3 = 0.035$, $\text{Y}_2\text{O}_3 = 0.033$).

X-ray fluorescence analysis was performed using an ARL-9900XP (Thermo Fisher Scientific) spectrometer (Sobolev Institute of Geology and Mineralogy, analyst N.G. Karmanova) and the QuantAS software, which was part of the software package of the apparatus. The detection limits of the elements were of 0.001–0.1%. Specimens were prepared by fusing (1:9) samples with the flux on the base of a lithium tetraborate–lithium metaborate mixture.

The dominant minerals were determined by X-ray powder diffraction (XRD) analysis using an ARL X'TRA (Thermo Fisher Scientific, Switzerland) diffractometer at the Sobolev Institute of Geology and Mineralogy (analyst L.V. Miroshnichenko).

The grain-size characteristics were studied by classical sedimentation analysis (decantation) using the procedures described in (Novikov, 1952; Rukhin, 1957). Weighed portions of 100 g of each sample were placed in 5-L battery glasses and soaked for 24 h. For five months, upper ten centimeters of the water column (suspension) were daily poured in new glasses to separate the fraction $<1\ \mu\text{m}$. The process took place with the daily addition of a few drops of ammonia to the upper glass to keep the particles in suspension and a few drops of hydrochloric acid to deposit the fraction in the lower glass. Afterward the fractions 1–10 and 10–50 μm were separated. On agitation of the substance, 10 cm of the water column was poured out after settling for 5 and 2.5 min until the solution in the glass became transparent within the given time interval. Larger fractions were obtained by sieve analysis.

The particle sizes were also determined using a Fritsch Analysette 22 MicroTec laser analyzer. The samples were prepared by the standard method with preliminary ultrasonic dispersion. The samples were crushed in a china mortar using a pestle with a rubber tip, and the fraction $>0.5\ \text{mm}$ was sifted out. Ten grams of the fraction $<0.5\ \text{mm}$ was placed in a flask

with 300 mL distilled water. The obtained solution was stirred for 5 min in a shaker, and then part of the solution was transported to the laser particle sizer. The other portion ($<0.5\ \text{mm}$ fraction) was placed in the ultrasonic radiator before the analysis, and the solution was subjected to ultrasonic treatment at 22,500 Hz for 3 min. The fraction $>0.5\ \text{mm}$ was also soaked in a flask, placed in the ultrasonic radiator, and then the preserved particles $>0.5\ \text{mm}$ in size were sifted out. The portion of the coarse fraction was estimated by the gravimetric method. Analysis was carried out at the Institute of Soil Science and Agrochemistry by A.S. Chumbaev.

The composition and micromorphology of the minerals of ores were studied using a MIRA 3 LMU (Tescan Ltd.) SEM and an INCA Energy 450+ XMax 80 (Oxford Instruments Ltd.) (Sobolev Institute of Geology and Mineralogy, 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 $\sim 12\ \text{nm}$, but the locality of the analysis was determined by the size of the focal spot diameter, which reached 5 μm 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% (criterion 3σ), 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 two times.

Also, the ore samples were analyzed by high-resolution electron microscopy using a JEM-2010 (Japan) device with a resolution of 1.4 Å (Boreskov Institute of Catalysis, analyst E.Yu. Gerasimov). The X-ray microanalysis of the element composition of the samples was carried out using an energy-dispersive X-ray spectrometer and a Si(Li) detector with an energy resolution of 130 eV. The samples were prepared by two methods: They were placed on perforated carbon supports fixed on copper grids with and without an UZD-1Uch2 sonicator.

Results

Composition of the substance under study

The studied rocks, which have a thin-banded structure, are high-grade ores typical of the Burannnyi site of the Tomtor massif. Dry samples are very fragile and break easily. The content of major elements in the ores under study mainly corresponds to the previous data (Table 1) (Lapin, 2011; Tolstov, 2006). The content of Nb_2O_5 is 5.6%; that of the total rare-earth oxides, 14.6%; and that of Y, 0.75%; besides that, the main components of the ores include 12.6 wt.%

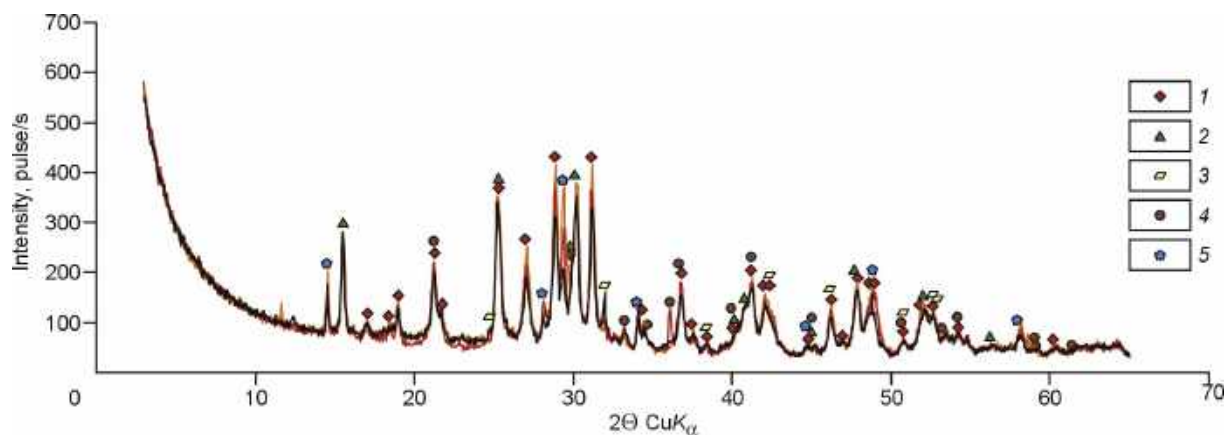


Fig. 5. Mineral composition of ore from the northern part of the Buranniy site, Tomtor deposit, according to XRD. 1, monazite; 2, goyazite; 3, siderite; 4, goethite; 5, pyrochlore.

Al_2O_3 , 12 wt.% Fe_2O_3 , and 15.4 wt.% P_2O_5 , which is somewhat lower for Al_2O_3 and higher for Fe_2O_3 , P_2O_5 , and REE_2O_3 than the average contents in the ores of the Buranniy site (Table 1). Also, high contents of V (1.4%), Sr (4%), Ba (3.3%), Pb (1600 ppm), and Th (2140 ppm) are observed. The contents (ppm) of Cl (1800), Rb (27), Hf (167), and Ta (500) have been first determined.

According to XRD, the ore samples under study are dominated by pyrochlore, monazite, and goyazite (mineral of the crandallite group), whose relative content shows minor variation (Fig. 5). Also, the XRD pattern clearly shows siderite and goethite.

The decantation showed that during interaction with water, 18% of the substance passes into dissolved and/or colloid form and eluded deposition (Fig. 6). Therefore, data on the size of the mineral particles were obtained using a Fritsch Analysette 22 MicroTec laser analyzer. With no preliminary ultrasonic treatment, particles >0.5 mm in size make up 18–20%. The rest of the substance consists of particles no larger than

20 μm , most of them <10 μm (Fig. 7a). The particles were grouped into four size intervals with average values of 0.75, 2, 5, and 10 μm . After preliminary ultrasonic treatment, the fraction >0.5 mm made up only 3% of the total mass of the sample. The particles constituting the total mass became smaller: The portion of particles whose average size was 0.75 μm increased considerably, whereas the number of ~ 5 and 10 μm particles decreased dramatically (Fig. 7b). Thus, the ore in the northern part of the Buranniy site consists mainly of clay (<2 μm) and fine silt (2–8 μm) particles. Some grains make up aggregates which break easily as a result of ultrasonic dispersion. This fact is confirmed by analysis of the content of major elements in grain-size fractions obtained by decantation. The contents of Ti, Fe, Zn, Sr, Y, Zr, Nb, La, Ce, Pb, Th, and U are similar in different fractions of each ore sample (Table 2). Only the contents of elements in the coarsest fraction are different.

Minerals and forms

The previous researchers considered more than 80 minerals in the Tomtor high-grade ores (Konoplev et al., 1995; Lapin, 2011). The ores are oxides (pyrochlore, goethite, hematite, rutile, and ilmenorutile), phosphates (monazite, minerals of the crandallite group, fluorapatite, and xenotime), and carbonates (siderite). Sulfides (pyrite, galena, sphalerite, and chalcopyrite) are widespread, though their content in the ores is low, usually averaging no more than 4%. Also, silicates (kaolinite and illite) were observed (Lapin, 2011). The present paper is aimed at a detailed description of only ore-forming minerals: pyrochlore, goyazite, and monazite, which are easily determined by XRD.

The typical appearance of the ores is shown in Fig. 8. A very fine-grained mass of monazite, goyazite, and goethite makes up the laminated ore structure. The distinct laminate at some places are no more than 20 μm thick. This fine-grained mass contains cracked pyrochlore grains, which often have well-preserved faces.

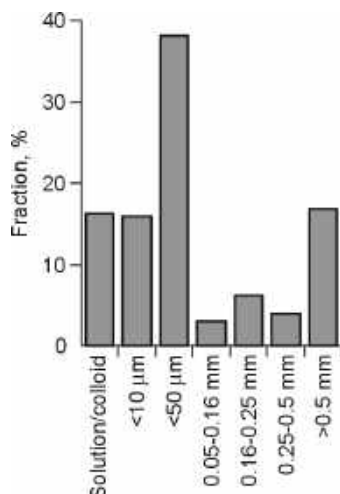


Fig. 6. Grain-size composition of high-grade ores in the northern part of the Buranniy site.

Table 1. Compositions of high-grade ores from the Buranniyi site, Tomtor deposit

Component	(Lapin, 2011)	(Tolstov, 2006), average for 100 samples	Present paper, average for 20 samples
Na ₂ O, %	0.24	0.2	0.68
MgO	0.15	0.27	0.22
Al ₂ O ₃	20.32	15.62	12.59
SiO ₂	7.2	9.78	1.68
K ₂ O	0.17	0.32	0.15
CaO	2.3	2.84	3.70
TiO ₂	9.95	6.81	9.77
Fe ₂ O ₃	10.17	9.05	11.98
FeO	4.55	6.82	N.d.
MnO	0.33	0.54	0.51
P ₂ O ₅	12.86	13.21	15.39
Nb ₂ O ₅	3.36	3.93	5.63
REE ₂ O ₃	7.2	10.28	14.58
CO ₂	2.03	3.27	3.6
SO ₃	0.51	0.77	2.2
LOI	N.d.	–	3.50
Be, ppm	71	N.d.	N.d.
B	48	N.d.	N.d.
Cl	N.d.	N.d.	1800
Sc ₂ O ₃	76 (Sc)*	500	N.d.
V, %	1	N.d.	1.40
Cr, ppm	120	N.d.	300
Co	17	N.d.	N.d.
Ni	30	N.d.	176
Cu	48	200	320
Zn	1000	900	670
Ga	100	N.d.	100
Rb	N.d.	N.d.	27.4
Sr, %	2	2.32	4.03
Y ₂ O ₃	0.78	0.78	0.92
Zr	0.21	N.d.	0.1
Mo, ppm	52	N.d.	N.d.
Cd	N.d.	N.d.	6.84
Sn	22	N.d.	17
Sb	N.d.	N.d.	17
Ba, %	3.6	N.d.	3.30
La ₂ O ₃	1.44 (La)*	2.38	3.16
Ce ₂ O ₃	N.d.	5.13	7.30
Pr ₂ O ₃	N.d.	0.58	0.67
Nd ₂ O ₃	N.d.	1.61	2.31
Sm ₂ O ₃	N.d.	0.24	0.21
Gd ₂ O ₃	N.d.	0.18	0.30
Hf, ppm	N.d.	N.d.	167
Ta	N.d.	N.d.	500
Pb	2600	1100	1600
Bi	19	N.d.	N.d.
Th	N.d.	1000	2140
U	N.d.	100	95

Note. In this study REE₂O₃ is a sum of oxides of La, Ce, Pr, Nd, Sm, Gd, and Y. Hereafter: N.d., no data; dash, not determined.

* The content of the element (not its oxide) is given.

The pyrochlore group minerals are typical accessory minerals of carbonatites and different alkaline igneous rocks. In the Tomtor ores, pyrochlore is the major Nb mineral, as at many large deposits related to carbonatite massifs (Cordeiro et al., 2011). Pyrochlore group minerals have the general formula $A_{2-m}B_2O_6Y_{1-n}pH_2O$, where $A = \text{Na, Ca, Mn, Fe}^{2+}, \text{Sr, Ba, REE, Pb, Th, U, etc.}$, or vacancy; $B = \text{Nb, Ta, and Ti, Al, Si, Fe}^{3+}, \text{Zr, Sn, and W}$; $Y = \text{F, O, OH, or vacancy}$. Three main subgroups are recognized based on the proportion of elements at the B -site: pyrochlore ($\text{Nb} + \text{Ta} > 2\text{Ti}$, $\text{Nb} > \text{Ta}$), microlite ($\text{Nb} + \text{Ta} > 2\text{Ti}$, $\text{Ta} \geq \text{Nb}$), and betafite ($2\text{Ti} \geq \text{Nb} + \text{Ta}$) (Hogarth, 1977). The composition of the mineral is not constant. If the ratio of the major elements at the B -site ($\text{Nb}:\text{Ta}:\text{Ti}$) during different superposed processes remains close to the initial ratio, then the A -site is an open system. As a result of ion exchange processes and/or leaching, the original cations at the A -site are substituted by others. The A -site is characterized by almost continuous miscibility series between cations. Within the subgroups the name of the mineral was traditionally determined based on the predominant cation at that site (Hogarth, 1977, 1989). In the new classification, the mineral names were determined with regard not only to the predominant element at the A -site but also to the anion or vacancy at the Y -site (Atencio et al., 2010). The pyrochlore group minerals are characterized by reaction rims (sometimes, very complicated), in which minerals with different predominant elements at the A -site replace one another (Melgarejo et al., 2012). Such rims are a record of the geologic events following the mineral formation. The substitution of cations and anions in the pyrochlore structure was described in detail in (Lumpkin and Ewing, 1995), and conclusions were made on the possible physicochemical conditions of the alteration. Primary and secondary alteration was recognized, among which transitional and secondary reactions were distinguished. The first type consists in removal of Na from the structure, which is accompanied by the removal of F. In this case the vacancy at the A -site is partly replaced by Ba, Sr, Pb, REE, etc. The second type presupposes the removal of Ca from the structure (see below, pyrochlore II and III). Later on, these types were interpreted by some authors (Nasraoui and Bilal, 2000) as hydrothermal postmagmatic and supergene.

