Excess of REE in plant foods as a cause of geophagy in animals in the Teletskoye Lake basin, Altai Republic, Russia

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Abstract. Geological and hydrobiogeochemical studies carried out in two areas in the Teletskoye Lake basin in the Altai Mountains suggest that geophagy among wild and domestic herbivores in the studied areas develops in mountain-taiga with steppe landscapes on Proterozoic metamorphic rocks near the Paleozoic granitoids with high concentrations of magmatogenic minerals of rare earth elements (REE). This fact is the reason for high concentrations of REE in loose diluvial deposits and glacial deposits adjacent to granitoids, as well as in derivative soils and vegetation. REE concentrations in the vegetation of the studied territories were almost similar to the geophagy sites previously investigated in the Sikhote-Alin. The geochemical specificity of landscapes revealed both in the Altai Mountains and in the Sikhote-Alin may be the cause of REE imbalance in the hormonal system of the body. It forces animals to address the resulting problems with mineral sorbents of the quartz-feldspar-illite-chlorite type which can remove the excess of REE from the body. When selecting these, the animals tend to find sodium-enriched varieties if possible.

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Introduction

In some areas of the world, the consumption of mineral soils is common among wild and domestic animals. Regular geophagy leads to the formation of easily recognizable landscape complexes usually named salt licks or mineral licks in scientific literature. As will be demonstrated below, these objects are not always directly related to soluble salts and licking. That is why it was decided to use the term 'kudur' which originates from the Turkic shepherds (1). The term 'kudurit' derived from kudur, means mineral soil that is eaten at kudurs.

The geophagy of animals has been systematically studied since the 1930s. A number of researchers have tried to understand the reasons leading to the consumption of rocks and mineralized water from the springs by animals. However, currently, there are only a series of hypotheses with varying degrees of evidence. The most common of these are: The need for sodium and mineral sorbents to normalize the electrolyte balance in the digestive tract during the periods of seasonal transition of animals from roughage to green food (2-4); the replenishment of iron in the body; the renewal of microorganisms in the intestine; b the acteriostatic action of clay minerals against pathogenic microflora; parasite control; pH regulation in the digestive tract (5-8); and the removal of the toxic organic compounds from the body using mineral sorbents (9-11).

After analyzing the extensive material on the geochemistry of eaten earths in different regions of the world, it was hypothesized that there are only two main reasons for the desire for geophagy explaining all the cases worldwide. The first one is the electrolyte imbalance in the body most often associated with the lack of sodium in the diet. The other reason is associated with disorders of the metabolism of rare earth elements (REE). The second reason may be more common. The main point of the REE hypothesis (12,13) is that some elements from the light lanthanides group associated with nerve tissues and internal secretion gland enzymes can be replaced by heavy lanthanides, which, contrary to the light ones, are not able to perform the functions necessary for the body. As a result, vital systems of the body can be affected, which manifests in the decreasing adaptive capacity of the body to counteract adverse external factors (geochemical, cosmophysical, climatic and others). Animals under hormonal stress begin searching for substances that can be either a source of lacking REEs or their effective sorbents. This type of stress and the associated urge for geophagy were reproduced by American researchers on laboratory rats in the late 1970s. The experiment demonstrated that rats with artificially induced stress as a result of disturbed metabolic processes in the body (artificially induced arthritis) began to actively eat clay (14).

The research performed by the authors in the Sikhote-Alin in 2020 demonstrated that in the areas where geophagy is widespread among wild ungulates, acid volcanogenic and volcanogenic-sedimentary rocks enriched in REE are predominant. The weathering of these rocks leads to the formation of secondary readily soluble rare earth hydrous phosphates, carbonates, and fluorocarbonates over primary magmatic rare earth minerals. As a result, there is the accumulation of rare-earth elements in all landscape components (natural waters, soils, vegetation, and the hormonal system of herbivores), i.e., in fact, the development of landscape REE-abnormalities (15). It was concluded that an excess of REE in the neuroimmunoendocrine system of the body, which is a carrier of this group of elements, causes a stress response in animals making them seek mineral sorbents capable of correcting the REE imbalance in the body.

In 2021, to verify the REE hypothesis, similar studies were carried out in the Altai (16) Mountains, a region with a fundamentally different geological background, composition of rocks, climate and plants and animals compared to the Sikhote-Alin. The research was carried out on the coast of the Teletskoye Lake and in the estuary part of the Chulyshman River (hereinafter referred to as the Teletsky or T-area), and also in the upper reaches of the Chulyshman River near the Yazula settlement (hereinafter referred to as the Yazula or Y-area). These are the areas of the Altai Mountains with well-known cases of animal geophagy accompanied by the formation of well-defined kudurs. The location of the study areas with kudurs is shown on the geological map (Fig. 1).

