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Rare-Earth, Noble, and Rare Metals in the Ores of the Algama Zirconium Occurrence, Khabarovsk Krai

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Abstract—Samples of ore and gravity concentrate from the Algama zirconium occurrence were studied. Concentrations of rare-earth elements (REE), and rare and noble metals were determined. The REE content is 200–300 g/t in the ore and reaches 400 g/t in the gravity concentrate. REE distribution patterns show a clear negative Ce anomaly and MREE and Y predominance. The ore and the concentrate have elevated Hf, W, U, Ta, Au, and Pt contents. Their source is the ancient weathering crust developed after ultra-alkaline rocks of the Ingili massif. The presence of a buried weathering crust enriched in valuable components is inferred in the studied area.

Keywords: zirconium, baddeleyite, rare-earth elements, rare metals, gold, platinum, weathering crust, Algama deposit, Ingili massif, Khabarovsk krai, Far East Russia

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INTRODUCTION

Zirconium is a rare metal applied in different spheres of production owing to its metallophysical and chemical properties. The metal has the widest application in the metallurgical, nuclear, and energetic industries, as well as the production of refractory and ceramic raw materials. In addition, the main Zr-bearing minerals, zircon and baddelyite, are sources of Hf, which is an even rarer and more expensive metal [5]. The zirconium (hafnium) industry of Russia suffered significant losses after the collapse of the USSR. The discovery of the Algama baddeleyite–zirconium occurrence in the north of the Khabarovsk krai in 1984 would provide the raw base for the zirconium industry at the Far East.

The Algama occurrence is situated in the Ayan–Maya district of the Khabarovsk krai, 130 km north of the settlement of Nelkan. In 2014–2016, prospecting works at the deposit were undertaken by JC Sosnovgeo in cooperation with the JSC Dal'geofizika. To obtain additional data on the composition of ores and REE distribution in them, the JSC Dal'geofizika gave the collection of samples of rocks, ores, and gravity concentrates to the Kosygin Institute of Tectonics and Geodynamics.

The aim of this study was to determine the concentrations and speciation of rare-earth, rare, and noble metals in the zirconium-bearing ores of the deposit and their concentrates and to reveal their relations with the nearby Ingili ultra-alkaline massif.

MATERIALS AND METHODS

The studies were carried out for field samples, as well as for ores and rocks from the Algama project areas, which were collected in 2014–2015 in prospecting trenches and holes, as well as for six 20–25 kg samples of gravity concentrate obtained in the JSC Dal'geofizika.

The major rock-forming oxides were determined by X-ray fluorescence on a Bruker S4 Pioneer spectrometer (Germany, analyst L.M. Il'in) at the Khabarovsk Innovation Analytical Center for Collective Use, Kosygin Institute of Tectonics and Geodynamics of the Far Eastern Branch of the Russian Academy of Sciences. The rare, trace, rare-earth, and noble elements were determined by ICP-MS on an ELAN9000 Perkin Elmer (United States, analyst A.V. Shtareva) at the same institute. The species and composition of ore minerals were studied on a VEGA 3 LMH, TESCAN electron scanning microscopy (Czech Republic) equipped with an X-max 80 Oxford EDS (Great Britain, analyst V.O. Krutikova). Minerals were analyzed in spots and over selected area with a continuous counting of spectra.

The chemical preparation of samples was carried out by N.I. Il'ina, A.Yu. Petrova, and G.F. Zolotukhina. The rare-earth element abundances for spidergrams were normalized to continental crust [12].