The pyrochlore group minerals in the ores from the northern part of the Buranniyi site occur as crystals with preserved original faces and isometric, xenomorphic, and conchoidal fragments (Fig. 9). The observed crystals are from 10 to 250 μm in size; most of them are strongly cracked owing to secondary alteration. Some crystals contain relics of original magmatic Na–Ca pyrochlore (Fig. 9a, b). These might be whole crystals with a core of original magmatic pyrochlore, and a reaction rim. Also, rounded fragments with a thin secondary rim which lost their crystallographic outlines are observed. In the latter case, the grains coexist with conchoidal fragments (Fig. 9a). Completely altered large crystals ($>200 \mu\text{m}$) retain their original shape, because the formed cavities and cracks are filled with cementing other minerals (Fig. 9c, d). Minerals of the crandallite group, pyrite, chalcopyrite, sphalerite, galena, vanadinite ($\text{Pb}_5(\text{VO}_4)_3\text{Cl}$), etc., evolve in the cavities independently or in assemblages.

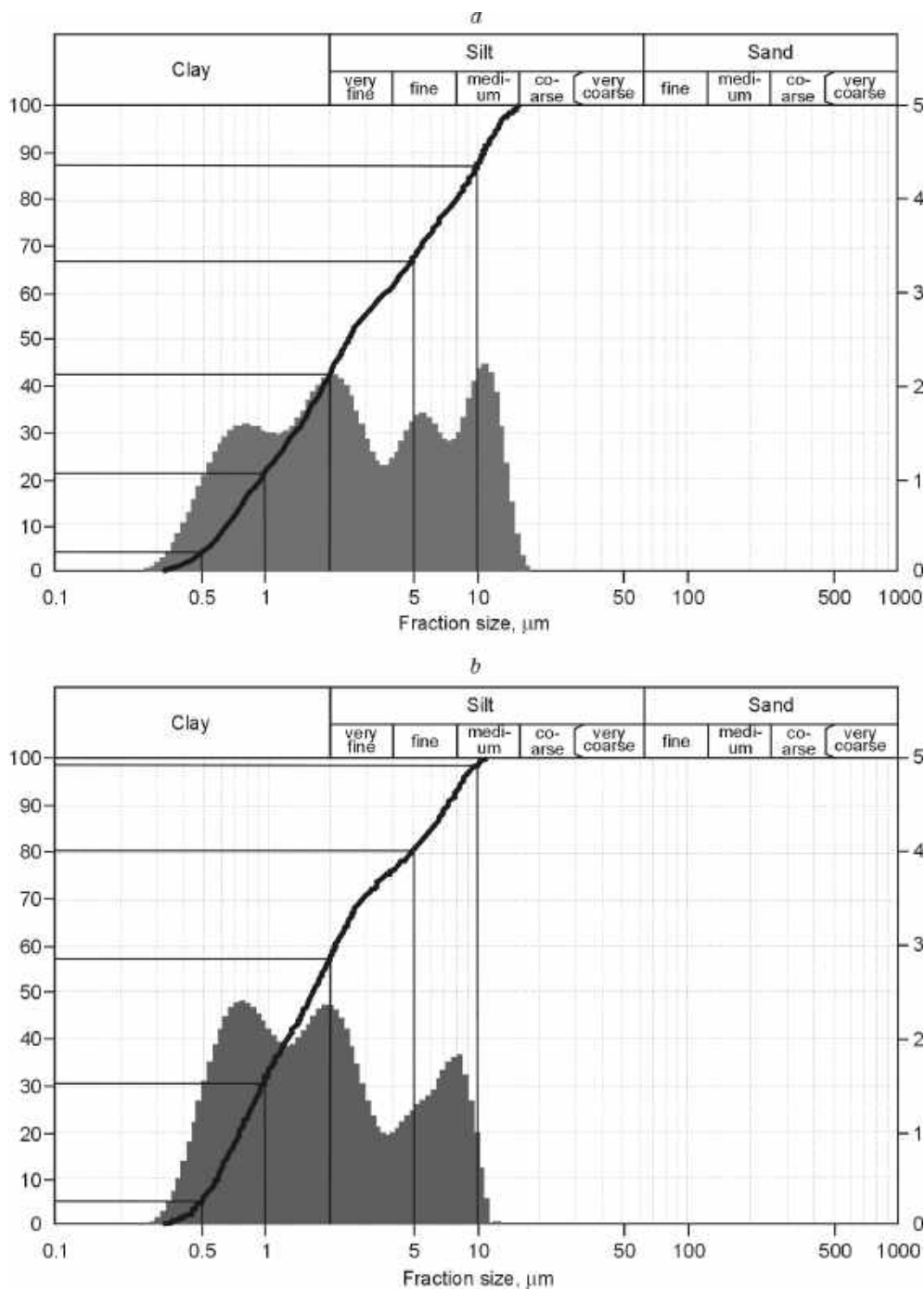


Fig. 7. Results of particle size analysis in ore from the Burannyi site, Tomtor deposit, using a Fritsch Analysette 22 MicroTec laser particle sizer by the standard technique (a) and with preliminary ultrasonication (b). Right vertical scale shows the percentage of fractions for the heavy line, whereas left scale shows the percentage of fractions for the histogram.

Smaller pyrochlore crystals are also cracked, but deposits of other minerals are rarely observed in the cavities (Fig. 9e, f).

In all analyzed pyrochlore samples, the B-site is occupied mainly by Nb (54.2–67.9 wt.% Nb₂O₅, 1.65–1.97 apfu). The second place is taken by Ti, whose content in some crystals reaches 4 wt.% TiO₂ (0.22 apfu). Some crystals contain considerable amounts of Zr (up to 3.8 wt.% ZrO₂, 0.04–0.13 apfu). The content of Fe₂O₃ in some crystals reaches 1.8 wt.%. The content of SiO₂ is no more than 0.4 wt.%,

usually 0.2 wt.%. Tantalum was not detected in any of the analyzed pyrochlore crystals.

Based on the predominant element at the A-site, three varieties of pyrochlore group minerals are recognized. Pyrochlore I is typical magmatic Ca–Na pyrochlore (Table 3), which occurs as relict zones in large crystals (Fig. 9b) or their fragments (Fig. 9a). The content of Na₂O in the mineral is slightly higher than 7 wt.%, which corresponds to 0.88–0.89 apfu, whereas CaO makes up ~10.8 wt.% (0.73–

Table 2. Contents of elements in different grain-size fractions of ore from the Tomtor deposit

Component	Fracton size						
	< 1	5–10	10–50	0.05–0.16	0.16–0.25	0.25–0.5	> 0.5
	μm			mm			
Ti, %	4.7	4.5	4.6	2.7	2.5	3.1	0.8
Fe	3.1	2.7	2.8	2.8	3.7	3.7	1.7
Zn, ppm	436	581	553	501	617	749	199
Sr, %	2.2	2.2	1.9	1.9	2.0	2.0	1.5
Y, ppm	5370	5580	4690	4500	5500	6800	1070
Zr	825	815	940	1145	850	955	805
Nb, %	2.2	2.5	3.5	4.5	1.0	2.8	4.0
La	3.8	3.5	3.9	2.4	3.3	3.7	0.6
Ce	6.9	6.1	7.3	4.1	6.0	7.8	1.4
Pb, ppm	1300	1400	1740	2440	2200	1300	1660
Th	1930	2010	1970	2075	1960	2230	1340
U	41	71	80	127	90	68	138

0.75 apfu). Only this pyrochlore variety has a high LREE content; Ce_2O_3 content reaches 8.29 wt.%, and LREE makes up 0.26 apfu (Table 3), and 0.11 apfu remains vacant. The Y-site is almost completely occupied by F. According to the classification from (Atencio et al., 2010), the mineral should be called “fluornatropyrochlore.”

Pyrochlore II and pyrochlore III occur in close association. These two varieties form pseudo-oscillatory zoning in reaction rims in all the grains under consideration (Fig. 9). At some places the zones are very thin (<0.5 μm), which complicates the analysis of both. Assuming similarity between the compo-

sitions of pyrochlore II and III, the grains were analyzed at the places where the width of the zones approached 1 μm. In both pyrochlores the A-site is almost half vacant and the second part is occupied mainly by Sr, Pb, and Ba in different proportions, which determines the difference between the compositions of pyrochlores II and III (Table 3).

Pyrochlore II has high Na and Ca contents, and the elements make up 0.31–0.50 and 0.12–0.46 apfu, respectively (Table 3). The predominant cation or the cation close to Na at the A-site is Sr (9.79–13.7 wt.%, 0.36–0.49 apfu), and the other components are $\text{BaO} = 3.38\text{--}6.64$ wt.% ($\text{Ba} = 0.08\text{--}$

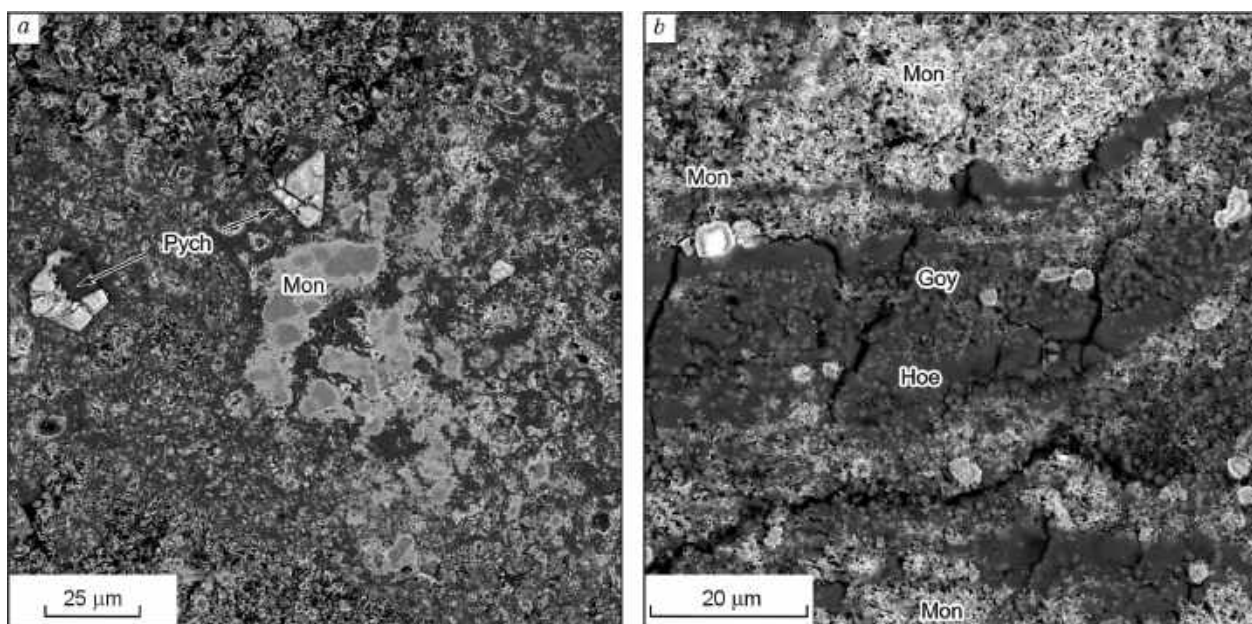


Fig. 8. Typical pyrochlore–monazite–crandallite ores of the Burannyi site, Tomtor deposit. *a*, Relict pyrochlore (Pych) crystals; *b*, monazite (Mon) aggregate, crandallite group minerals (in this case goyazite (Goy)) as colloform (And) globular segregations in a colloform goethite aggregate (Goe). *a*, Without visible layering; *b*, thin layering. Polished thin section, scanning microscope, BSE.

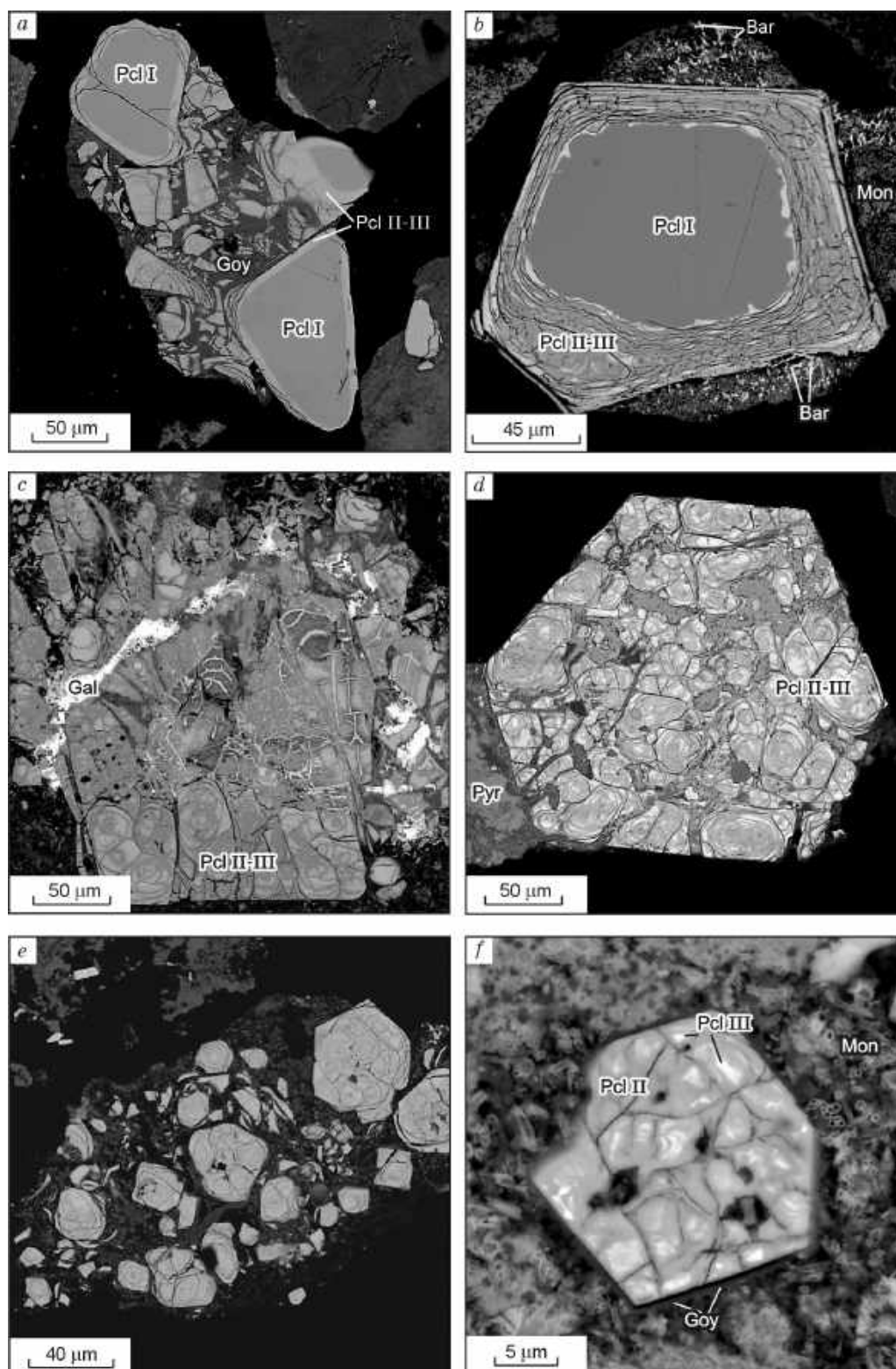


Fig. 9. Pyrochlore crystals from the high-grade ores of the northern part of the Burannyi site, Tomtor deposit. *a*, Fragments of pyrochlore I (Pcl I) crystals replaced by pyrochlore II and III (Pcl II and Pcl III) to a large extent or completely and cemented by goyazite; *b*, pyrochlore I crystal with a reaction rim of compositions II and III in monazite and barite (Bar); *c*, fragment of a pyrochlore crystal completely replaced by compositions II and III and cemented by later sulfides (galena (Gal) and pyrite (Pyr)); *d*, pyrochlore crystal completely replaced by compositions II and III and cemented by the minerals filling cracks (pyrite, chalcopyrite, sphalerite, and goyazite); *e*, pyrochlore crystal and fragments of crystals completely replaced by compositions II and III; *f*, small edged crystals of pyrochlore II and III in monazite and goyazite. Polished thin section, scanning microscope, BSE.