It should be noted that the authors have already studied soil eaten by animals in the coastal zone of Teletskoye Lake in 2016 (17). At that time, it was found that the Altai kudurits contained low sodium (Na) concentrations. However, there were higher REE concentrations compared to the Sikhote-Alin, which could be extracted with the hydrochloric acid solution. The authors also conducted similar studies in 2018 on the Shavla River and near the Yazula settlement. These data have not been published yet, and were also used in the present study.

The research objectives included: The analysis of the geological structure of the study areas according to the data of the state geological survey; field collection of factual material (samples of water, rock, and loose soil including the kudurits, and vegetation samples); and various laboratory studies of the collected material. Based on the data obtained and taking into account the information from literature sources, the authors aimed to draw a justified conclusion about the cause of geophagy.

Following is a brief description of the study areas and research objects in the present study:

The Teletsky area. The geology, geomorphology and the landscape of the Teletskoye Lake area, as well as the characteristics of the local kudurs have been previously described by the authors in sufficient detail (17). Herein, only the most critical points ares mentioned.

There are numerous kudurs in the Teletskoye Lake area; however, they appear only on the southeastern shore. According to the study by Sobanskiy (18), there are about 40 kudurs in this part of the lake shore. They are also found near the estuary of the Chulyshman River valley, in particular, near the Koo settlement (Fig. 1).

The majority of the local kudurs are dry, represented by outcrops of loose (sometimes poorly cemented) rocks with characteristic depressions eaten by animals. They are formed at the slopes and on the surface of a multi-level river and lake terraces on thinly dispersed aqueous and glacial (more often, glaciolacustrine) deposits. Sometimes they also appear on interlayers of eolian material in modern diluvial and landslide deposits. The main rocks in the area are strongly metamorphosed mainly primary sedimentary rocks of the Proterozoic represented mostly by quartz-albite-sericite schists and gneisses cut by granitoids of the Middle Paleozoic age (presumably, Silurian and Devonian) (Fig. 1).

The kudurs on the Teletskoye Lake are most often visited by red deer (*Cervus elaphus sibiricus*), also Siberian roe deer (*Capreolus pygargus*), hares (*Lepus timidus*) and rarely, wild boar (*Sus scrofa*). According to the local old residents, until the early 1930s, the kudurs were also actively visited by Siberian ibex (*Capra sibirica*), which at that time lived along the lake shores. According to the annals of the Reserve, the main peak of visits to kudurs is from April to July, with another slight increase in September-November. Near the Koo settlement, where Silurian granites outcrop in the river valley, kudurs are equally actively visited by domestic animals (Fig. 2B).

The Yazula area. The upper reaches of the Chulyshman River near the Yazula village is a deeply dissected mountain plateau with individual towering mountain massifs, with absolute marks from 1,500 to 3,000 m. The valleys of the main rivers are deeply incised, with terraces and floodplains of varying degrees of intensity. Plateau-shaped watersheds are swamped in some places, and the slopes of river valleys and floodplains are partly covered with forests snd steppe. The tree cover is mainly represented by larch (*Larix sibirica*). On the northern slopes and in river valleys, dark conifers mingle with larch: Siberian spruce (*Picea obovata*), Siberian fir (*Abies sibirica*) and Scots pine (*Pinus silvestris*). Siberian pine (*Pinus sibirica*) is predominant on the tops of slopes and in the watersheds.