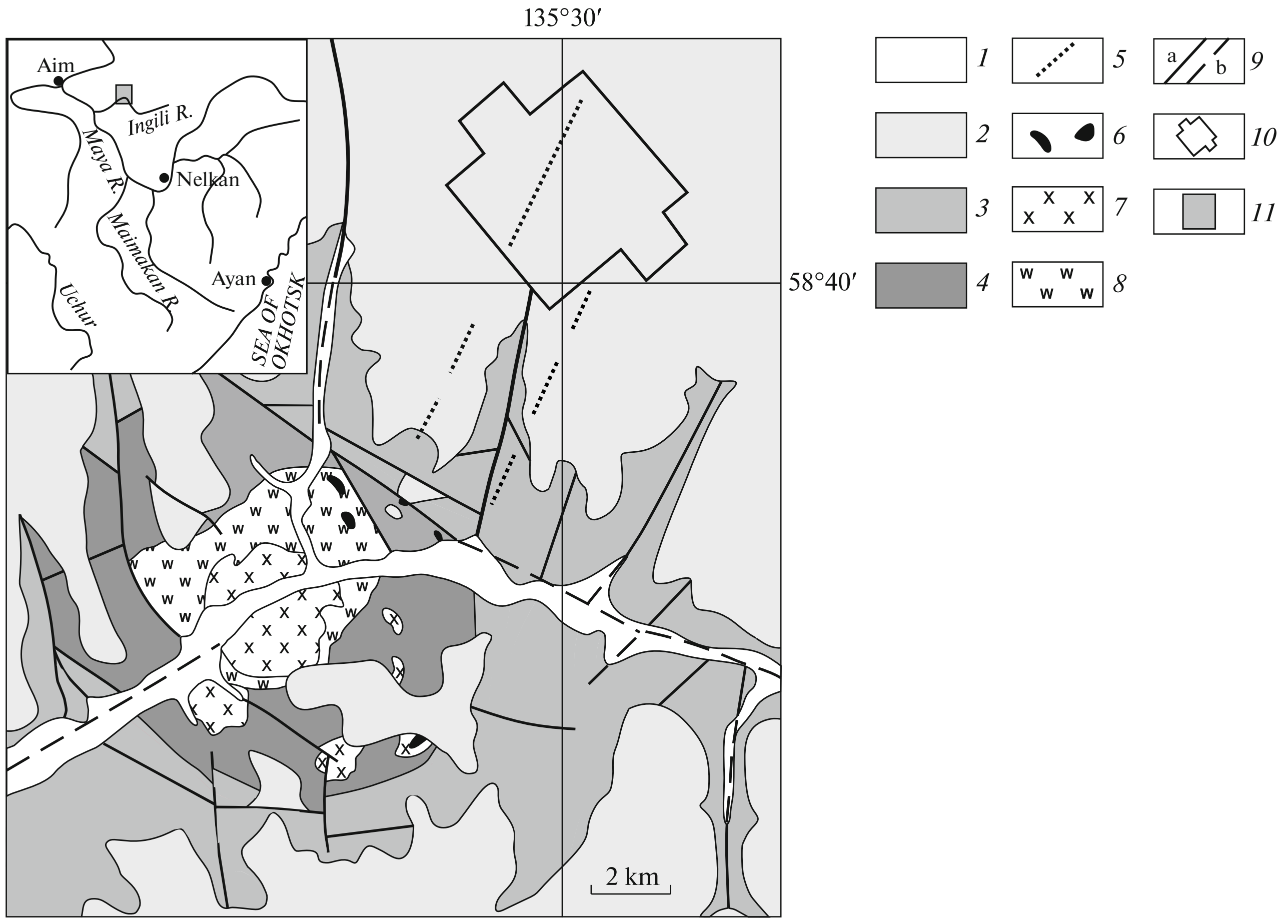

Fig. 1. A schematic geological map of the Ingili ore cluster modified after the Geological map of the Ingili ore district on a scale 1 : 100000 (modified after (Vyazunov, 2016). (*1*) Quaternary rocks, (*2*) Early–Middle Cambrian Yudoma and Pestrotsvetnaya formations, (*3*) Middle–Late Proterozoic rocks of the Kerpyl, Maisk and Ui groups, (*4*) Early Proterozoic Batomga Group, (*5*) gabbrodiabase dikes, (*6*) carbonatite bodies, (*7*) alkaline basic–ultrabasic rocks of the Ingili massif, (*8*) contact altered rocks, (*9*) faults mapped (a) and overlain by Quaternary sediments (b); (*10*) Algama project with the Algama zirconium deposit, (*11*) studied area shown in the inset.

THE GEOLOGICAL CHARACTERISTICS OF THE DEPOSIT AREA

The Algama zirconium deposit is located in the junction zone between the eastern Siberian Platform and the Yudoma–Maya pericratonic trough, which separates the Siberian Platform and the Okhotsk median massif. The deposit is restricted to the Ingili Rise, including the Ingili dome. The domal core exposes Proterozoic stratified rocks, which are intruded by Proterozoic alkaline basic–ultrabasic bodies and Paleozoic gabbrodiabase dikes. The dome is surrounded by Cambrian sedimentary rocks (Fig. 1).

The Early Proterozoic metamorphic rocks are represented by scapolite–amphibole–plagioclase gneisses, crystalline schists, amphibolites, and marbles of the Batomga Group. The rocks were strongly migmatized by small bodies and veinlets of gneissose plagiogranites. They are overlain with a sharp unconformity by weakly metamorphosed Middle–Late Proterozoic terrigenous–carbonate rocks. Vendian carbonate-rich sediments of the Yudoma Formation unconformably overlie Riphean and Lower Proterozoic rocks. This formation was deposited after a large hiatus, which was accompanied by the emplacement of the Ingili intrusive complex (Ingili alkaline basic–ultrabasic massif with small carbonatite bodies) with the formation of the Ingili domal structure. The latter is restricted to the intersection of the deep-seated Urakhan and Uchur–Ingili faults [2–4]. The formation of the Ingili dome was completed in the Devonian by the emplacement of gabbrodiabase dikes of elevated alkalinity.

The ore-bearing Vendian sediments of the Yudoma Group rest unconformably on Riphean and Early Proterozoic rocks, as well as on magmatic rocks of the Ingili Complex. Riphean–Cambrian carbonate rocks are represented by Mg varieties, while younger carbonates have a calcareous composition. The sediments of the Yudoma Formation are carbonate-rich rocks subdivided into two subformations. The lower subformation is mainly made up of terrigenous rocks. Mineralization is confined to the upper subformation consisting mainly of fine-grained chemogenic carbonaceous–magnesian sediments transformed into dolomites and calcareous dolomites. Based on the wide distribution of oncolithic structures in the ore-bearing rocks, these are coastal–shallow chemogenic sediments precipitated on the low-angle slopes of the Ingili swell-like rise. The rocks of the Ingili massif were introduced in the Yudoma dolomites during their formation, which follows from the elevated contents of zirconium (0.1–0.3%, rarely up to 1.5–2.5%), niobium (0.015–0.024%), and rare-earth metals (0.05–0.27%), as well as from the presence of weathered ultra-alkaline material in the basal conglomerates [4]. The Yudoma dolomitic sequence has existed for a long period of time (since the Paleozoic) under continental conditions, which provided the formation of the paleokarsts system with stratified and cross-cutting elements. The development of the karst was related to the elevated porosity of dolomites and restriction to faults associated with thick zones of fracturing and sulfidization. The karst zones are confined to faults healed with gabbrodiabase dikes (L.S. Vyazunov, 2016). The faults provided favorable conditions for groundwater circulation and karst formation.

The Cambrian system is represented by sediments of the Pestrotsvetnaya and Inikan formations that lie conformably on the rocks of the Yudoma Group.

Modern sediments are alluvial shingles, sands, and loam up to 25 m thick, as well as eluvial, eluvial–talus, talus, and proluvium sediments, and colmatolites (sediments of karst cavities). The latter are precipitated in karst cavities as gravity-exchangeable breccias, influvium, and chemogenic material. The composition, sorting, and proportions of clastic and sandy–clayey fractions of colmatolites depend on the shape, size, and duration of formation of karst cavities, as wells as on the water content and flow of an underground chamber (O.D. Lysenko, 1998).