Table 3. Chemical compositions of minerals of the pyrochlore (I, II, and III) group in the Tomtor high-grade ores

Component	I	I	II	II	II	III	II	III	II	II	III	II	III
	1-1	1-2	1-3	2-1	3-1	3-2	4-1	4-2	5-1	6-1	6-2	7-1	7-2
Na ₂ O, wt. %	7.28	7.01	4.06	3.26	2.83	1.39	2.70	1.62	1.74	3.19	1.48	2.48	1.13
CaO	10.87	10.84	4.06	2.70	2.15	0.94	1.68	1.41	6.31	4.09	0.59	4.18	0.34
SrO	B.d.l.	B.d.l.	9.79	13.07	12.71	9.00	12.22	9.57	10.64	11.52	6.65	10.84	7.12
BaO	B.d.l.	B.d.l.	3.38	6.35	6.10	3.93	6.14	4.34	5.73	6.64	4.81	4.82	5.34
PbO	B.d.l.	B.d.l.	1.75	1.17	2.56	18.08	3.92	16.32	1.64	0.78	19.83	1.59	18.68
Ce ₂ O ₃	7.77	8.26	1.85	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	1.12	B.d.l.	B.d.l.	B.d.l.	B.d.l.
La ₂ O ₃	0.95	0.93	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	0.77	B.d.l.	B.d.l.	B.d.l.	B.d.l.
Pr ₂ O ₃	0.99	0.68	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.
Nd ₂ O ₃	1.92	1.26	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.
ThO ₂	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	0.63	B.d.l.	0.88	0.61	1.45
Nb ₂ O ₅	61.18	59.74	67.82	67.89	65.76	54.99	63.77	59.20	54.22	66.89	58.57	60.97	50.90
TiO ₂	3.64	3.47	B.d.l.	B.d.l.	2.19	3.97	0.83	3.12	2.99	2.57	2.50	2.49	2.47
ZrO ₂	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	1.69	3.20	N.d.	N.d.	1.30	3.38
Fe ₂ O ₃	1.83	1.76	0.89	0.67	0.83	0.80	0.59	0.53	1.86	B.d.l.	0.59	1.07	1.39
Al ₂ O ₃	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	0.23	0.94	B.d.l.	B.d.l.	B.d.l.	B.d.l.
F	4.59	4.84	3.42	3.50	3.16	2.10	3.26	2.22	3.48	4.25	2.11	2.4	0.77
Total	101.2	98.8	97.01	98.62	98.30	95.19	95.11	100.24	95.27	99.29	99.56	94.17	94.69
Structural formula <i>B</i> (Nb + Ti + Zr + Fe + Al) = 2													
Na, f.u.	0.89	0.88	0.50	0.41	0.34	0.19	0.35	0.21	0.23	0.39	0.20	0.31	0.16
Ca	0.73	0.75	0.28	0.19	0.14	0.07	0.12	0.10	0.46	0.27	0.04	0.29	0.03
Sr	–	–	0.36	0.49	0.46	0.37	0.47	0.37	0.42	0.42	0.27	0.41	0.30
Ba	–	–	0.08	0.16	0.15	0.11	0.16	0.11	0.15	0.16	0.13	0.12	0.15
Pb	–	–	0.03	0.02	0.04	0.34	0.07	0.29	0.03	0.01	0.37	0.03	0.37
Ce	0.18	0.20	0.04	–	–	–	–	–	0.03	–	–	0.00	0.00
La	0.02	0.02	–	–	–	–	–	–	0.02	0.00	–	0.00	0.00
Pr	0.02	0.02	–	–	–	–	–	–	–	0.00	–	0.00	0.00
Nd	0.04	0.03	–	–	–	–	–	–	–	0.00	–	0.00	0.00
Th	–	–	–	–	–	–	–	–	0.01	0.00	0.01	0.01	0.02
Σelements _A	1.89	1.89	1.30	1.26	1.14	1.08	1.18	1.07	1.33	1.25	1.03	1.17	1.03
A vacancy	0.11	0.11	0.70	0.74	0.86	0.92	0.82	0.93	0.67	0.75	0.97	0.83	0.97
Nb	1.74	1.75	1.96	1.97	1.86	1.75	1.93	1.76	1.65	1.88	1.84	1.79	1.67
Ti	0.17	0.17	–	–	0.10	0.21	0.04	0.15	0.15	0.12	0.13	0.12	0.13
Zr	–	–	–	–	–	–	–	0.05	0.11	0.00	–	0.04	0.12
Fe	0.09	0.09	0.04	0.03	0.04	0.04	0.03	0.03	0.09	0.00	0.03	0.05	0.08
Al	–	–	–	–	–	–	–	0.02	0.07	0.00	–	0.00	0.00
Σelements _B	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
F	0.91	0.99	0.69	0.71	0.62	0.47	0.69	0.46	0.74	0.84	0.46	0.49	0.18

Note. Hereafter: B.d.l., below detection limit. Grain numbers and spectra in the grains are in bold type. Exposure time is 30 s.

0.16 apfu) and PbO = 0.78–3.92 wt. % (Pb = 0.01–0.07 apfu). The vacancy makes up 0.64–0.75 apfu. With rare exceptions, the F content of the site *Y* remains high and usually equals at least 0.6 apfu. This variety can be called “barium–strontium pyrochlore,” according to the classification in (Hogarth, 1977), or “fluorstrontio-pyrochlore,” according to (Atencio et al., 2010).

In pyrochlore III, the contents of Na and Ca at the A-site are lower than in pyrochlore II, whereas the number of vacancies is larger. Sodium and calcium make up only 0.16–0.21 and 0.03–0.10 apfu. The highest Pb content at the A-site is PbO = 16.32–19.83 wt. % (Pb = 0.29–0.37 apfu); SrO = 6.65–9.57 wt. % (Sr = 0.27–0.37 apfu); and BaO = 3.93–5.34 wt. % (Ba = 0.11–0.15 apfu). Thus, the Sr and Pb

contents in atoms per formula units are almost equal. Pyrochlore III has the lowest F content, which equals mainly 0.47 apfu (sometimes, it decreases to 0.18). This variety can be called “strontio-plumbopyrochlore” (Hogarth, 1977) or “keno-plumbopyrochlore” (Atencio et al., 2010). Plumbopyrochlore is described in the alkaline rocks of the Kola Peninsula (Chakhmouradian and Mitchell, 2002) and in the carbonatites of Angola (Melgarejo et al., 2012), but their PbO contents (38 wt.%) are much higher than that in pyrochlore III from the Tomtor ores. It might be that, actually, an alternation of barium–strontium pyrochlore and plumbopyrochlore is observed and the zoning is too fine for their analytical discrimination.

The change in the ratio of the elements at the *B*-site in pyrochlore from the high-grade ores in the northern part of the Buranniy site of the Tomtor massif is described by two trends (Fig. 10a): Trend I corresponds to an increase in Ti content, whereas trend II corresponds to an increase in Ti and Zr contents. More detailed studies of magmatic pyrochlore from the Tomtor massif may show what rocks were the source of the identified mineral varieties.

The compositions of Tomtor pyrochlore in the three-component diagram Na–Ca–vacancy, which shows the ratio at the *A*-site, do not match the trends in the composition of magmatic pyrochlore which are described as transitional (trend III, Fig. 10b) and secondary (trend IV, Fig. 10b) (Lumpkin and Ewing, 1995; Nasraoui and Bilal, 2000). In the rims after pyrochlore at the *A*-site, high Na content is preserved; note that most of the *A*-site remains vacant or occupied by Sr, Pb, and Ba. In the reaction rims after Tomtor pyrochlore, the Ba/Sr ratio, actually, remains constant, whereas the Sr/Pb ratio changes (Fig. 10d), which is reflected in the zoning of varieties II and III. Comparison of the compositions with the trends for pyrochlore from the carbonatites of the Tchivira massif, Angola (Melgarejo et al., 2012), showed high convergence (Fig. 10c), though the cloud of compositions is displaced toward the peak Sr + Ba + Pb with respect to the trend formed in the diagram by pyrochlore with predominant Sr, which forms reaction rims. Based on the observed mineral assemblage, the authors define such replacement as caused by superposed hydrothermalism (Melgarejo et al., 2012). Not all authors explain the formation of pyrochlore with predominant Sr and Pb at the *A*-site in the same way, by supergene processes (Nasraoui and Bilal, 2000; Williams et al., 1997). A more justified hypothesis appears to be that such replacements are a result of hydrothermal alteration (Chakhmouradian and Williams, 2004; Melgarejo et al., 2012). Both views can be reconciled, because hydrothermalism is possible under surface conditions. That is how we explain the substitutions in pyrochlore from the Tomtor high-grade ores. The mineral assemblage in the cavities of pyrochlore crystals also confirms our hypotheses.

The pyrochlore crystals and fragments completely replaced by varieties II and III are more abundant than the crystals and grains with relics of magmatic pyrochlore. The presence of partly replaced crystals whose cracked parts are not cemented by later minerals (Fig. 9b) shows that those crystals did not move after the replacement and did not experience mechanical

destruction, which is inconsistent with the hypothesis of their mechanical redeposition. On the other hand, the total mass contains a considerable number of isometric fragments in association with conchoidal fragments (Fig. 9a,e), which testify to the mechanical destruction of partly or completely replaced pyrochlore crystals.

The crandallite group minerals, which belong to the alunite supergroup, have the general formula $AB_3(XO_4)_2 \cdot (OH)_6$, where *A* is a large cation (Na^+ , K^+ , Ag^+ , NH_4^+ , H_3O^+ , Ca^{2+} , Ba^{2+} , Sr^{2+} , Pb^{2+} , Ce^{3+} , and other REE). The *B*-site is occupied by Al^{3+} , Fe^{3+} , Cu^{2+} , or Zn^{2+} , whereas XO_4 is represented by PO_4^{3-} , SO_4^{2-} , and AsO_4^{3-} , which can be substituted by CO_3^{2-} , SbO_4^{3-} , CrO_4^{2-} , and SiO_4^{2-} (Dill, 2001; Jambor, 2000; Scott, 1987; Stoffregen and Alpers, 1987). Minerals with predominant SO_4 make up the alunite–jarosite group. Phosphates are assigned to the crandallite group, which includes crandallite ($CaHA_3(PO_4)_2(OH)_6$), goyazite ($SrHA_3(PO_4)_2(OH)_6$), gorceixite ($BaHA_3(PO_4)_2(OH)_6$), plumbogummite ($PbHA_3(PO_4)_2(OH)_6$), and florencite ($(REE)Al_3(PO_4)_2(OH)_6$, $-(Ce)$, $-(La)$, $-(Sm)$, $-(Nd)$). At the *A*-site, continuous miscibility series are observed between the elements. Crandallite group minerals are very widespread in different geologic environments and under different geologic conditions: postmagmatic, hydrothermal, diagenetic, weathering, and oxidation processes (Dill, 2001).

In the high-grade ores from the northern part of the Buranniy site, the crandallite group minerals seldom occur as single-mineral aggregates (Fig. 11a), but mainly exist in close association with other minerals (Fig. 11b–d). In most cases they occur as colloform segregations in fine layered polymineral material mainly of goethite and monazite-(Ce) (Figs. 8b, 11b). The segregations of crandallite group minerals are globules ~0.7 μm in diameter. The crandallite group minerals can coexist with a Ti–Nb mineral (presumably, ilmenorutile) and Y-phosphate (presumably, churchite) (Fig. 11c). Sometimes they form pseudomorphs around pyrochlore crystals (Fig. 9f) or fill cracks (Fig. 9b, c), where they occur independently or as inclusions in later sulfides (Fig. 9b). Alteration structures filled with crandallite group minerals after other minerals are rarely observed (Fig. 11d). A corroded grain was detected among these pseudomorphs; analysis showed that it was rhabdophane ($Ca,L_aPO_4(H_2O)$), which, most likely, replaced monazite (Fig. 11d).