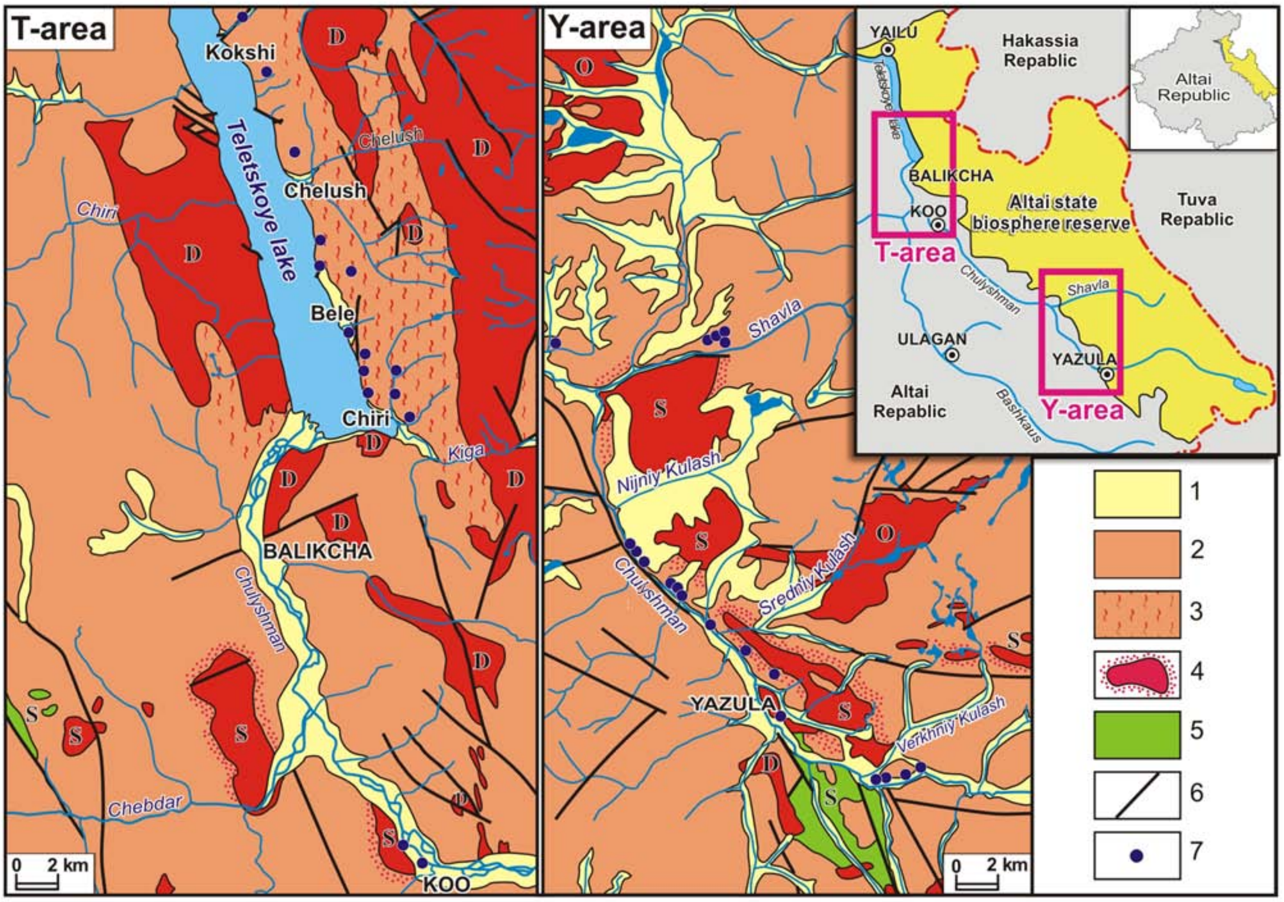

Figure 1. Geological structure of the study areas and their location relative to the territory of the Altai State Biosphere Reserve and the Altai Republic: 1, Quaternary aqueous and aqueoglacial deposits (pebble, boulders, sandy loam and loam); 2 and 3, Proterozoic and Early Paleozoic metamorphic rocks [mainly quartz-albite-sericite and quartz-sericite-chlorite schists (2) and gneiss (3)]; 4, Devonian, Ordovician and Silurian granitoids, including those with the contact metamorphism aureoles; 5, Silurian diorites and gabbro-diorites; 6, tectonic faults; 7, kudurs.

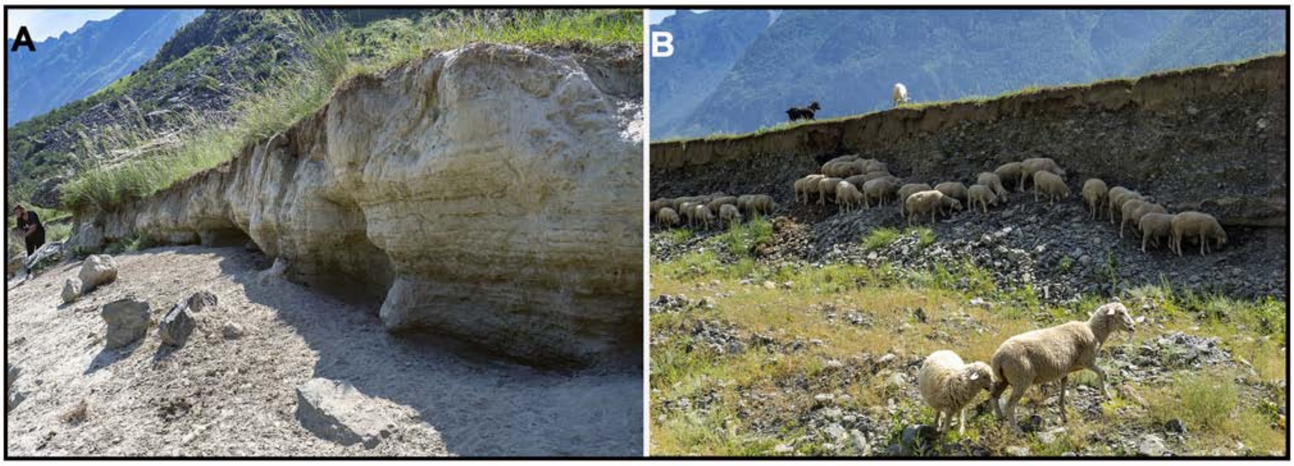

Figure 2. (A) A fragment of a kudur 5 km north of the Koo settlement (aqueoglacial loam in the Chulyshman River floodplain); (B) sheep eating fine soil in the roadside ditch near the Koo settlement (floodplain deposits of the Chulyshman River).