Intrusive rocks are represented by complexes of different ages (Fig. 1). The first stage of platform magmatism in the Riphean was responsible for the emplacement of central-type intrusions (Ingili Complex) as well as diabase and gabbrodiabase sills and dikes of the trap formation. Intrusions of the first type are developed on the platform, while the latter occur not only on the platform, but also in the Yudoma–Maya pericratonic trough.

The Ingili massif is a central-type ultrabasic alkaline intrusion with carbonatites, which composes the core of a large (6–8 km across) diapir-type domal structure. The massif has a zoned structure. Its central part is made up of metasomatically altered pyroxenites (apopyroxenites) intruded by a system of subparallel and cross-cutting veins of ijolite–melteigites up to 50 m long. The core of the massif is rimmed by a ring of silicate and carbonate metasomatites (theralites), which were formed after metamorphic rocks and ijolite–melteigites. The metasomatites, along with metamorphic and sedimentary rocks, are intruded by bodies and dikes of nepheline and cancrinite syenites. The later calcitic and dolomitic carbonatites compose stocks and sills in all of the aforementioned rocks [2, 4]. The apex of the dome was strongly eroded in the Precambrian.

Genetically, the rocks of the Ingili massif are ascribed to the mantle-derived concentric-type basic–ultrabasic associations and classified as sodic alkaline ultrabasic rocks associated with carbonatites. These complexes are restricted to the marginal parts of cratonized crustal blocks (Siberian Platform) that experienced compression [3].

Another type of ultrabasic rock is represented by the bodies of kimberlite-like ingilites (picrites), which are widespread as explosion pipes and dike bodies, which terminate the emplacement of the Ingili Complex. These bodies are usually overlain by sediments of the Yudoma Formation, but are mapped with confidence by magnetic anomalies (I.G. Korsakova, 1989).

Paleozoic intrusions are represented by Middle–Late Devonian diabase, gabbrodiabase, and olivine diabase dikes. Most of them are extended in the sublongitudinal and northeastern direction. They are from 5–10- to 30–60-m thick, and from 0.5 to 3–5 km, rarely more, in strike.

Mineral resources. The studied area comprises several mineral occurrences. In addition to the Algama and other zirconium occurrences, there are also occurrences of iron ores and base metals confined to the sedimentary rocks of the platform cover, as well as the occurrences of niobium and tantalum, rare-earth elements, apatite, diamond, and gold, which are associated mainly with the Riphean central-type intrusions (Ingili massif). Signs of petroleum potential were found in the rocks of the Yudoma Formation in 2016 [7].

THE GEOLOGICAL STRUCTURE OF THE DEPOSIT

Over 30 project areas of zirconium and associated mineralization and dozens of promising gamma-spectrometric anomalies were recognized within the Ingili ore cluster. Five areas were studied in detail: Algama, Anomaly 501, Tas-Yuryakh, Kandyk, and Nizhnyaya Algama. The best studied among them is the Algama project area, which spans the Algama zirconium occurrence and its nearby flanks (Fig. 1).

The Algama occurrence is located on the northern slope of the Ingili massif, 15 km from its central part. The area is made up of terrigenous–carbonate rocks of the upper subformation of the Vendian Yudoma Formation, including marbled dolomites and calcareous dolomites with numerous karst cavities filled with loose clastic and sandy–clayey material (influvium). The thickness of the karst sediments varies from a few centimeters to 28 m. In section, the karst cavities have a lenticular, stratal shape. Karsting is developed both in subsurface conditions and at some depth. Sediments of karst cavities occur at different hypsometric levels, from 560 to 620 m, and are unevenly distributed throughout the sequence. The karst sediments are gradually pinched out in the northeastern direction. The sediments of the formation lie horizontally with a weak northward slope, conformably with a general slope of the northern limb of the Ingili dome (O.D. Lysenko, 1998).

Ore bodies are located in the upper part of the Yudoma Formation and are spatially restricted to zones of intense karst formation in dolomites. In total, three zones are distinguished within the studied part of the ore field: the Western, Main, and Southern ones. The best studied Main ore body is 5.8 km long and 500–800 m wide. It is localized in the northern part of the ore field, has an average thickness of 1.6 m (varying from 1 to 5 m), and contains from 0.9 to 55% ZrO_2. The mineralization occurs at three horizons separated by dolomites with a vertical span of 300 m (L.S. Vyazunov, 2016).

The ore is represented by grussy–clayey rocks among loose karst sediments of similar appearance. Therefore, the ore-bearing zones in geological section have no clear outlines and are distinguished by the elevated radioactivity in the gamma-logging curve. The ore bodies have a complex morphology, which is determined by variable sizes, high variabilities of karst formations, and ZrO_2 contents. Ores of the upper horizons are represented by breccias of disintegrated carbonate rocks with baddeleyite–clayey cement. These are sometimes compact fine-grained brecciated ores cemented by gangue collomorphic quartz and calcite. In addition to calcite, dolomite, quartz, baddeleyite, and zircon, the ore contains an admixture (up to 1%) of apatite, scheelite, magnetite, chromite, pyrochrlore, hematite, and REE phosphate.

The ore bodies have elevated radioactivity and show a high positive correlation between U and ZrO_2, which was used to mark potential ore bodies.

Zirconium minerals are accumulated in material with grain size less than 2.5 mm. Thereby, the valuable components tend to be accumulated in less than 0.05 mm material (slime concentrate). The slime likely represents silty pelitic component of variably carbonated and ferruginated terrigenous sandy–clayey rocks.

The valuable ore minerals are baddeleyite and zircon, which occur as separate grains, collomorphic segregations, and polymineral aggregates. There is an opinion that the main ore mineral of the Algama ores is a finely dispersed zircon gel [1, 4]. However, high-precision mineral–technological studies of the ores in IMGRE and VIMS did not find this mineral [8].