It was a challenge to obtain reliable information on the chemical composition of the crandallite group minerals. Some grains are very small. Single-mineral aggregates are very rare and extremely porous (Fig. 11a). As a rule, the crandallite group minerals are aggregated with other minerals. Nevertheless, some analyses are perfectly consistent with the composition of crandallite group minerals (Table 4). Some “grains” contain (wt.%) Mn (≤0.09), Ti (≤2.71), V (≤1), Nb (≤2.37), Zr (≤1), Na (≤0.55), Y (≤3.78), Pb (≤1.78), and Sc (≤0.05) impurities. These elements were not included in the calculation of the formula, because their presence is mostly due to association with micro- or nanosized Ti, Nb, and Zr or by sorption processes. Owing to the complicated character of the analysis and the presence of $(OH)_n$, it was rarely possible to

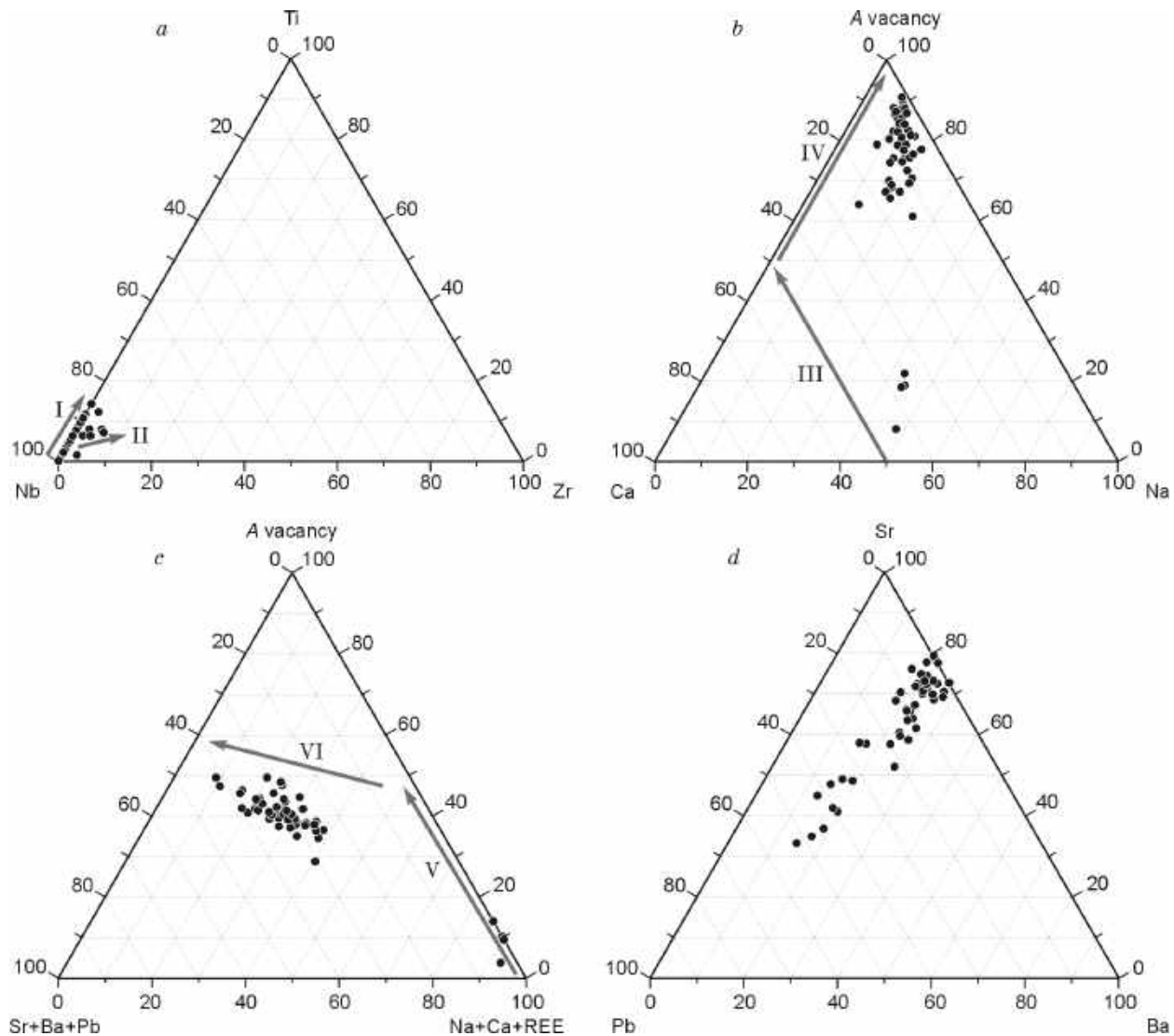


Fig. 10. Compositions of pyrochlore from the Tomtor high-grade ores. *a*, Relative contents of Nb, Ti, and Zr at the *B*-site, trends I and II, see text for explanation; *b*, comparison of the pyrochlore compositions with the trends of transitional (hydrothermal postmagmatic) (III) and secondary (supergene) (IV) substitutions (Lumpkin and Ewing, 1995; Nasraoui and Bilal, 2000); *c*, comparison of the pyrochlore compositions with the trends of substitutions regarded for pyrochlore from the carbonatites of the Tchivira massif as postmagmatic (V) and hydrothermal (VI), which cause the formation of strontipyrochlore (Melgarejo et al., 2012); *d*, Sr, Ba, and Pb in pyrochlore.

obtain a good sum; therefore, contents are quoted in apfu rather than in wt.%.

At the *X*-site, P (from 1.95 to 2.00 apfu) strongly dominates over S (Table 4). At the *B*-site, in all the analyzed cases, Al dominates over Fe (Fe content is from 0.07 to 0.47 apfu) (Table 4). At the *A*-site, the largest portion belongs to Sr. The portion of goyazite varies from 21 to 52%, averaging 36.5% (Fig. 12, Table 4). Goyazite predominates in 29 of 38 samples under study. The second important end-member is florencite; its content varies from 17 to 38%, averaging at 26.5% (Fig. 12). Florencite predominates in only four of 38 cases. The third important end-member is crandallite; its content varies from 7.7 to 34.5%, averaging 22.7% (Table 4). Crandallite predominates in 5 of 38 cases. The least important end-member is gorceixite, varying from 8 to 19%, averaging 14% (Fig. 12). These results permit calling the mineral

“goyazite,” which is confirmed by XRD. The F content in some samples reached 1 apfu (Table 4).

The morphology of goyazite testifies to its supergene sedimentary origin. We discuss in the final part of the paper whether it was a hydrothermal–sedimentary or biogenic–sedimentary process.

Monazite group. Monazite is a phosphate of REE (predominantly, LREE), $(\text{La-Gd})(\text{PO}_4)$. Depending on the predominant element, the following varieties are recognized: monazite-Ce, monazite-La, monazite-Nd, and monazite-Sm. Since monazite group minerals are geologically and economically significant, a great number of research works and overviews have been published on this subject (Mariano, 1989; Ni et al., 1995; Rosenblum and Mosier, 1983; Smith and Barreiro, 1990; Spear and Pyle, 2002). The minerals are widespread in different rocks, and, owing to high U and Th

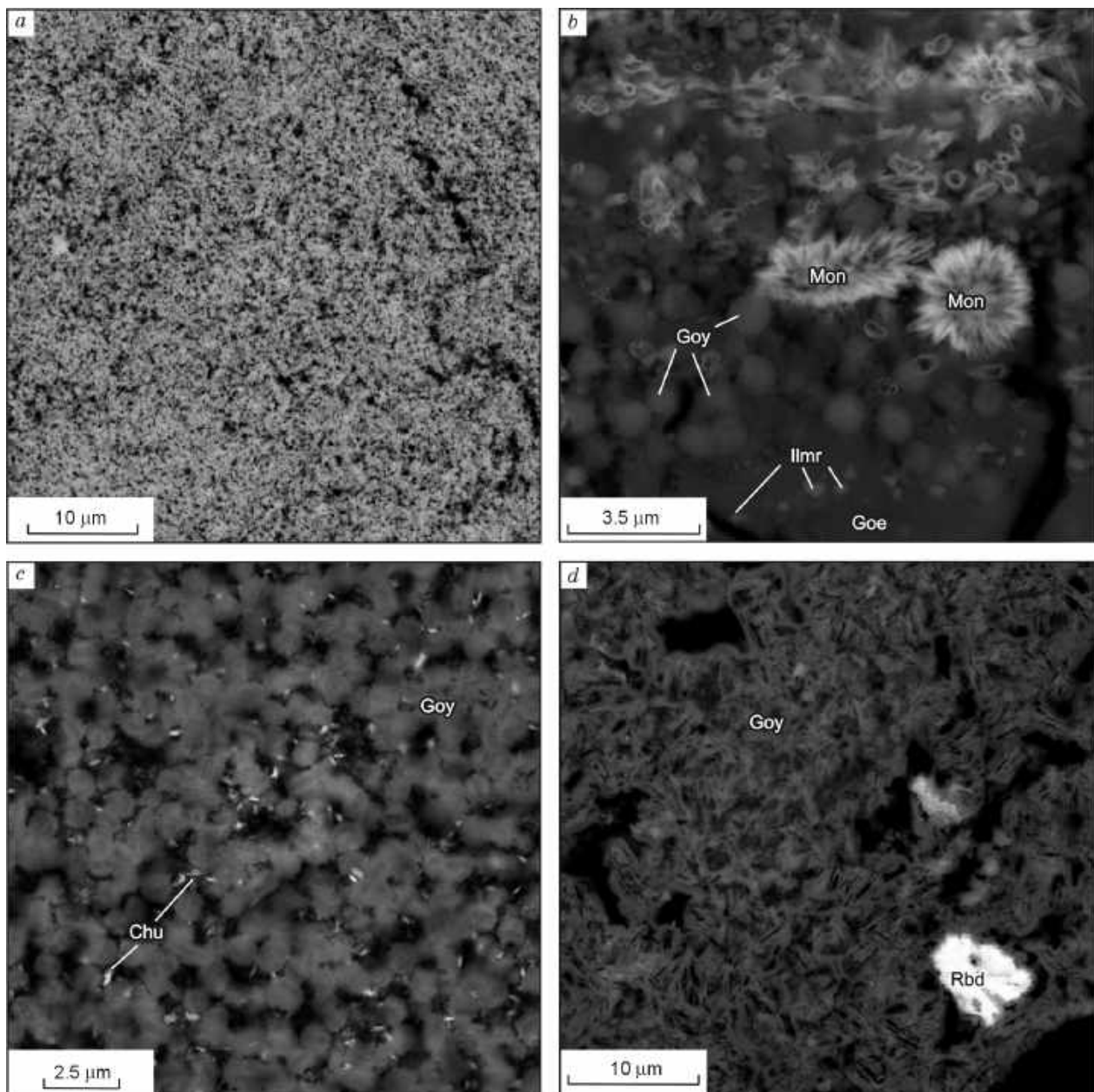


Fig. 11. Crandallite group minerals from the Tomtor high-grade ores. *a*, Continuous goyazite field; *b*, globular goyazite segregations in a layered structure composed of goethite (Goe) and monazite-Ce; light zone in goethite is a Ti-Nb mineral (presumably, ilmenorutile (Ilmr)); *c*, goyazite with Y-phosphate (presumably, churchite $\text{YPO}_4 \cdot 2\text{H}_2\text{O}$ (churchite-y, Chu)); *d*, substitution structures, with corroded grains of rhabdophane $(\text{Ce,Lu})\text{PO}_4(\text{H}_2\text{O})$ (Rbd) and goyazite pseudomorphs after monazite. Polished thin section, scanning microscope, BSE.

contents, they are widely used as isomorphous impurity for U/Pb and Th/Pb dating (Catlos, 2013; Harrison et al., 2002; Montel et al., 1996; Parrish, 1990; Williams et al., 2007). Commercial contents of monazite as a rock-forming mineral are known in alkaline rocks and carbonatites.

Owing to resistance to weathering, large monazite placers are known (Dill et al., 2012; Nash, 1984; Overstreet, 1967; Rosenblum and Mosier, 1983). Monazite group minerals also form in hydrothermal veins and hydrothermally altered rocks. Supergene monazites are observed in laterite after carbonatites, in which they form large commercial accumulations (Mariano, 1989) (e.g., in massifs: Mt. Weld, Australia (Lot-

termoser, 1988); Araxá and Catalão I, Brazil (de Toledo et al., 2004; Mariano, 1989); the Poços de Caldas alkaline complex, Brazil (Waber, 1992); Mrima Hill, Kenya (Castor and Hedrick, 2006; McKie, 1962; Onuonga and Bowden, 2000); and Mabouni, Gabon, Africa (Mariano and Mariano, 2012). Supergene monazites were detected as earthy aggregates of euhedral crystals from 1 to 10 µm in size (Mariano, 1989; Waber, 1992). The geologic settings and mineral and geochemical features reported in the cited papers are very similar to those observed in the Tomtor massif.