There are numerous kudurs near the Yazula settlement. They are very similar to the Teletsky area kudurs both in appearance and place of occurrence. All the kudurs studied appeared on stepped surfaces of different steepness, mostly on southern slopes. The vegetation is represented mainly by fescue-sagebrush and forb-sagebrush steppe with the main dominants of the Artemisia genus: *Artemisia gmelinii*, *A. frigida*, *A. viridis*, *A. commutata* and *A. dracunculus*. In the grasses, fescue is predominant: *Festuca pseudovina*, *F. vallesiaca* and feather grass (*Stipa capillata*). Mixed herbs include cinquefoil (*Potentilla acaulis*), stonecrop (*Orostachys spinosa*), crassula (*Sedum hybridum*), and sedge

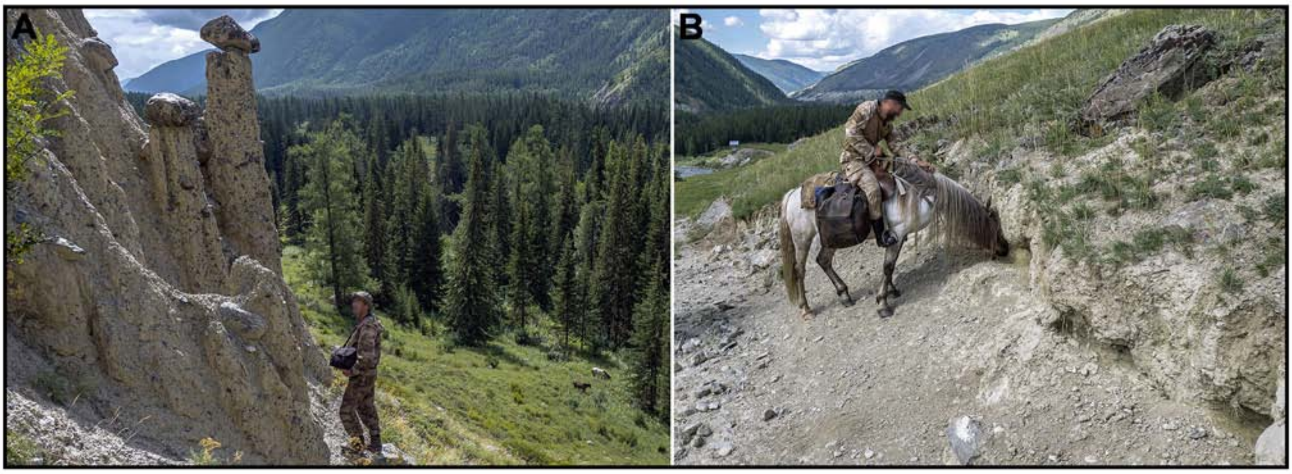

Figure 3. (A) Glacial moraine deposits on the right bank of the Chulyshman River (8.5 km north of the Yazula settlement); (B) a horse eating aqueoglacial loam on the right bank of the Chulyshman River (7 km to the north of the Yazula settlement).

(*Carex supina* and *C. pediformis*). The majority of these species are food for herbivores. On the sides of river valleys, kudurs are often confined to remnants of glacial moraines with rounded boulders (Fig. 3A), and on the sides and the surface of river terraces, to outcrops of glaciolacustrine loam and sandy loam.

According to the geological materials (map of the Russian Federation at a 1:200,000 scale; sheets M-45-XI and M-45-XVII), all studied glacial deposits with kudurs near the Yazul settlement lie on the Proterozoic age rocks similar to the Teletsky area (quartz-sericite-chlorite schists and gneiss), which are cut by the Ordovician and Silurian granitoids (Fig. 1).

The kudurs near the Yazula settlement are mostly visited by livestock (cows, sheep and horses), while the remote kudurs are visited by red deer, Siberian roe deer, hares and moose (*Alces alces*). Domestic and wild animals consume kudurits almost all year round. The peaks of visits to kudurs are the same as those in the lake area.