Baddeleyite forms mainly fine-grained and nodular aggregates with characteristic radial and concentrically zoned texture with jointing fractures and rare spherulitic minerals. It also occurs in polymineral aggregates in a tight association with rock-forming minerals, sometimes with zircon. The sizes of the aggregates and grains of the mineral vary from thousandths to a few tenths of a millimeter, rarely reaching 1–2 mm.

Zircon is present as individual and collomorphic grains, which contain a significant mechanical admixture of rock-forming minerals, first of all, layer aluminosilicates. Zircon grains are usually from 0.1 to 7 μm in size, but also are smaller, a few nm in size. The collomorphic aggregates of zircon usually have a nodular and flake-like shape, reaching 80 μm. Finely dispersed zircon grains usually occur on the surface of quartz, carbonate, and clay aggregates as 15-μm crusts. Zircon grains no more than 5 μm in size also form intergrowths with iron hydroxides.

The ZrO_2 content varies from 41.22 to 65.03% in zircon and from 74.94 to 93.17% in baddeleyite. Zircon has elevated contents of yttrium (up to 0.44%) and uranium (up to 0.52%). According to Bagdasarov [1], the ore contains uranium silicates, coffinite, as up to 2-μm inclusions in association with zircon and baddeleyite. Baddeleyite contains oxides of tungsten (0.9–2.63%) and silica (1.30–14.18%).

The ores rarely contain larger (a few tenths of a millimeter) grains of apatite, which is mineralogically close to xenotime, as well as weakly alkaline amphibole, pyrite, hydrogoethite, and locally, the finest scheelite. The modern supergene zone after ore dolomites consists of the abundant montmorillonite and other hydrosilicates and shows an increase of hydrogoethite and especially quartz.

According to [4], the ores were formed after intense pre-Yudomian weathering, which led to the accumulation of an ancient weathering crust on the magmatic rocks of the Ingili pluton. Weathering during this and the next periods caused pervasive chemical reworking of the material, with its disintegration up to the dispersed size. During long-term laterite weathering under supergene conditions, zirconium became more mobile and, depending on pH conditions, could redistribute, reprecipitate, and dissolve.

During Paleozoic activation leading to the emplacement of diabase and gabbrodiabase dikes, dolomites were subjected to karst leaching with successive infilling by weathered magmatic rocks of the Ingili intrusion. The process was multistage and began from the precipitation of crystalline quartz, which cemented dolomite breccias and covered karst cavities at 180–80°C [10, 11]. Practically monomineralic small layers (bands) of baddeleyite and zircon crystals were precipitated directly on quartz. The karst cavities were then filled with compositionally heterogeneous colloid–suspension material.

The ore bodies are karstified dolomites, in which the morphology and position of Zr-bearing minerals were determined by the level of groundwaters, which circulated during filling and subsequent precipitation and reprecipitation of supergene material. A significant part of the material consisted of soluble compounds.

RESULTS

The compositions of ores and zirconium minerals were investigated in detail during technological studies [8] and comprehensively described (L.S. Vyazunov, 2016). Therefore, our attention was focused on the study of rare-earth elements, their distribution, and sources, as well as on the speciation of PGE, gold, and some trace elements in the ores.

Based on the zirconium content, the studied samples from the Algama deposit are subdivided into four groups.

The first group (three samples) includes ore-bearing dolomites of the Yudoma Formation containing 200–250 g/t Zr. The second group (eight samples) involves disintegrated dolomites from karst cavities with Zr contents from a few hundredths to a few tenths of a percent. In the ores of the third group (eight samples), Zr accounts for from a tenth of a percent to a few percent or more. The fourth group includes gravity concentrates (six samples) with 38–55% Zr. Rock samples from the Ingili massif and dike gabbrodiabases from the deposit area were united in a separate group (Table 1).

The Zr content was analyzed by mass spectrometry (ICP-MS), which allows the determination of maximum contents of no more than 0.3–0.4%. Therefore, samples with higher Zr contents were distinguished using data from the JSC Dal'geofizika (gravity concentrates).

Rare-earth mineralization of the Ingili massif was related to the veined bodies of late carbonatites and apatite-bearing pyroxenites.

According to Korsakova (1989), the apatite-bearing pyroxenites, which were intruded by ijolite and syenite dikes and recovered by prospecting holes to verify magnetic anomalies, contained up to 2.5 kg/t REE. The high total REE contents up to 11.054 kg/t were established in apatite monofractions. These rocks contain 4–6% apatite and have elevated contents of zirconium, gold, and platinum.

Carbonatites compose stock-like and equant bodies in the marginal parts of the complex and in the Lower Proterozoic contact metamorphic rocks. According to Bagdasarov [2], the carbonatites are subdivided into five types, four of which are ore-bearing and contain disseminated REE carbonates, as well as accumulations of zeolites and dissemination of pyrite, fluorite, and barite. In addition, they are accompanied by bodies of quartz–carbonate breccias with TR_2O_3 0.008–0.056%, while mineralogical analysis of crushed samples showed that they contain up to 4000 g/t REE minerals. The rocks also contain zircon, apatite, monazite, fluorite, and barite. REE are dominated by Ce, La, and Y. Fluorite–carbonate rocks developed after syenites contain 60% fluorite, 0.24% Nb_2O_3, and 0.38% TR_2O_3.

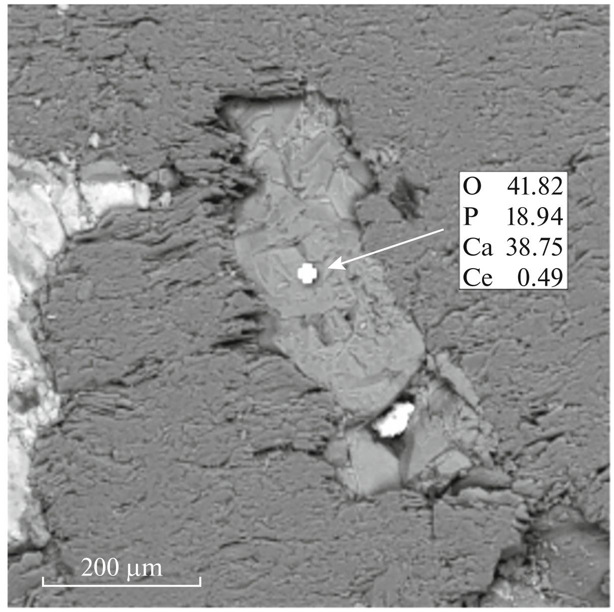

Fig. 2. An apatite grain in pyroxenite.