In the northern part of the Buranniyi site, monazite-Ce was detected, whose segregations have a very characteristic ap-

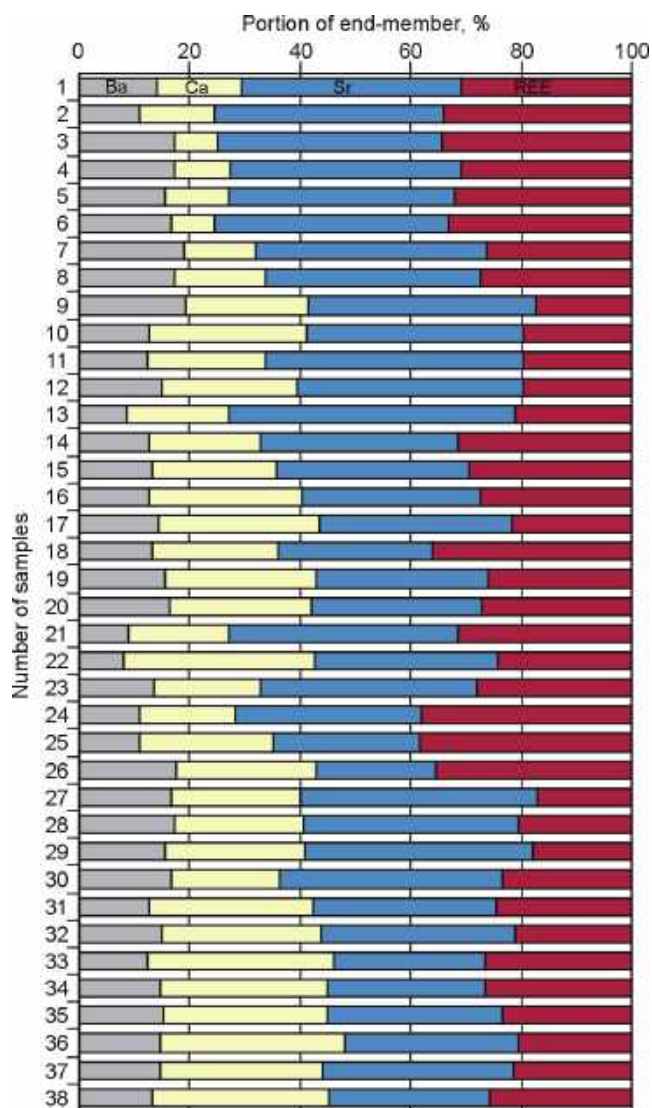


Fig. 12. Composition of a crandallite group mineral from the high-grade ores of the northern part of the Burany site, Tomtor massif. Ba—Portion of the goerxite end-member $\text{BaAl}_3(\text{PO}_4)_2(\text{OH})_6$; Ca—portion of the crandallite end-member $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_6$; Sr—portion of the goyazite end-member $\text{SrAl}_3(\text{PO}_4)_2(\text{OH})_6$; REE—portion of the florencite end-member $(\text{REE})\text{Al}_3(\text{PO}_4)_2(\text{OH})_6$.

pearance. Aggregates consisting of hollow calibrated tubes 800–1200 nm in length and 300 nm in diameter (Fig. 13) are observed everywhere. The most widespread aggregates are beautiful spherulitic aggregates resembling biomorphic structures, in which the monazite tubes diverge from a single center (Fig. 13c) or make up a ring with a hollow center (Fig. 13b, d). Less often, the monazite tubes overgrow plates or needles of an unpreserved object in the same way (Fig. 13e). The tubes are either aligned (Fig. 13f) or randomly oriented (Fig. 13h, i). Sometimes the tubes overgrow irregularly shaped fragments which also consist of rare-earth phosphate (Fig. 13h). The walls of the tubes are either very thin, so that the aggregate looks light (Fig. 13b, i), or thick (Fig. 13d, e, h); rare accumulations of thick tubes form aggregates looking like a single mass (Fig. 13h). Figure 13d shows aggregates in which the inner part of the tube is thicker looking like a denser ring

inside a lacy one, making the aggregate absolutely similar to a flower.

In all this variety of “tubular” aggregates, rare monazite-Ce segregations of a different shape are observed. An aggregate was detected with distinct short-prismatic grains from 200 to 500 nm in length (Fig. 13i). Sometimes monazite-Ce forms absolutely exotic zonal microsegregations (Fig. 13j) or oval segregations. Figure 11d shows a corroded grain, which, judging by the results of analysis, consists of rhabdophane $((\text{Ce}, \text{La})\text{PO}_4\text{H}_2\text{O})$. The appearance of the grain and its coexistence with a goyazite aggregate replacing an unknown mineral suggests that it is monazite substituted by rhabdophane.

The composition of monazite-Ce in such heterogeneous porous aggregates is extremely hard to analyze. Eventually, a few zones with the densest texture were detected, and satisfactory results were obtained (Table 5). The content of Ce_2O_3 varies from 26 to 31 wt.% (from 0.36 to 0.4 apfu Ce) (Table 5). The content of La_2O_3 varies from 12.4 to 20.95 wt.% (0.16–0.27 apfu La). The content of Nd_2O_3 is high, 4.58–9.83 wt.% (from 0.06 to 0.13 apfu Nd). The content of the oxides of other REE is <0.7 wt.% or, often, below the detection limit (Table 5). Note that a considerable Eu_2O_3 content (up to 0.25 wt.%) is observed in some grains as the spectrum accumulation time increases to 150 s. The content of Th in monazite is not constant; it is usually below the detection limit but reaches 1 wt.% in some places. Along with REE, the analysis of the mineral shows Ca, Ba, Sr, Fe, Al, Ti, and Si (Table 5). The content of the S admixture in the mineral is very low, no more than 0.75 wt.%. F impurity (up to 1 wt.%) is often detected.

The observed forms of monazite-Ce are similar to bacteriomorphic structures consisting of rare-earth phosphates which were obtained in laboratory experiments on precipitation of La and Ce by microorganisms (Fig. 14) (Jiang et al., 2010; Kazy et al., 2006; Langley and Beveridge, 1999; Mullen et al., 1989). The hypothesis that these tubes are sheaths on microorganism cells determined the subsequent direction of studies.

The morphology of the monazite tubes was determined by transmission electron microscopy. Studies of samples prepared without ultrasonication showed that the tubes were a complicated aggregate (Fig. 15). Short-prismatic isometric grains of monazite-Ce, no more than 50 nm in length, are irregularly located on a tube of different composition (Fig. 15). For a more detailed study of the composition of the tube, the samples were placed on a substrate with the use of a sonicator.

As a result of the ultrasonic exposure, the monazite grains easily separated from the tubes, which consist of aluminum silicate with Fe and Mn impurities (Fig. 16a, b). The Al and Si contents in the mineral turned out to be equal (Fig. 16c). The mineral looked amorphous in FFT images (Fig. 16f), but the Al–Si composition and the tubular shapes indicated that it may be halloysite.

The subsequent identification of the mineral was carried out by X-ray phase analysis. It appeared impossible to identify a minor content of a clay mineral in the diffraction patterns for the ore samples behind the peaks of monazite, pyrochlore,

Table 4. Chemical compositions of crandallite group minerals in the Tomtor high-grade ores

Component	1	2	3	4	5	6	7	8	9	10
	Exposure time, s									
	30	30	30	30	30	30	30	30	150	150
CaO, wt. %	1.86	1.62	0.90	0.91	2.27	2.27	2.28	3.22	2.69	2.83
SrO	7.00	7.78	8.62	9.22	7.83	7.05	7.52	7.24	7.04	6.67
BaO	3.54	4.08	5.44	5.39	5.37	3.80	3.94	4.52	3.78	3.63
Ce ₂ O ₃	4.66	4.87	6.41	5.91	2.93	2.58	4.30	3.44	4.90	4.33
La ₂ O ₃	1.82	3.72	4.23	4.00	2.19	2.12	5.32	2.65	5.21	2.79
Pr ₂ O ₃	B.d.l.	B.d.l.	B.d.l.	0.74	B.d.l.	B.d.l.	B.d.l.	B.d.l.	0.34	0.29
Nd ₂ O ₃	1.40	0.99	0.84	0.76	B.d.l.	0.63	0.82	0.72	1.03	0.91
Al ₂ O ₃	26.05	25.69	28.45	28.16	25.88	24.46	27.32	27.66	31.14	26.74
Fe ₂ O ₃	2.06	4.69	1.62	1.10	4.20	6.42	2.13	3.22	2.27	3.32
P ₂ O ₅	23.35	24.86	26.35	27.02	25.18	23.56	26.88	26.64	28.07	25.62
SiO ₂	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	B.d.l.	0.50	B.d.l.	0.37	0.50
SO ₃	0.43	0.33	B.d.l.	B.d.l.	0.65	0.70	B.d.l.	B.d.l.	B.d.l.	B.d.l.
F	B.d.l.	B.d.l.	1.26	B.d.l.	B.d.l.	2.82	B.d.l.	2.28	2.46	3.51
Total	72.17	78.63	84.12	83.21	76.50	76.41	81.01	81.59	89.30	81.14
Structural formula X(P + S + Si) = 2										
Ca, f.un.	0.20	0.16	0.09	0.09	0.22	0.24	0.21	0.31	0.24	0.27
Sr	0.40	0.42	0.45	0.47	0.42	0.40	0.38	0.37	0.34	0.35
Ba	0.14	0.15	0.19	0.18	0.19	0.15	0.13	0.16	0.12	0.13
Ce	0.17	0.17	0.21	0.19	0.10	0.09	0.14	0.11	0.15	0.14
La	0.07	0.13	0.14	0.13	0.07	0.08	0.17	0.09	0.16	0.09
Pr	–	–	–	0.02	–	–	–	–	0.01	0.01
Nd	0.05	0.03	0.03	0.02	–	0.02	0.03	0.02	0.03	0.03
Al	3.01	2.80	2.96	2.86	2.75	2.77	2.73	2.85	2.99	2.80
Fe	0.15	0.33	0.11	0.07	0.29	0.47	0.14	0.21	0.14	0.23
P	1.97	1.98	2.00	2.00	1.96	1.95	1.96	2.00	1.97	1.96
Si	–	–	–	–	–	–	0.04	–	0.03	0.04
S	0.03	0.02	–	–	0.04	0.05	–	–	–	–
F	–	–	0.36	–	–	0.87	–	0.73	0.64	1.00
Crandallite, %	19.3	15.3	7.8	7.7	22.2	24.4	20.1	28.94	22.76	26.64
Goyazite	39.3	39.7	40.7	42.4	41.4	41.1	35.8	35.23	32.27	34.03
Gorceixite	13.4	14.1	17.3	16.7	19.2	14.9	12.7	14.87	11.73	12.51
Florencite	27.9	30.9	34.2	33.1	17.2	19.6	31.4	20.96	33.24	26.82

Note. 1, Fig. 12a; 3, 4, Fig. 12d.

and goyazite; therefore, additional studies of the fraction 5–10 μm , obtained by the decantation of material were required. Along with those of well-defined monazite and goethite, the diffraction pattern shows peaks testifying to the presence of halloysite (Fig. 17).

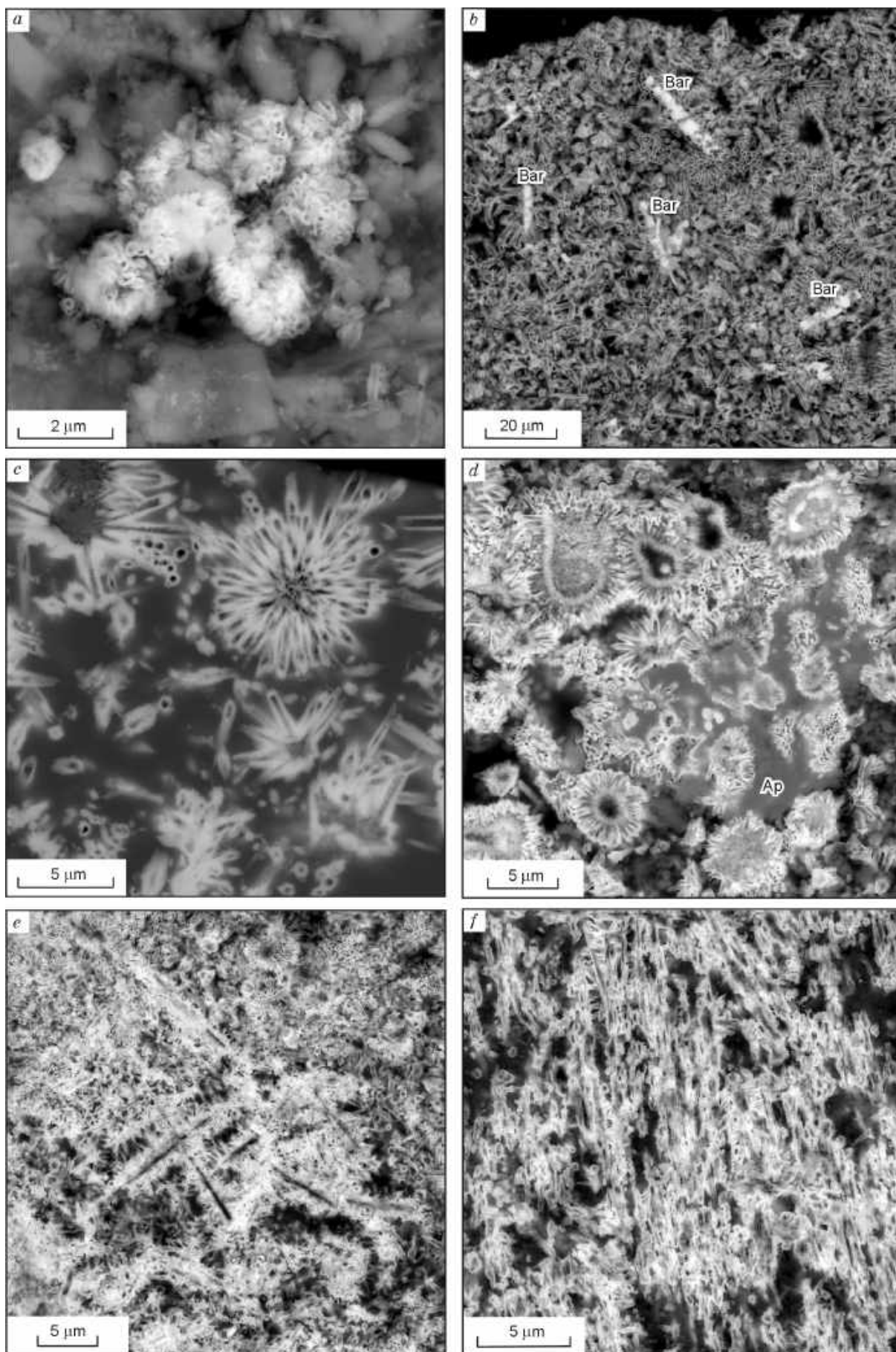
Halloysite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4n\text{H}_2\text{O}$, where $n = 0$ or 2) occupies a special position among clay minerals. The extensive overview (Joussein et al., 2005) summarized the information obtained by different researchers on the genesis, forms, and chemistry of the mineral and the ways of its identification.