The attractiveness of the studied kudurs to domestic animals is illustrated by the fact that all four expedition horses (2018 expedition), once on the kudur after a seven-day walk, began eating the soil, which they licked and chewed for about 20 min on average, consuming ~0.5 kg of kudurit in the process (Fig. 3B).

Materials and methods

Factual material and sampling methods. In the Teletsky area, the research was carried out from July 24 to August 2, 2021, using motorboats and a car. In total, 28 hydrochemical samples, 37 rock samples and 64 vegetation samples were collected. The sampling locations are presented in Fig. 4. In the Yazula area, the research was carried out from August 1 to 8, 2018 using horses, and from August 3 to 8, 2021 on foot. A total of 20 hydrochemical samples, 50 rock samples and 28 vegetation samples were collected (Fig. 4).

Sampling sites were added to a 1:50,000 scale topographic base using GPS receivers. Water was sampled in 250 ml bottles stored in a car fridge during the fieldwork. Rock material samples (rocky and earthy varieties), up to 300 g each, were placed in strong polyethylene bags. Kudurits were collected from depressions eaten by animals to a depth of 10 cm. Aboveground plant parts were sampled within a 10-m radius. In total, three plant species were collected at all sites: One of the ferns (collected species were: *Matteuccia struthiopteris*, *Pteridium aquilinum*, *Dryopteris filix-mas* and *Dryopteris expansa*); one of the sedges (*Carex supina*, *C. pediformis*, *C. caryophyllea* and *C. globularis*), and one of the sagebrushes (*Artemisia gmelinii*, *A. frigida*, *A. viridis*, *A. commutata* and *A. dracunculus*). Ferns were collected as they are the accumulators of REE (19) common in Siberia and the Russian Far East. In addition, some of these are a part of the feed for ungulates. Sagebrushes are also occasionally used as food plants and they are widespread in the study areas (20). Sedge was sampled as the most common food plant for animals. Plant samples were collected into a paper bags.

Analytical methods. Chemical analyses of water and rock samples were performed at the Analytical Center of the Far East Geological Institute of the Far East Branch of the Russian Academy of Sciences (AC FEGI FEB RAS) in Vladivostok, Russia. X-ray diffraction analysis of minerals was performed at the Department of Engineering and Environmental Geology, Faculty of Geology, Lomonosov Moscow State University (Moscow, Russia). Plant samples and biological samples were analyzed in research laboratories of the Tomsk Polytechnic University (TPU) in Tomsk, Russia.

Plant samples were further prepared for inductively coupled plasma (ICP)-mass spectrometry (MS) analysis. They were ground, weighed, placed in 200 mg plastic test tubes, and dissolved in a mixture of nitric acid and hydrogen peroxide. Biological samples were decomposed with a mixture of nitric acid (HNO_3) and hydrofluoric acid (HF) acids in HP500 autoclaves with the Mars 5 microwave decomposition system (CEM Corporation). The maximum magnetron power was 1,200 W, the pressure was 150 psi, and the temperature was 150˚C.

The analytical studies of the collected samples are almost completely identical to those performed earlier. Further details on the methodology of these studies have been previously published (15).