The ore-bearing carbonatites are enriched in pyrochlore, allanite, zircon, and titanite and are characterized by their elevated thorium and uranium radioactivity.

In other rocks of the massif, the REE content varies from a thousandth or a hundredth of a percent to a few percent, usually, a few tenths of a percent. The composition and proportions of useful components at different sites show wide variations, but ubiquitously contain Nb, Ta, Y, Yb, La, Ce, Sr, Zr, Sc, and less commonly Pt and Au (a few tenths of a g/t) and Ag (up to 30 g/t). The REE carriers are zircon, pyrochlore, cobeite, titanite, and apatite (Fig. 2). The latter occurs practically in all rocks of the massif, reaching maximum contents in pyroxenites (from 6 to 12%).

We studied pyroxenite samples with elevated P_2O_5 contents (up to 7.08%). According to ICP-MS data, sample CK-1 has the highest REE content of up to 1540.8 g/t (Table 1). Thus, Ce partially occurs as an isomorphic admixture in the rock matrix. Sample CK-7 contains prismatic and oval small inclusions of linearly oriented REE mineral (Fig. 3). Compositionally, it is close to parisite from carbonatites. REE are represented by LREE (La–Nd) with the predominance of Ce (up to 15.2 wt %) and La (up to 9.14 wt %). Two pyroxenite samples with elevated REE contents have similar REE distribution patterns.

Table 1. The contents of rare-earth and rare metals in the rocks of the Ingili Massif and diabase dikes

Elements	CK-1	CK-2	CK-7	805	146
La	270.88	1.24	82.15	25.53	40.53
Ce	692.98	5.80	185.30	53.79	83.26
Pr	86.76	1.08	22.97	6.08	9.30
Nd	298.28	5.64	80.66	22.57	33.51
Sm	51.81	1.89	12.87	4.18	5.79
Eu	13.07	0.63	3.29	0.90	1.26
Gd	47.67	2.45	12.16	4.42	6.04
Tb	4.85	0.37	1.36	0.58	0.78
Dy	16.56	0.84	5.14	3.00	4.21
Ho	2.41	0.40	0.83	0.56	0.80
Er	5.51	0.94	2.05	1.63	2.26
Tm	0.46	0.17	0.22	0.23	0.31
Yb	2.31	0.92	1.26	1.59	1.98
Lu	0.28	0.13	0.18	0.24	0.28
Y	47.02	6.89	18.59	13.95	20.48
Total TR	1540.85	29.41	429.04	139.26	210.79
Sc	44.49	31.48	39.56	12.01	9.46
Co	62.03	50.30	50.70	16.41	19.03
Ni	22.39	79.52	96.08	15.73	17.84
Sr	1597.78	85.12	603.91	172.08	281.61
Zr	324.91	2108.67	1280.15	744.31	5447.60
Nb	129.95	10.22	100.69	19.70	80.95
Ba	416.92	427.67	452.95	276.98	525.27
Hf	12.21	54.52	33.43	14.94	103.27
Ta	5.73	0.35	8.26	1.12	1.15
W	n/a	n/a	0.48	77.40	150.28
Th	12.57	0.32	8.54	9.52	10.93
U	2.05	12.61	7.72	2.86	7.24
Ru	<0.001	<0.001	<0.001	0.00008	0.0003
Rh	<0.001	<0.001	<0.001	0.00007	0.00055
Pd	0. 00157	0.006	<0.001	0.020	0.044
Ir	0.00054	0.002	<0.001	0.0024	0.023
Pt	0.00171	0.007	0.0057	0.006	0.0549
Au	1.0	16.946	0.128	0.03	0.079

(CK-1, CK-2, CK-7) pyroxenites of the Ingili massif, (805) gabbroid, (146) gabbrodiabase. Element contents, in g/t.

They show LREE and MREE predominance and low contents of HREE, especially Yb and Lu, and a small Eu anomaly (Fig. 4a). Sample CK-2 with low REE contents is an LREE-depleted rock with MREE predominance.

All samples have elevated Zr, Hf, Sr, and Ba contents, with sporadically elevated Th and Pd (up to 0.09 g/t) and Pt (up to 0.12 g/t) contents. They also have elevated Au contents (>1.0 g/t), reaching 16.9 g/t in sample CK-2 (Table 1). Pyroxenites are sulfidized and contain disseminated pyrrhotite, chalcopyrite, and arsenopyrite.

In two samples from Devonian diabase dikes (samples 805 and 146), the REE content is no more than 210 g/t. Their spidergrams differ from those of pyroxenites. They are flat, with insignificant predominance of LREE and MREE and an insignificant positive Gd anomaly (Figs. 4b). Pyroxene shows an isomorphic admixture of Eu and Ho. Diabases have elevated Zr contents (up to 0.5%). Zirconium minerals contain an