Halloysite is widespread in different supergene environments: It is produced by weathering and low-temperature hydrothermal alteration of rocks (most often, in the case of weathering of alkaline ultramafic and mafic rocks, including volcanics). The mineral is detected in karst deposits, in which it forms owing to chemical weathering or low-temperature hydrothermal alteration. It is known to form under marine conditions, but these cases are usually also related to deep-water hydrothermal activity. The mineral is observed in laterite which form in humid climates. Based on the structural characteristics

Table 5. Compositions of monazite-Ce and rhabdophane from the Tomtor high-grade ores

Component	1	2	3	4	5	6	7	8
Exposure time, s								
	30	30	150	150	150	30	150	30
SiO ₂	B.d.l.	B.d.l.	0.39	0.30	0.22	0.50	0.37	0.51
TiO ₂	B.d.l.	B.d.l.	0.25	B.d.l.	0.52	B.d.l.	B.d.l.	B.d.l.
Al ₂ O ₃	B.d.l.	B.d.l.	0.12	0.13	0.42	1.77	0.13	2.72
Fe ₂ O ₃	1.77	1.39	1.02	0.80	0.73	1.87	0.66	B.d.l.
CaO	3.71	3.96	4.28	3.97	2.73	2.46	1.39	1.29
BaO	1.36	1.38	B.d.l.	1.32	B.d.l.	1.83	0.60	1.02
SrO	1.14	1.25	1.43	1.10	1.58	1.64	2.20	2.53
Ce ₂ O ₃	31.19	26.33	31.96	26.75	26.46	22.55	30.98	27.99
La ₂ O ₃	14.07	17.46	12.42	20.95	13.39	15.07	16.44	12.35
Pr ₂ O ₃	2.19	2.62	1.88	1.65	2.31	2.34	3.19	2.49
Nd ₂ O ₃	6.81	8.58	6.03	4.58	7.14	8.05	9.83	8.48
Sm ₂ O ₃	B.d.l.	B.d.l.	0.27	0.48	0.64	B.d.l.	0.46	B.d.l.
Eu ₂ O ₃	B.d.l.	B.d.l.	B.d.l.	0.25	B.d.l.	B.d.l.	B.d.l.	B.d.l.
Gd ₂ O ₃	B.d.l.	B.d.l.	B.d.l.	0.41	0.68	B.d.l.	B.d.l.	B.d.l.
Tb ₂ O ₃	B.d.l.	B.d.l.	B.d.l.	0.37	0.46	B.d.l.	B.d.l.	B.d.l.
Dy ₂ O ₃	B.d.l.	B.d.l.	B.d.l.	0.31	0.56	B.d.l.	B.d.l.	B.d.l.
ThO ₂	B.d.l.	B.d.l.	B.d.l.	B.d.l.	0.18	B.d.l.	1.02	0.84
P ₂ O ₅	28.62	28.18	28.99	28.51	27.91	26.56	32.35	27.38
SO ₃	B.d.l.	B.d.l.	B.d.l.	0.13	0.25	0.75	0.25	B.d.l.
F	B.d.l.	1.05	0.27	0.77	B.d.l.	0.68	0.46	B.d.l.
Total	90.9	91.2	89.5	92.8	86.9	85.9	99.9	86.6
Structural formula O = 4								
Si, f.un.	–	–	0.01	0.01	0.01	0.02	0.01	0.02
Ti	–	–	0.01	–	0.02	–	–	–
Al	–	–	0.005	0.01	0.02	0.09	0.01	0.14
Fe	0.05	0.04	0.03	0.02	0.02	0.06	0.02	–
Ca	0.16	0.18	0.16	0.17	0.12	0.12	0.05	0.06
Ba	0.02	0.02	–	0.02	–	0.03	0.01	0.02
Sr	0.03	0.03	0.03	0.02	0.04	0.04	0.05	0.06
Ce	0.46	0.40	0.40	0.38	0.38	0.36	0.40	0.43
La	0.21	0.27	0.16	0.30	0.19	0.24	0.21	0.19
Pr	0.03	0.04	0.02	0.02	0.03	0.04	0.04	0.04
Nd	0.10	0.13	0.07	0.06	0.10	0.13	0.12	0.13
Sm	–	–	0.003	0.003	0.01	–	0.01	–
Eu	–	–	–	0.00	–	–	–	–
Gd	–	–	–	0.005	0.009	–	–	–
Tb	–	–	–	0.005	0.006	–	–	–
Dy	–	–	–	0.004	0.007	–	–	–
Th	–	–	–	–	0.002	–	0.01	0.01
P	0.98	1.00	0.84	0.94	0.93	0.98	0.97	0.98
S	–	–	–	0.004	0.01	0.02	0.01	–
F	–	0.14	0.03	0.10	–	0.09	0.05	–

Note. 1, Fig. 13c; 4, Fig. 13g; 5, Fig. 13h; 6, Fig. 13d; 7, Fig. 13i; 8, Fig. 10d. 1–7, monazite-Ce; 8, rhabdophane.



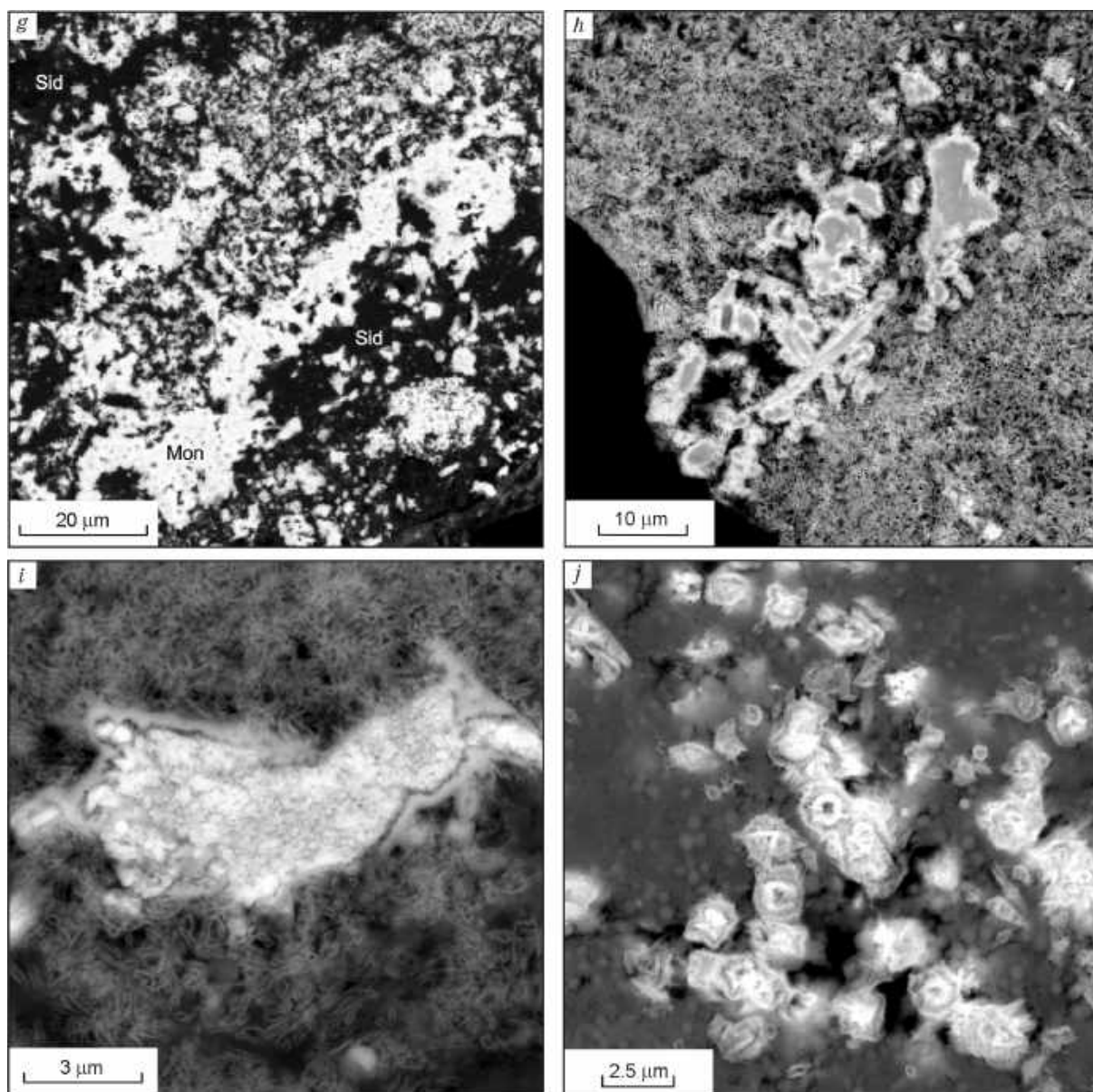


Fig. 13. Forms of monazite in ores from the northern part of the Burannyi site: *a*, Aggregate of hollow monazite tubes; *b*, barite metacrysts in the aggregate of monazite tubes; *c*, aggregate of monazite tubes diverging from the center; *d*, aggregate of monazite tubes of different thicknesses, cemented by apatite (Ap); *e*, monazite tubes overgrow a tabular object, which was not preserved; *f*, aggregate of aligned monazite tubes; *g*, monazite tubes with such thick walls that the aggregate looks almost solid in association with siderite (Sid); *h*, thick monazite tubes overgrow rare-earth phosphate; *i*, monazite aggregate consisting of short-prismatic grains in a lacy aggregate of monazite tubes; *j*, complicated zonal monazite segregations. Photo with the use of a scanning microscope, BSE; *a*, Unpolished sample; all others are polished sections.

related to the hydration of the mineral, halloysite-10 Å (hydrated) and halloysite-7 Å (dehydrated) are distinguished (Churchman and Carr, 1972, 1975). Bound water can be replaced by organic molecules with the formation of organomineral complexes. Halloysite particles can be tabular, globular, and tubular (the most widespread), but they are rarely >0.5 µm in size in the former case and 1 µm in the latter. Attempts of synthesizing this mineral in laboratory experiment have failed.

Although halloysite is applied as the main component of antimicrobials owing to its unique sorption capacity (Barr,

1957; Barr and Arnista, 1957a,b; Carroll, 1958; Chen et al., 2012; Kulok et al., 2005; Smith, 2005), it is hypothesized in the literature that the formation of clay minerals (Ueshima and Tazaki, 2001), including halloysite, in soils, laterite, karst, etc., may be due to microbial activity (Cunningham et al., 1995; Folk and Lynch, 1997; Minyard et al., 2011). Originally, this hypothesis was based on numerous observations of natural interaction between clay minerals and microorganisms. Japanese researchers (Asada and Tazaki, 2000; Tazaki, 1997, 2000; Ueshima et al., 2000) recorded cases of biomineralization of living cells of microorganisms with kaolinite, nontronite, and

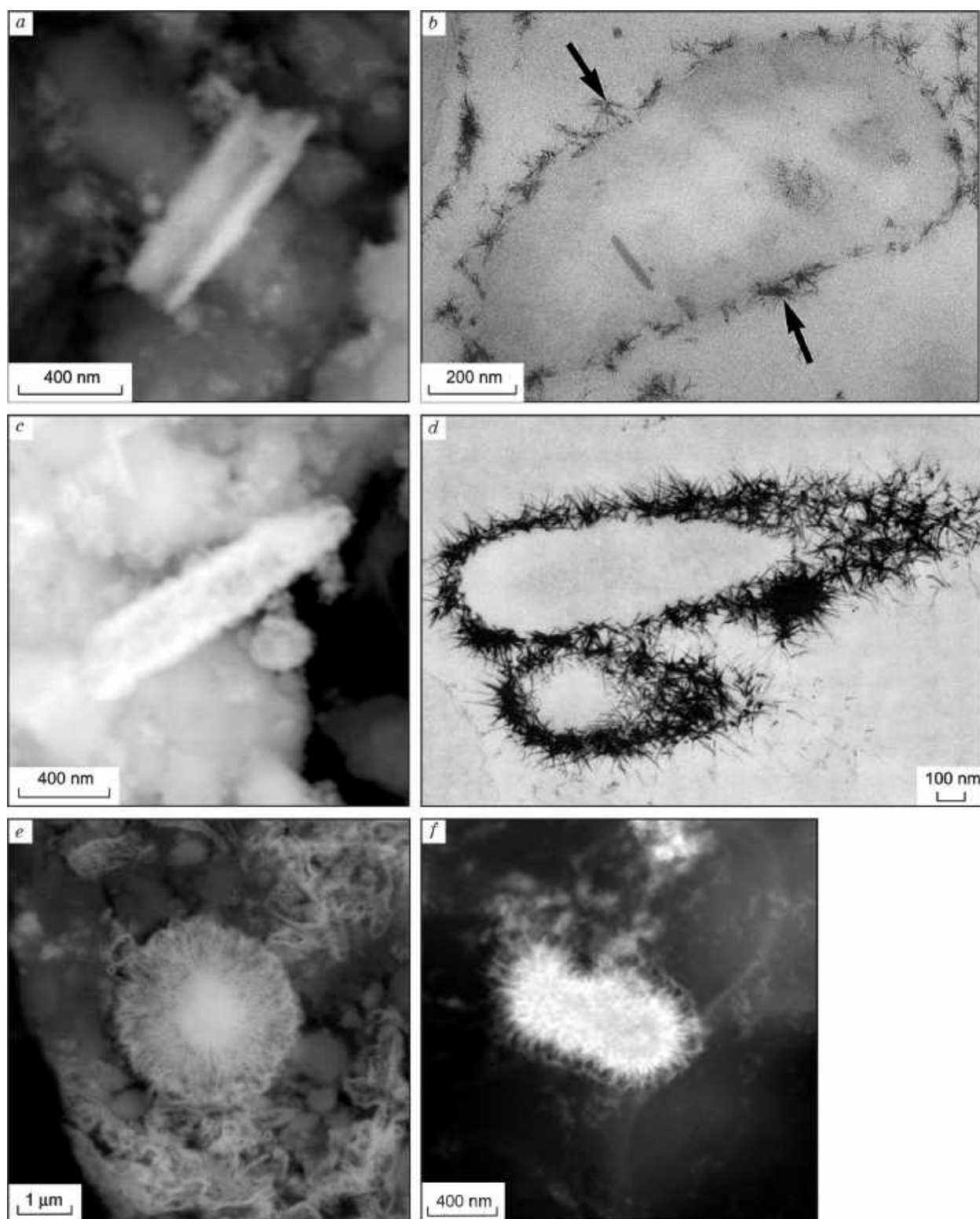


Fig. 14. Comparison of the forms of monazite from the high-grade ores of the Burannyi site, Tomtor deposit (a, c, e), with pseudomorphs of lanthanum phosphate after the *Pseudomonas aeruginosa* cells obtained in a laboratory experiment (b, d) and the cerium phosphate aggregate produced by precipitation of Ce by the bacteria *Saccharomyces cerevisiae* (f). b, (Langley and Beveridge, 1999); d, (Mullen et al., 1989); f, (Jiang et al., 2010).