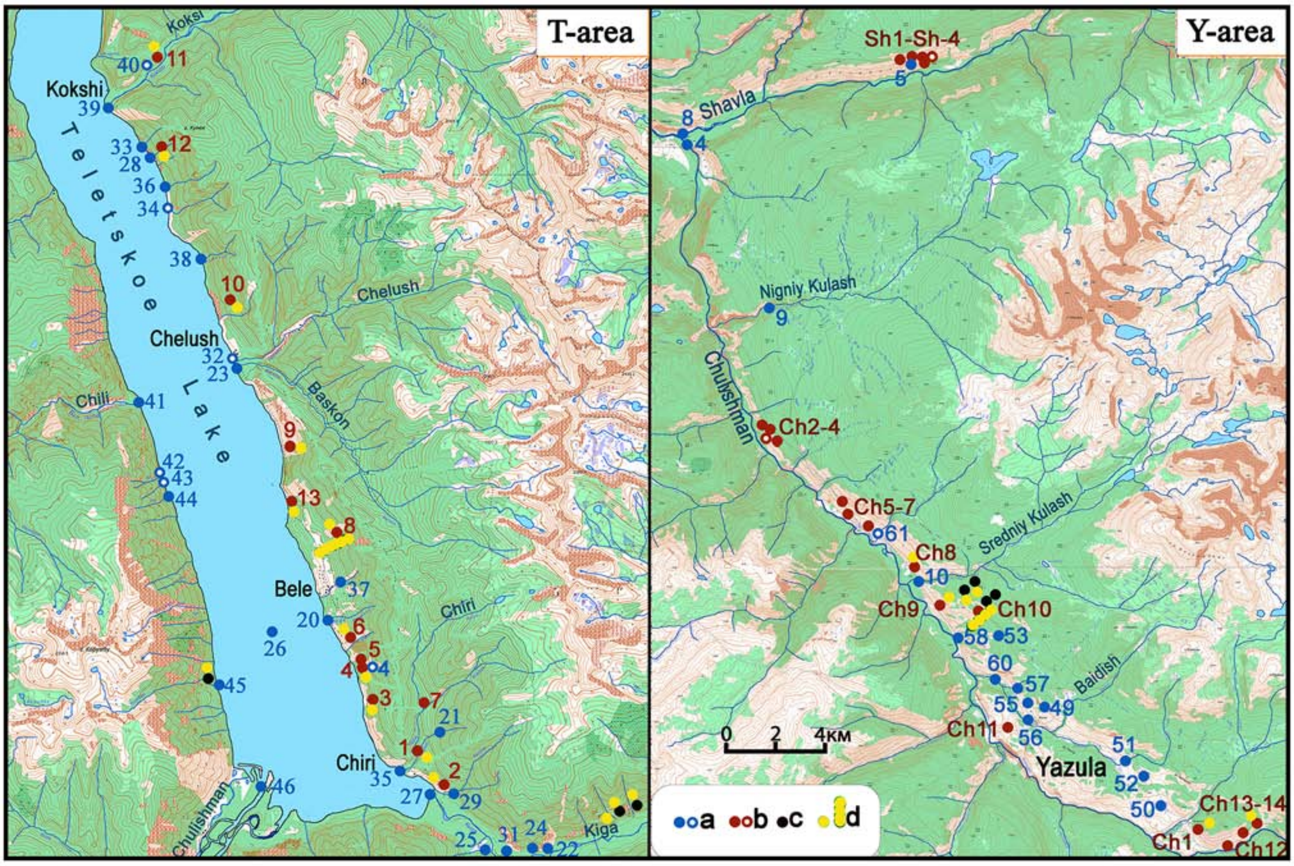

Figure 4. The sampling points of factual material: a, water samples, including those with high REE concentrations; b, kudurits and visually similar uneaten earths; c, granitoids; d, vegetation, including samples on profiles.

The micromineral composition of kudurit samples was determined in AC FEGI FEB RAS on the scanning electron microscopes Lyra 3 XMH (Tescan) with analytical attachment EDS AZtec X-Max 80 and JSM-6490LV (JEOL Ltd.) with attachments EDS INCA Energy, X-max, and WDS INCA Wave. A loose sample was glued onto carbon tape, placed on an aluminum column and sprayed with carbon coating. To automate the search process, INCAFeature software (version 5.03) by Oxford Instruments was used.

The particle sizes in the kudurit samples were determined using an Analysette 22 NanoTech plus laser particle analyzer (Fritsch GmbH).

To determine the yield of chemical elements under acidic conditions in the abomasums of ruminant mammals, 11 samples were treated with hydrochloric acid extracts in the Laboratory of Geochemistry of the PGI FEB RAS. Rock samples weighing 5.00 g were treated with 50.00 ml of hydrogen chloride (HCl) solution (pH 1.0; close to the rennet of large cattle). Subsequently, the suspension was shaken for 30 min and left for a day. The supernatant was centrifuged in plastic beakers for 30 min at 4,500 rpm (3,5 x g) at 22˚C. The transparent centrifugate was transferred to be analyzed for the studied elements. Distilled extra-pure HCl and triple purified distilled water were used to prepare the solution.

To reveal the ability of some minerals and mineral mixtures to sorb REE in conditions close to the environment of the abomasum, as well as the intestines of ruminants, laboratory experiments were performed. To simulate the electrolyte in the abomasum, an HCl solution with pH 2.00 was prepared in tridistilled water, in which La, Pr and Sm compounds were diluted (one of them appeared to have an admixture of Gd). First, $La_2(CO_3)_3$ salt (0.1648 g) and PrO_2 (0.1129 g) and SmO (0.1106 g) oxides were dissolved in 3.3 ml of 10% distilled hydrochloric acid. The solution was then diluted to 1 liter and allowed to stand for 24 h; 1 ml was then taken from the prepared solution and diluted with a HCl solution (pH 2) to 1 l. Subsequently, 5 g each of minerals (quartz, chalcedony, albite, calcite and smectite) and three varieties of quartz-hydromica-chlorite kudurits grinded to 1-10 μm were placed in flasks and 50 ml REE salt solution was added to each flask. This was followed by 12 h in a shaker and 12 h of settling. The liquid was separated from the minerals in a centrifuge for 30 min at 4,500 rpm (3,5 x g) at 22˚C. The analysis was performed using the ICP-MS method.