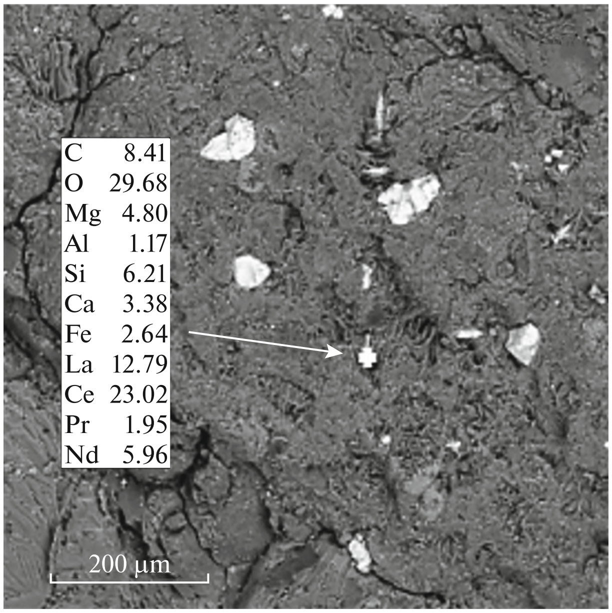

Fig. 3. An elongate prismatic grain of REE carbonate in pyroxenite. White oval grains are arsenopyrite and chalcopyrite.

isomorphic admixture of Hf and W. The diabases are weakly sulfidized. Sulfides are represented by pyrrhotite, galena, sphalerite, and pyrite, which make them different from pyroxenites of the massif.

Rare-earth mineralization of the ores and rocks of the Algama deposit. The chemical composition of ores and rocks of the deposit are listed in Table 2.

The first group, ore-bearing dolomites of the Yudoma Formation, are represented by fine-grained calcareous magnesian, weakly brecciated varieties cemented by calcite and quartz, and contain up to 0.3 wt % Cl. Their precipitation is related to the transgression of a shallow sea of elevated salinity on a peneplaned surface of older rocks. The terrigenous material was supplied from the weathering crust of the Ingili massif, as follows from the presence of small grains of Hf and W-bearing baddeleyite (Fig. 5). Along with zircon, they contain pyrite, apatite, and platinum. This also caused the high Au content (up to 0.24 g/t, sample 210-49), averaging 0.114 g/t. The REE content of this group is low, while their spidergram (Fig. 4c) is similar in shape to those of ore samples and apatite-bearing pyroxenites of the Ingili massif. They show the predominance of MREE and Y, at low contents of Yb and Lu, weak negative Ce and Pr anomalies, and positive Eu and Gd anomalies.

The second group is a breccia of disintegrated dolomites with baddeleyite–clayey, quartz, or calcite–quartz cement. These are mainly so-called “solid” ores or influvium of karst cavities with the predominance of rock material. They more resemble a mechanical mixture of karst influvium, with wide

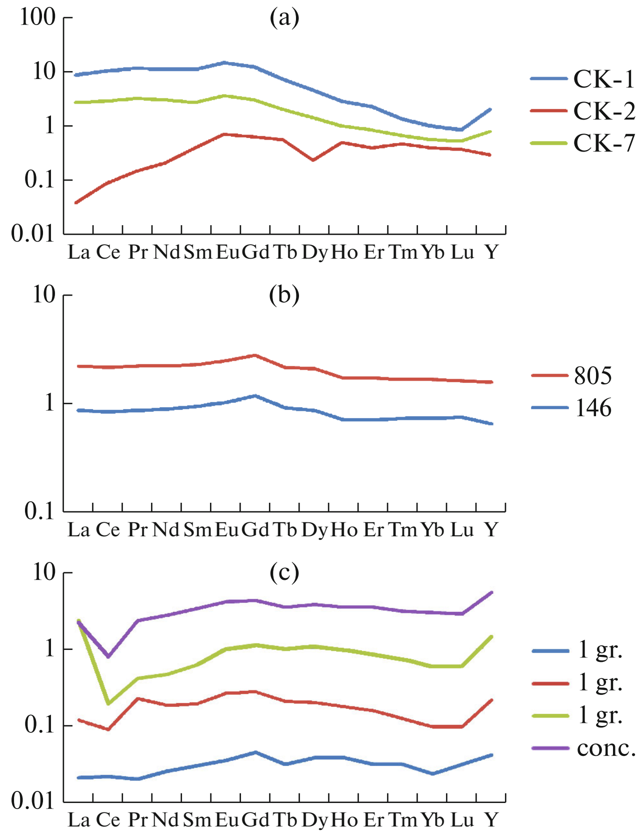

Fig. 4. The REE distribution pattern in the ores and rocks of the Algama deposit. Normalized to the upper continental crust: (4a) pyroxenites of the Ingili massif; (4b) rocks from diabase dikes; (4c) ores and rocks from the Algama deposit. (1 gr.) dolomites of the Yudoma Formation; (2 gr.) disintegrated dolomites; (3 gr.) zirconium ores; (conc.) gravity concentrate.

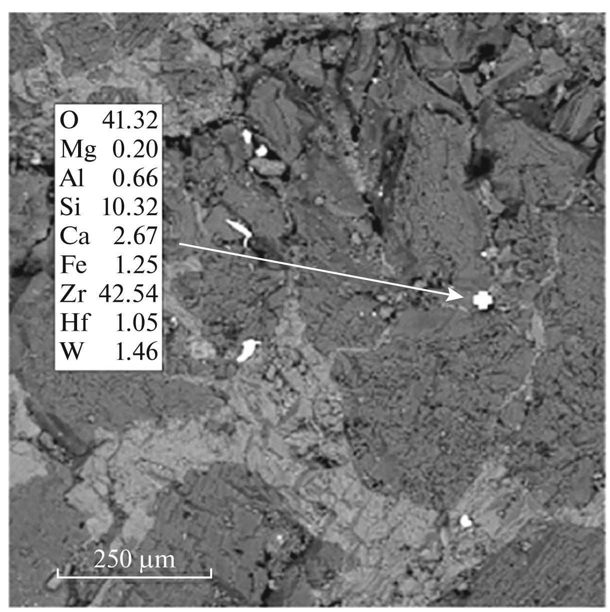

Fig. 5. Dolomites with fine baddeleyite dissemination.