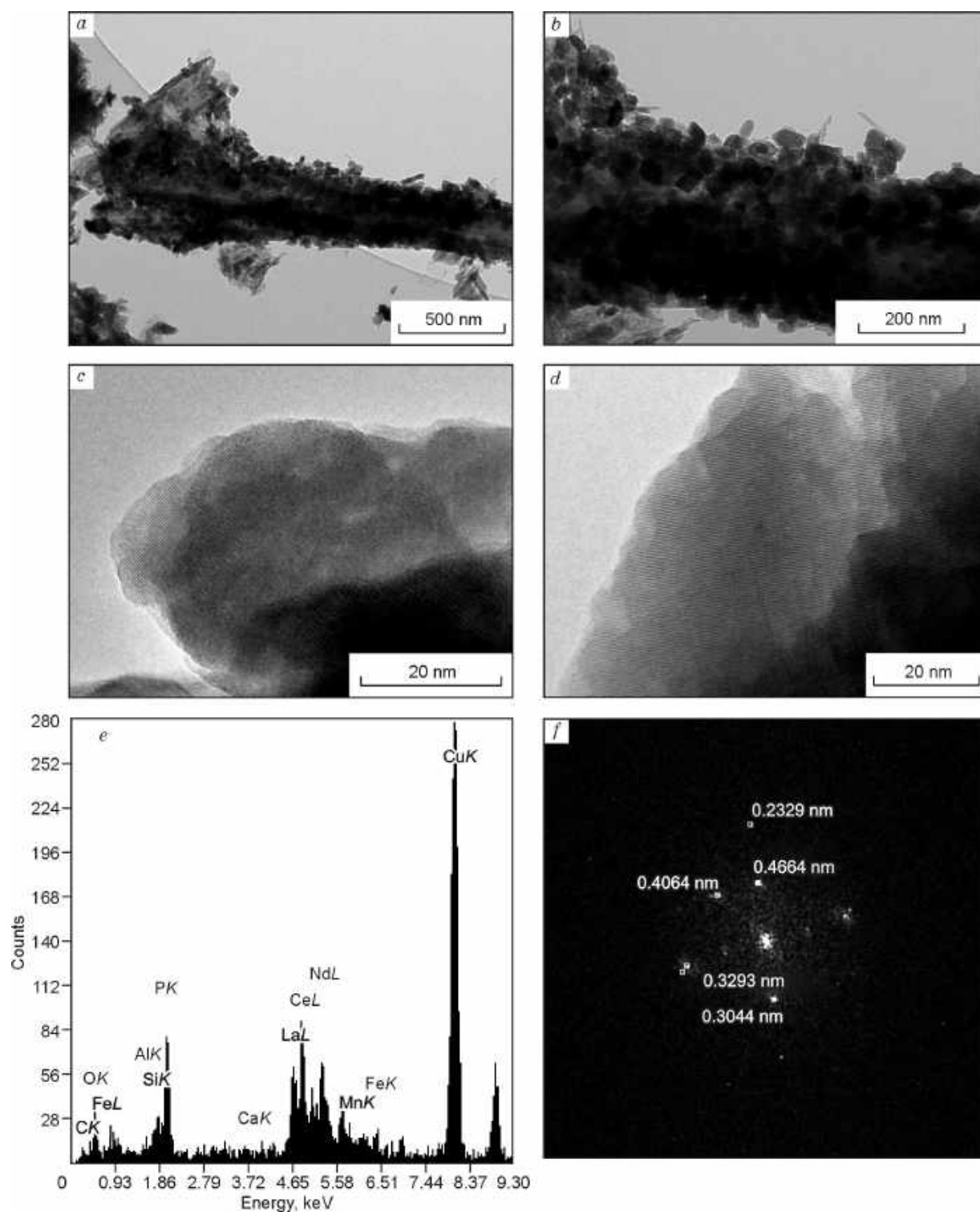


Fig. 15. Monazite nanocrystals chaotically cover a tube consisting of a different mineral. *a, b*, Aggregate at different magnifications; *c, d*, monazite grains; *e*, EDX spectrum for monazite particle; *f*, FFT image obtained from Fig. 15e, diffraction pattern corresponds to monazite-Ce ((Ce,La,Nd)PO₄). Transmission electron microscope.

bentonite. Experimental studies (Tazaki, 2005) showed the formation of a mineral similar to globular halloysite on cell walls, for which the name “biohalloysite” was proposed. Also, laboratory experiments with the participation of bacteria yielded prismatic and tubular varieties of halloysite, which

form during alteration of K-feldspar in the presence of cyanobacteria *Phormidium* sp. (Tazaki, 2006). It was shown that supergene alteration of volcanics proceeds with active participation of globular and rod-like bacteria, whose interaction with the rocks gave rise to clay minerals, including tubular

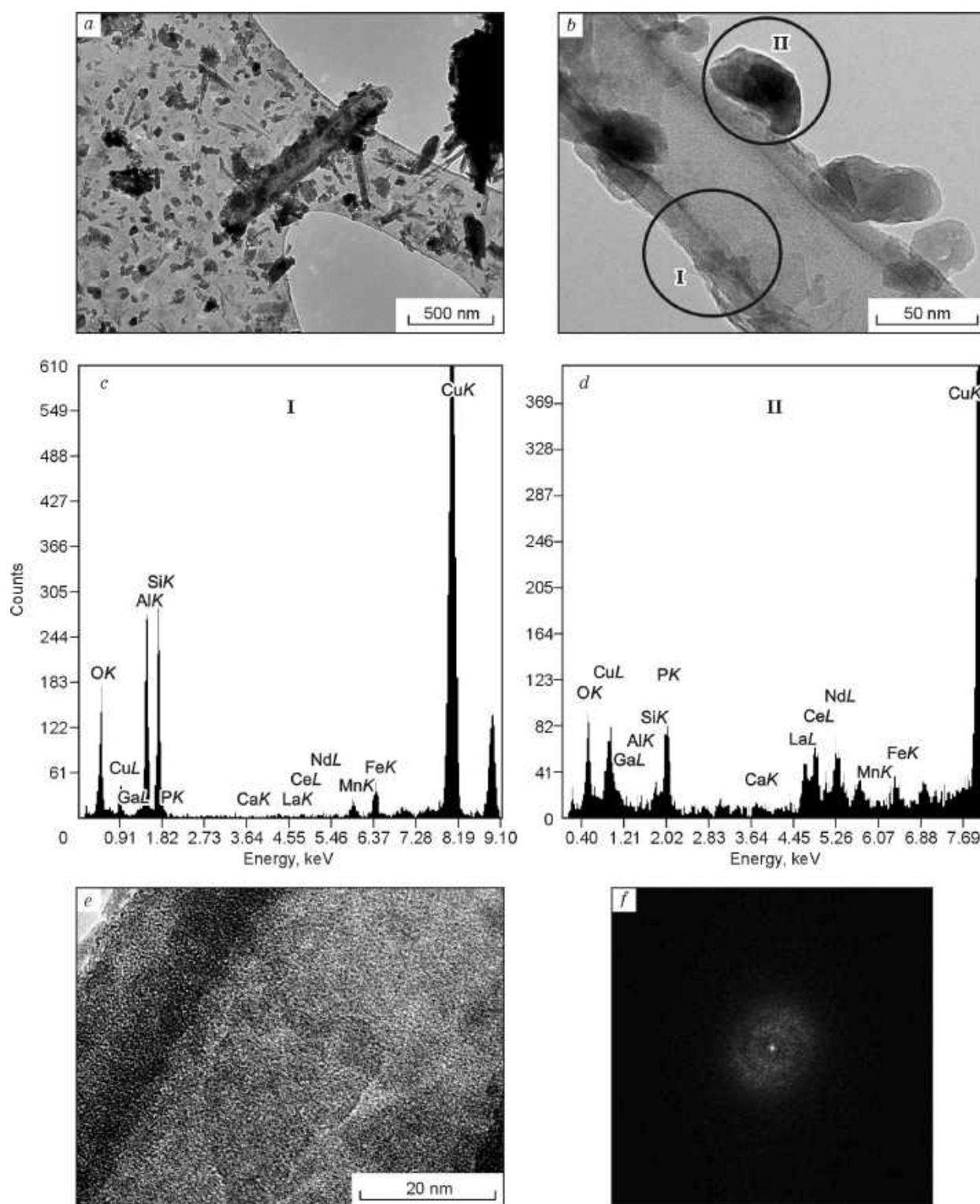


Fig. 16. Aluminum silicate (halloysite) tube covered by an aggregate of monazite nanocrystals. *a, b*, Tube at different magnifications; *c*, EDX spectrum in zone I of micrograph 16*b*, which illustrates the chemical composition of the tube; *d*, EDX spectrum in zone II of micrograph 16*b*, which shows the chemical composition of monazite; *e*, microstructure of the mineral, which illustrates its amorphous state; *f*, FFT image obtained from micrograph 16*e*. Transmission electron microscope.

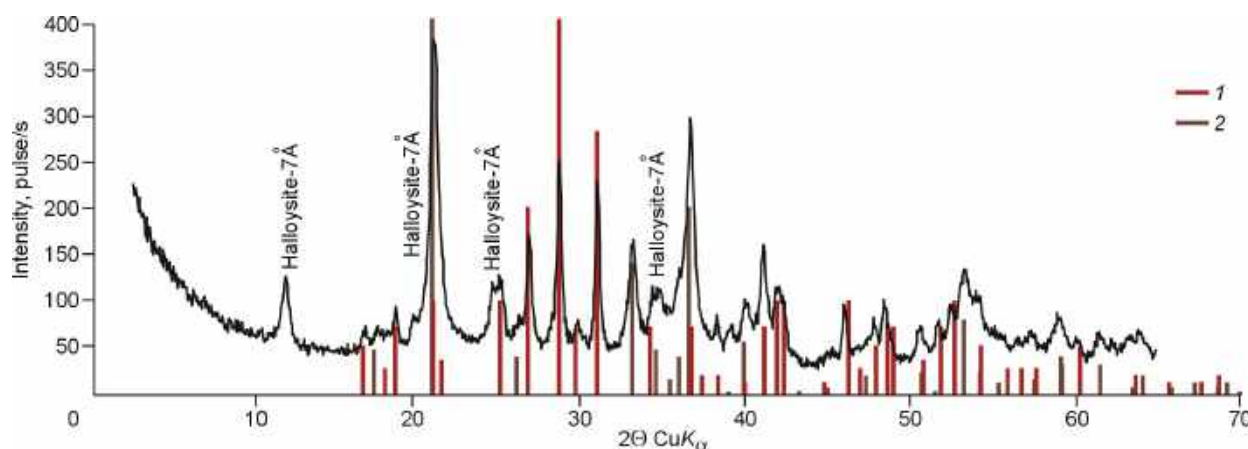


Fig. 17. XRD pattern for the fraction <0.01 mm of ore from the Burannyi site, Tomtor deposit. 1, monazite; 2, goethite.

halloysite (Kawano and Tomita, 2002). The latest studies have demonstrated high biocompatibility of halloysite; its presence in the system stimulates cell growth (Lvov et al., 2014). The unsuccessful attempts of synthesizing halloysite may be explained by the fact that some physicochemical parameters (first and foremost, microorganisms and/or organic substances) were not considered in planning the experiment.

Halloysite has unique sorption capacity with respect to many inorganic ions and organic compounds; most importantly, with respect to the phosphate ion (Haseman et al., 1950; Low and Black, 1950; Theng et al., 1982). It is currently known that tubular halloysite has the maximum sorption capacity when the solution has a pH value of 6.

Organic remains. Tubular halloysite–monazite aggregates coexisting with goyazite are detected within organic remains (Fig. 18), which are fragments of a multicellular organism (probably, plant). The thickness of cell walls is from 5 to 20 μm at their joints. Analysis of the plant remnant with the use of a scanning microscope showed the highest contents of TiO_2 (6.3–7.9 wt.%) and Fe_2O_3 (3.2–7.2 wt.%, Table 6). Besides that, almost all the components characteristic of ores are present: P_2O_5 , Al_2O_3 , Ce_2O_3 , La_2O_3 , Nb_2O_5 , SrO , and BaO (Table 6).

Discussion

The reported study showed that ores at the northern Burannyi site of the Tomtor massif mostly have <20 μm grains. Dry ore material is friable. Main ore minerals and their particles, including nano- and micrometer grains, show almost no morphological signatures of deformation or transport (in a water flow), except some pyrochlore grains. Judging by preserved crystal morphology in both relict and authigenic minerals, exotic (flower-like, radiated–fibrous, or biomorphic filamentous) forms of aggregates, and the laminated structure, the ores underwent minor or no transport while most minerals were chemically precipitated from thermal waters, possibly with participation of biota.

The magmatic pyrochlore group minerals in the Tomtor ores are strongly altered. The observed substitutions apparently result from supergene hydrothermal alteration (see above). The minerals occur mainly as fully altered crystals, though retaining the original faces, or as numerous conchoidal fragments; less often they are crystals with reaction rims or rounded crystal fragments. Alteration of some magmatic pyrochlores may have been syngenetic with ore deposition, as one may infer from the presence of strongly altered and heavily cracked large crystals, which retain their habits being cemented by other ore minerals (iron, copper, or lead sulfides and goyazite). The conchoidal fragments testify to transport and deformation of already altered grains, most likely to a short distance; otherwise the fragments of altered pyrochlore would have been completely disintegrated.

Goyazite can form in environments of weathering, hydrothermal alteration, coal deposition, etc. (Dai et al., 2012; Dill, 2001). Note that colloform goyazite coexisting with boehmite (AlOOH) in coals fills cavities in mineralized plant remnants. The occurrence of goyazite in the Tomtor ores mainly as colloform micro- or nanometer globules suggests its origin by microbially mediated (?) hydrochemical precipitation.

Halloysite–monazite aggregates in the ores are of special interest. The abundance of radiated aggregates is unique to the ores at the northern Burannyi site: This morphology has never been reported for fossil microorganisms (Rozanov, 2012). Among living organisms, colonies of this kind are known in diatoms (Jaworski et al., 1988). The genesis of halloysite–monazite structures waits to be revealed. Halloysite forms mainly during chemical weathering or hydrothermal alteration of rocks. It is the most widespread in altered volcanic ashes and pumices and is often found in soil, which contains organic matter and is subject to microbial activity.