A solution of salts in ammonium acetate buffer with pH 8.6 on tridistilled water was prepared as a model of animal intestinal electrolyte. At the first stage, individual solutions of each salt were prepared: $Lu_2(SO_4)_3 \times 8H_2O$ (0.0224 g), $Eu_2(SO_4)_3 \times 8H_2O$ (0.0242 g) and $Gd(CH_3COO)_3 \times 3H_2O$ (0.0248 g) were dissolved in 100 ml water; the salts $Tb_2(CO_3)_3 \times 3H_2O$ (0.0173 g), $Dy_2(CO_3)_3 \times 8H_2O$ (0.0178 g) and $Y_2(CO_3)_3 \times 3H_2O$ (0.0232 g) were dissolved in 3 ml of 2 M acetic acid solution, then brought to 100 ml with water. A total of 0.1 ml was then taken from the obtained solutions and diluted with ammonium acetate buffer solution to 1 l. Following this, 5 g each of quartz

Table I. Averaged REE concentrations in seawater for the recalculation to the seawater standard.

Units	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
pmol/kg	5.26	3.02	1.06	4.97	1.26	0.36	1.70	0.31	2.12	0.58	1.82	0.25	1.35	0.21	71.21
ppb	0.73	0.42	0.15	0.72	0.19	0.06	0.27	0.05	0.34	0.09	0.30	0.04	0.23	0.04	6.33

Table II. Content of main ions in water samples with the maximum REE content collected from water sources and surface watercourses in the Teletsky and Yazula areas.

			Concentration of ions, mg/l (ppm)										
Area	Sample	pH	HCO_3	SO_4^{2-}	Cl^-	Br^-	NO_3^-	F^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
Teletsky	T4	6.27	7.24	35.7	0.44	<0.001	0.66	0.08	7.36	7.67	34.3	9.25	0.06
	T32	6.05	15.6	1.86	0.12	<0.05	1.52	<0.3	1.07	0.89	3.94	0.72	<0.1
	T34	6.68	49.5	3.89	0.15	<0.05	2.56	<0.3	1.71	2.24	14.8	1.29	<0.1
	T40	6.79	39.8	3.16	0.19	<0.05	0.22	<0.3	3.12	2.07	6.58	3.54	<0.1
	T42	5.64	5.40	2.56	0.10	<0.05	1.58	<0.3	1.23	0.25	3.11	0.76	<0.1
	T43	5.70	19.5	1.22	0.10	<0.05	2.07	<0.3	1.29	0.31	6.07	0.51	<0.1
	T26-Lake	6.66	57.80	3.89	0.52	<0.05	0.61	<0.3	1.51	0.61	13.80	2.81	<0.1
Yazula	Y61	6.25	31.50	1.68	0.15	<0.05	0.25	<0.3	2.30	0.88	6.93	1.74	<0.1

Please see Fig. 4 for water sources with high REE concentrations. REE, rare earth elements.

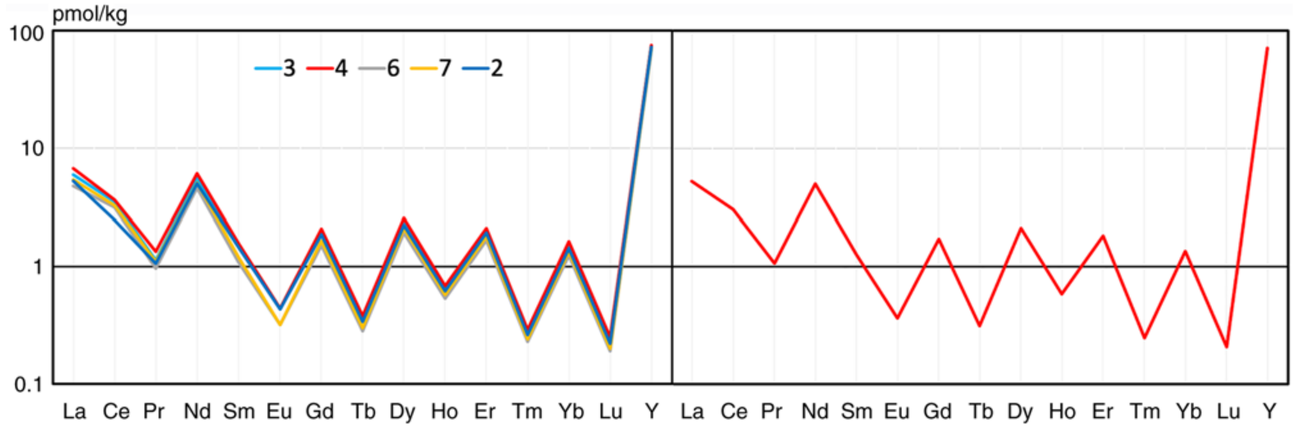

Figure 5. Left panel, concentration profiles for three, four, six and seven measurements at different depths; right panel, an averaged profile for seven measurements.

and albite minerals grinded to 1-10 microns were placed in flasks and 50 ml of the prepared REE salt solution was added.