Table 2. The chemical composition of the ores and rocks of the Algama deposit (average over groups)

	1 gr.	2 gr.	3 gr.	4 gr.
SiO_2	27.61	21.94	33.13	31.62
TiO_2	0.02	0.05	0.05	0.05
Al_2O_3	0.31	0.47	0.81	1.58
Fe_2O_3	0.63	0.92	1.73	0.91
MnO	0.04	0.39	0.40	0.19
CaO	25.07	36.67	30.32	2.34
MgO	17.52	9.55	6.25	2.19
Na_2O	0.06	0.08	0.84	4.88
K_2O	0.02	0.09	0.10	0.04
P_2O_5	0.01	0.03	0.31	0.99
L.O.I.	31.39	33.96	27.06	7.44
Total	102.68	104.15	101.00	52.22
Sc	0.03	0.72	13.71	111.22
V	1.79	10.48	20.64	85.28
Cr	38.01	33.61	33.08	19.19
Co	4.96	7.99	9.44	6.08
Ni	5.22	17.07	31.66	33.18
Cu	7.12	29.47	42.86	76.63
Zn	4.93	29.69	63.45	34.63
Ga	0.24	0.74	2.06	12.10
Rb	0.70	2.08	2.56	1.72
Sr	31.19	42.39	24.48	205.80
Y	0.88	4.72	31.98	119.60
Zr	135.41	643.5	8221.42	ZrO_2, 42.40
Nb	2.21	4.79	265.01	2402.41
Ag	5.39	0.82	13.00	124.74
Sn	0.34	0.65	0.48	0.54
Cs	0.05	0.14	0.23	0.18
Ba	3.66	300	295.85	272.30
Hf	2.61	12.81	545.43	4991.15
Ta	0.05	0.07	0.11	0.03
W	20.89	37.97	456.92	4690.05
Pb	2.73	2.95	3.61	33.49
Th	0.05	1.07	0.34	0.37
U	0.98	7.41	78.52	438.78
		TR		
La	0.62	3.52	70.99	66.94
Ce	1.38	5.59	12.31	49.41
Pr	0.14	1.60	2.91	16.61
Nd	0.66	4.68	12.02	72.81
Sm	0.13	0.87	2.81	15.13
Eu	0.03	0.23	0.87	3.62
Gd	0.17	1.03	4.28	16.30
Tb	0.02	0.13	0.65	2.23
Dy	0.13	0.68	3.85	13.30
Ho	0.03	0.14	0.78	2.83
Er	0.07	0.35	1.97	8.12
Tm	0.01	0.04	0.24	1.04
Yb	0.05	0.21	1.30	6.58
Lu	0.01	0.03	0.19	0.92
Y	0.88	4.72	31.98	119.6
Total TR	4.33	23.82	147.15	395.44
Pd	0.001	1.87	137.88	7.09
Ir	0.33	4.11	53.81	92.79
Pt	1.17	12.18	129.43	241.14
Au	114.78	249.45	37.8	62.75

(1 gr.) dolomites of the Yudoma Formation, (2 gr.) disintegrated dolomites; (3 gr.) zirconium ore; (4 gr) gravity concentrate of the ore. Oxides and ZrO_2 are in wt %, elements, in g/t. PGE and gold, in ppb.

variations of their contents of rock-forming elements. In general, they have a mainly calcareous composition (a significant CaO predominance over MgO). The REE content is higher than in the dolomites (on average the REE total is 23.2 g/t), with the predominance of MREE and Y. Some samples have a negative Ce anomaly, weakly positive Eu and Gd anomalies, and low HREE (Tb, Yb, and Lu) (Fig. 4c). The average contents of trace elements are given in Table 2. The PGE content is low (on average 0.012 g/t, at a maximum of 0.04 g/t). Gold is unevenly distributed, averaging 0.24 g/t and reaching 1.8 g/t in one sample, which in general is higher than in the dolomites. The samples have high contents of Ba and, especially, barite.

The third group included samples with economic Zr contents. They are represented by disintegrated dolomites in the form of calcareous–clayey material, gruss, and ore breccias variably reworked by iron hydroxides. The typical structure of the ore is shown in Fig. 6, where the brecciated quartz–carbonate rock is cemented by a baddeleyite–clayey groundmass. The REE content in general is low, from 20.6 to 247.3 g/t, averaging 83.24 g/t. REE are dominated by MREE and Y, at a slightly lower HREE content. The distribution patterns display a negative Ce anomaly and small positive Gd and Dy anomalies. The trace-element contents (Table 2) in this group generally are much higher than those of the first and second groups. This is especially the case for the Hf, Nb, W, and U contents, which as admixtures are involved in baddeleyite and zircon. The Pt content on average is 0.13 g/t, at a maximum of 0.57 g/t. Some samples have high Pd contents (up to 1.06 g/t) at an average of 0.14 g/t. The Au content is slightly lower than in samples of the second group, averaging 0.038 g/t and reaching 0.13 g/t.

The fourth group is represented by samples of gravity concentrate in form of fine-grained ferruginated sand. The study of the grain-size composition and distribution of zirconium dioxide over grain-size fractions showed that 64% of the ore is fragments of quartz and rocks of the +1.25 mm fraction, 20% sands of the productive grain-size fraction (−1...+0.044 mm), and 16% slime (−0.044 mm fraction). The coarse-clastic (+1.25 mm) and sand-size (−1...+0.044 mm) fractions are depleted in zirconium. The high-grade ores are −0.44 mm slimes containing 7.1% ZrO_2. They contain 63% ZrO_2 of all ores. Gravity enrichment provides extraction of 79% ZrO_2 in heavy fraction. The ores have higher contents of trace and ore elements: Sc, Co, Ni, Sr, Nb, Hf, W, Th, U, PGE, and Au compared to high-grade ores. The elevated contents of rare and ore elements are caused by the gravity concentration. They also have elevated REE contents from 352.5 to 454.9 g/t, averaging 395.4 g/t. The REE distribution pattern (Fig. 4c) shows a distinct negative Ce anomaly, which indicates that material was supplied from the weathering crust [12], with the predominance of MREE and Y and an insignificant decrease of HREE.