Supergene monazite forms in carbonatitic laterite. Monazites morphologically and compositionally similar to those from Tomtor were reported from the ores of the Catalão I deposit, Brazil (de Toledo et al., 2004; Ribeiro et al., 2005), but no presence of halloysite in the aggregates was mentioned. Note that hydrothermal alteration was detected at all sites of

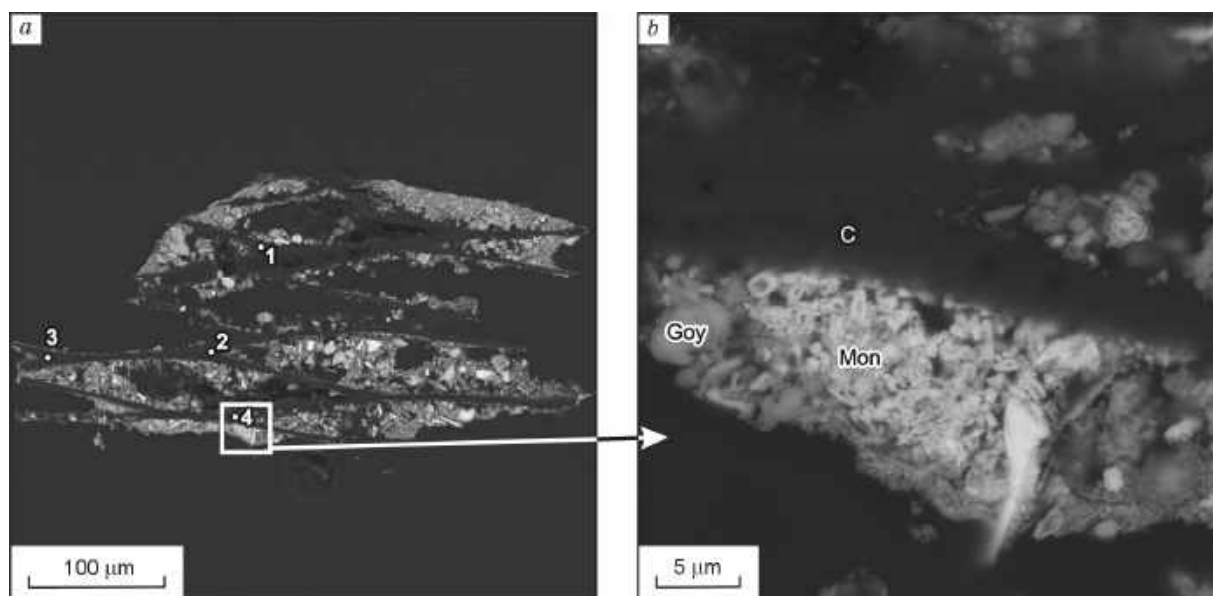


Fig. 18. Aggregates of monazite tubes in the cavities of a plant fragment. *a*, Whole fragment; *b*, magnified part. C, plant remnants. 1–4, points of analysis of the organic remains (Table 6).

supergene monazite, and the presence of thermal waters was observed in some places (Dill, 2001; Ribeiro et al., 2005). In the Tomtor ores, monazite coexists with minerals of hydrothermal origin: crandallite group minerals, sulfides (pyrite,

sphalerite, galena, and chalcopyrite), and barite (de Toledo et al., 2004; Ribeiro et al., 2005).

Plant remnants in the ore indicate ore deposition on the surface.

Thus, the high-grade ores at the northern Buranniyi site of the Tomtor massif formed in supergene conditions. The particle size of ore minerals suggests hydrochemical precipitation for most of them. The ore-forming minerals (pyrochlore, goyazite, and monazite-Ce, in combination with halloysite) were either precipitated (halloysite, goyazite, and monazite-Ce) or altered (pyrochlore group minerals) together in the same events. So, the ores may have been chemically precipitated from thermal water, i.e., have hydrothermal–sedimentary or volcanic–hydrothermal–sedimentary genesis.

This genesis is consistent with the existence of the N–S Chymara zone of REE mineralization produced by hydrothermal alteration of Neoproterozoic sediments south of the Tomtor massif (Fig. 1). It was its discovery that gave an impetus for exploration of the Tomtor massif.

The physicochemical conditions in a hot spring or a thermal lake or a pool which became the source of the Tomtor ore minerals can be deduced from mineral chemistry. Crandallite group minerals were precipitated from waters with pH from 4 to ~8 depending on the phosphate ion content (Dill, 2001). Halloysite–monazite aggregates may have formed as halloysite adsorbed the phosphate ion from waters if the hydrochemical process was the dominant mechanism; the adsorption is the most efficient at pH = 6 (Theng et al., 1982). The great amount of carbonates, both inside (carbonatite) and outside (host limestone and dolomite) the massif, must have neutralized the waters, if they were acid, and they became alkaline or neutral when reaching the surface. Recent data (Stepanchikova et al., 2014) show an important role of REE hydroxyl complexes ($\text{Ln}(\text{OH})^{2+}$, $\text{Ln}(\text{OH})_2^+$, $\text{Ln}(\text{OH})_3^0$).

Table 6. Contents of oxides in the organic remains, according to SEM analysis

Component	1	2	3	4
SiO ₂ , wt.%	0.21	0.11	0.19	0.19
TiO ₂	5.1	7.9	6.3	6.6
Al ₂ O ₃	4.38	0.74	4.74	0.87
FeO	5.2	7.2	3.3	3.2
MnO	B.d.l.	0.15	0.13	0.22
CaO	1.02	0.31	0.91	0.5
BaO	1.52	0.68	1.33	0.74
SrO	1.87	0.32	1.76	0.37
V ₂ O ₃	0.54	0.62	0.46	0.31
Ce ₂ O ₃	3.8	0.4	3.0	1.36
La ₂ O ₃	2.0	0.46	1.9	0.94
Pr ₂ O ₃	0.36	B.d.l.	0.16	B.d.l.
Nd ₂ O ₃	1.13	B.d.l.	0.8	0.37
Sm ₂ O ₃	0.17	B.d.l.	B.d.l.	B.d.l.
Eu ₂ O ₃	0.17	B.d.l.	B.d.l.	B.d.l.
ZrO ₂	B.d.l.	B.d.l.	0.26	B.d.l.
Nb ₂ O ₅	1.3	0.57	1.56	0.43
P ₂ O ₅	8.4	1.08	7.2	1.9
Cl	0.1	0.19	0.13	0.06
Total	37.2	20.7	34.1	18.1

Note. 1–4, see numbers of points in Fig. 18. Exposure time is 150 s.

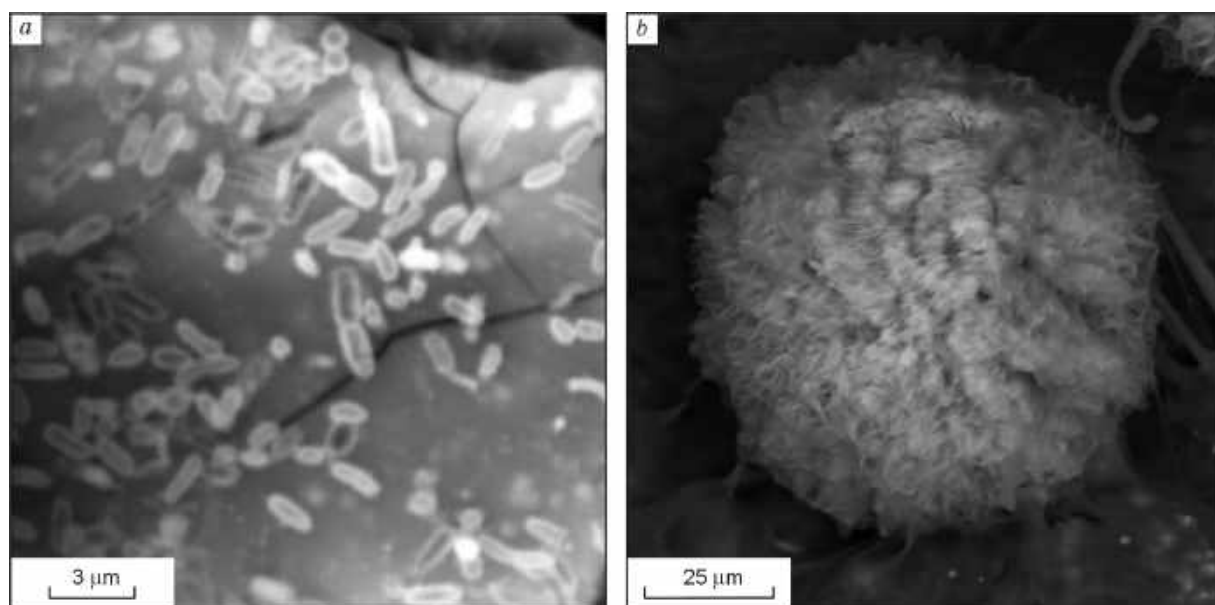


Fig. 19. Precipitation of phosphates in present-day microbial communities. *a*, Precipitation of iron and calcium phosphates on the cell walls of microorganisms in the cyanobacterial community of the Eskalator waterfall, Valley of Geysers; *b*, globular segregation of manganese, calcium, and iron phosphates in the cyanobacterial community of the Termofil'nyi spring, Uzon Caldera.

Which processes caused accumulation of rare-earth phosphates?

We infer that microbial activity may have been an agent in the Tomtor ore genesis. Microorganisms live in all present hot springs and thermal lakes and pools. During studies of cyanobacterial communities in thermal waters (Lazareva et al., 2010–2012), we often observed biomorphic mineral aggregates as silica sheaths or sometimes as dense “cotton”. The sediments of thermal lakes, e.g., in the Uzon–Geyser depression, consist of diatom and clay mud. Although the systems of thermal vents in the present Uzon–Geyser volcanic belt are very different from what is observed in the Tomtor massif both in geology and chemistry (Dobretsov et al., 2015), some analogy is possible. In the microbial communities of the Uzon–Geyser springs, calcium, iron, and manganese phosphates precipitated upon bacterial cells (Lazareva, 2014) at low P contents in the water (to 160 ppm, Fig. 19). Note that such precipitates are quite widespread.

The development of microbial communities in thermal waters is controlled mainly by temperature and pH. The pH value (6–8) inferred for the Tomtor thermal waters (see above) likely created a favorable environment. It may be important that REE contents are the highest in the orebody margins (Fig. 4), exactly in the place of most intense microbial activity and high bioproductivity in the hypothetical thermal lake (Zhmur et al., 1994). In contrast, pyrochlore, possibly a relict mineral of carbonatitic eluvium, is the most abundant near the lake bottom. Organic matter is known to be critical for the formation of present phosphorites and calcium phosphate nucleation to be much faster and more efficient in the presence of protein (Titov and Baturin, 2008).

Halloysite may be of biogenic origin (Kawano and Tomita, 2002; Lvov et al., 2014; Tazaki, 2000, 2005, 2006). Its crystals

produced by different processes vary in size from 0.02 to >30 μm (Joussein et al., 2005), being most often 0.5 to 2 μm (Tazaki, 2006). The halloysite tubes in the ores of the Burannyyi site make up distinct 1 to 3 μm biomorphic aggregates.

Recent studies have shown great importance of bacteria, including cyanobacteria, in Precambrian sedimentation (Rozanov, 2002). The oldest sediments contain fossil microorganisms, which evidence that their communities were key agents of sedimentation for a very long period of the Earth's history. Biological (including bacterial) mineralization is a widespread process in different geochemical conditions in the presence of liquids.

Bacteria, which have a large surface area per unit weight because of their small size, are known as efficient absorbers of dissolved metal ions. There are at least two sites of possible REE sorption on the surface of bacterial cells: carboxylated and phosphate groups. There are reports of REE bioaccumulation in some natural microbial communities (Takahashi et al., 2005).

The microorganisms responsible for REE accumulation in the Tomtor paleoecosystem may have been thermo- or mesophilic bacteria which belonged to a cyanobacterial mat or developed beneath it in bottom sediments. Otherwise, methanotrophic bacteria, which are resistant to high salinity and temperature (Gal'chenko, 2001) and are morphologically similar to the bacteriomorphic structures from the Tomtor ores, might have been REE concentrators, but no evidence for REE bioaccumulation by methanotrophs has been reported so far.

La compounds show antibacterial activity with respect to many organisms, including gram-positive ones, but not to gram-negative organisms which have thick and low-permeable cell walls (Balusamy et al., 2012). Gram-negative bacteria are

very diverse: Proteobacteria, Aquificae, Chlamydiae, Bacteroidetes, Chlorobi, Cyanobacteria, Fibrobacteres, Verrucomicrobia, Planctomycetes, Spirochetes, Acidobacteria, and others. Moreover, some gram-negative microorganisms are capable of accumulating La and other REE, as well as *Pseudomonas* sp. (Proteobacteria) (Kazy et al., 2006).

The mechanisms of La accumulation by bacteria have been a subject of research, as well as the possibility of using REE accumulation to identify syndimentary bacterial activity (Takahashi et al., 2005). A very important role in the biosorption of metals by bacteria belongs to extracellular polymer substances, which are a mixture of polysaccharides, mucopolysaccharides, and proteins (Vijayaraghavan and Yun, 2008).

Thus, the accumulation of rare-earth phosphates in the thermal lake of the Tomtor massif was mediated by thermo- or mesophilic single-celled and/or colonial bacteria (Cyanobacteria and others), which can form an extracellular polymer matrix and grow inside or immediately beneath cyanobacterial mats.

Conclusions

Comprehensive studies have shown that the Tomtor high-grade ores (natural concentrates of Nb, REE, Sc, Th, P, and Ti) precipitated in supergene conditions from thermal waters in a shallow-water lake. The ore minerals underwent short-distance or no transport and result mainly from hydrothermal alteration; most minerals were chemically precipitated from thermal waters, possibly with participation of biota. This origin was inferred from several features: morphology of the ore minerals and particles, including nano- and micrometer ones, free from signatures of deformation or transport in a water flow; preservation of primary crystal habits in both “relict” and authigenic minerals; exotic shapes of mineral aggregates; and laminated structure.

The abnormal concentration of rare metals has at least two causes: (i) accumulation of the heavy fraction on the lake bottom and the concentration of pyrochlore widespread in the Tomtor weathering profile (particularly, in weathered carbonates), and (ii) precipitation of crandallite group minerals, halloysite, and, partly, monazite from thermal waters. Microbial activity may have been an important agent in ore genesis, which is implicitly evidenced by bacteriomorphic micro- and nanostructures and co-occurrence of organic remains with ores.

Of course, many issues of the Tomtor ores still remain unresolved, such as details of their secondary and accessory minerals; the lifespan of hydrothermal systems; the water body type (a spring, a pool, a lake, etc); bedrock hydrothermal alteration; mechanisms of trace element and REE sorption; bio-accumulation rate (*in vivo* or *ex vivo*), etc. These issues will be the subject of our future studies, with implications for prediction of microbially-mediated mineralization and for biotechnological recovery and separation of trace and rare-earth elements.

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