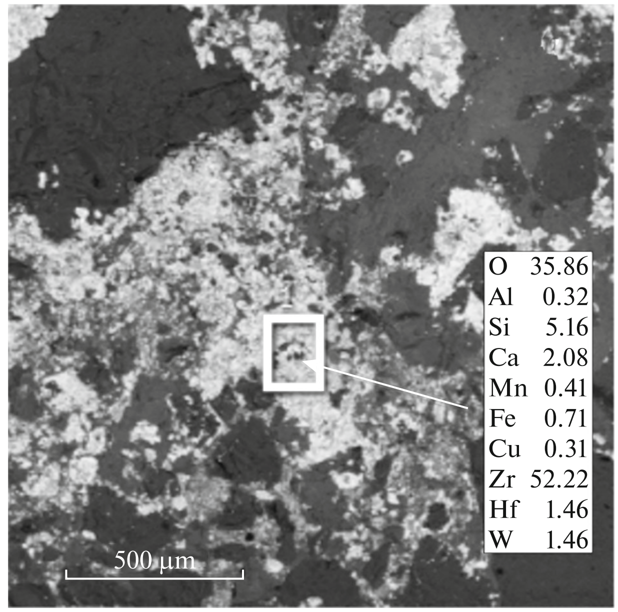

Fig. 6. Zirconium ore. Quartz and dolomite fragments are cemented by fine-grained baddeleyite–zirconium material.

DISCUSSION

Economic (>400 g/t) contents of total REE were found in carbonatites and apatite-bearing pyroxenites of the Ingili massif. In the Algama deposit, the minimum economic contents were found in gravity concentrates. In the ores and host rocks, the total REE content is no more than 200–300 g/t. However, it should be noted that REE in the ores were introduced from the weathering crusts developed after the Ingili massif. The material was transferred in a finely dispersed and colloid state. An increase of REE content in weathering crusts was provided by the redistribution of elements and extraction of LREE [12]. The upper continental crust-normalized REE distribution patterns show a relative decrease of their concentrations, first of all, Ce, and, to lesser extent, Nd and Sm typical of primary weathering (Fig. 4c). Thus, REE extracted from the weathering crust could occur in a dissolved or ion-sorption state, which are easily extracted and concentrated.

Two ore samples (nos. 4113-2 and 4113-3) and two samples of gravity concentrates (KD-1 and KD-3) were studied using bifluoride technology [14]. The percentage of REE extraction was 33–35% for ore and 45–73% for concentrate.

The Zr concentration and extraction from ores is a multiple complex procedure (L.S. Vyazunov, 2016) based on the application of different acids. Bifluoride technology [4] allows the associated REE extraction.

It is necessary to search for a possible buried weathering crust enriched in REE and other trace metals in the Ingili massif and surrounding areas. A similar geological situation is observed at the Tomtor deposit (Yakutia) [13], where a weathering crust was formed for a long period of time after silicate rocks (Riphean–Carboniferous) under hot and humid climatic conditions. The subsequent erosion and transfer of enriched sediments in potholes on the weathering crust after carbonatites was accompanied by the hydrochemical precipitation of REE with formation of high-REE sediments (up to 12%). The formation of weathering crusts and their enrichment in REE also occurred on the Ingili massif. However, their weathering products were more enriched in zirconium.

Alkaline complexes of such massifs could be a source of not only known secondary deposits, that is, weathering crusts lying directly on source rocks (mostly of carbonatite massifs) or in the potholes, which were fed by material of disintegrated rocks along their periphery, or in the zone of erosion and redeposition of crustal material, but also of occurrences related to the chemogenic removal of ore material. The transfer occurred in aqueous conditions, which provided the extraction, dissolution, and dispersal of the material [2]. The material could be precipitated in structurally favorable areas both within the massif and many kilometers away from the massif. This follows from the hydrochemical La anomaly to the north of the Algama deposit. According to available data, weathering crust is practically absent on the Ingili massif at the present-day erosion level. However, it is necessary to search for buried weathering crusts, especially along diabase dikes, which form positive landforms.

The distribution of rare and ore elements in the ores of the Algama deposit is related to their geochemical features and relations with weathering crust after the rocks of the Ingili massif. Carbonatites of the massif and apatite-bearing pyroxenites host occurrences with economic Ta–Nb–La, Ce, Sr, Th, U, PGE, and apatite mineralization [4, 9]. These elements are the main rare-metal admixtures in the ores of the deposit.

Hf isomorphically replaces Zr in baddeleyite and zircon. This is also partially the case for W, U, Y, and Th, which are incorporated in the zirconium minerals of the deposit and massif. It is pertinent to mention that these elements are absent in zircons from granites and other rocks unrelated to the Ingili massif. Niobium does not form its own minerals, including in the massif rocks. The tungsten in the ores was found not only as an isomorphic admixture in baddeleyite, but also as the finest scheelite grains. The technology of the associated extraction of tungsten oxide was developed by L.S. Vyazunov (2016). Uranium is present not only in an isomorphic form, but also as coffinite, which occurs as small inclusions in zircon and baddeleyite [6]. PGE and Au in the ores and host dolomites were also derived from massif rocks, which host occurrence of these metals. PGE were supplied mainly with terrigenous material, whereas gold was likely transferred in the colloid state.

CONCLUSIONS

The ores of the Algama occurrence have low REE contents. The main sources of REE, as well as rare and noble metals, in the ores are old weathering crusts after the rocks of the Ingili massif. The analogy of the formation of weathering crusts on the Ingili massif and on the Tomtor deposit in Yakutia [13], the duration of this process, and the enrichment in useful components make it possible to recommend searching for a buried weathering crust both within the massif (weathering potholes on carbonatites) and beyond it (along emerging diabase dikes).

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CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

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