To optimize the presentation of REE concentration profiles for water and biological samples, our standard for seawater was introduced. The hypothesis is that the REE concentration in seawater should be close to that in the animal blood. In turn, the optimal concentration of REE in seawater should be where the highest density of nekton is, as it is the marine environment that is the source of REE for fish. For the calculations, data from the literature (21,22) were adopted on REE concentrations in seawater for four water areas in the depth interval up to 30 m. The concentration profiles for three, four, six and seven measurements at different depths from 3 to 30 m on the left, and an average profile for seven measurements on the right are illustrated in Fig. 5. The numerical values used for the recalculation to the seawater standard are presented in Table I.

The mathematical processing of data was performed using Excel and STATISTICA software, which are parts of the licensed software package of Tomsk Polytechnic University (software package Microsoft Office 2016 Standard Russian Academic and StatSoft Statistica 13 Ultimate Academic Russian Concurrent). Statistical non-parametric analysis using the Mann-Whitney U test was applied to evaluate the significance of differences between the samples. Differences were considered significant at the critical value of Mann-Whitney U test for the significance level β=5% and confidence level P=0.95, i.e., $P<0.05$.

To obtain the objective and reliable information about the concentrations of La, Ce, Nd, Sm, Eu, Tb, Yb and Lu, 91 vegetation samples were also analyzed by the instrumental neutron-activation method. According to the statistical processing of the results of comparison of samples analyzed by two methods, the deviation in Ce, Nd and Lu concentrations was not >15%, and in La, Sm, Eu, Tb, and Yb, the concentrations were not >10%. The results were obtained using the equipment of the Center for Collective Use of Scientific Equipment of Tambov State University (Tambov, Russia) named after G.R. Derzhavin.

Results

Hydrochemistry. Analytical data for the water samples indicate that all the waters sampled in the studied areas are ultra-fresh with salinity <0.3 g/l. The pH values of waters in the Teletsky area range from 5.64 to 7.76 (6.67 on average; herein and below, the authors are referring to the arithmetic mean) and in the Yazula area, from 6.25 to 8.20 (7.50 on average). By the basic salt composition, the majority of the waters are hydrocarbonate-calcium, with only a few samples with a significant proportion of sulfate ions (Fig. 6).

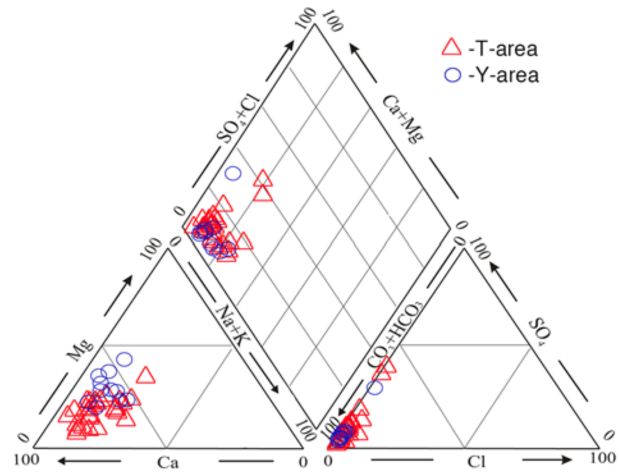

Figure 6. Macrocomponent composition of surface and spring well waters taken in the Teletsky (n=28) and Yazula (n=20) areas (Piper diagrams).

In the Teletsky area, the HCO_3^- concentration in samples varies from 2.1 to 206.9 ppm and the average value is 68.25. The average for SO_4^{2+} is 6.53 (1.14-30.6). The average chloride ion content is 0.57 ppm, ranging from <0.1 to 3.86. The average NO_3 content is 2.44 ppm (0.1-13.80). The concentrations of F and NO_2 ions are <0.1 (the detection limit). The average Ca content is 17.75 ppm (2.87-52.3). The average Na^+ content is 2.29 ppm (0.81-8.15). The content of Mg is 2.87 ppm on average (0.44-7.32). The content of K varies from 0.21 to 5.44 (1.91 on average). The dissolved organic carbon content ranges from 0.1 to 20.7, with an average of 3.72 ppm (data not shown).

In terms of the content of most trace elements (in ppb), the analyzed waters are distinguished by significant variations (within one order of magnitude) of Al (from 3.74 to 581 with an average of 53.2), Sr (8.37-180/52), Mo (0.12-8.32), U

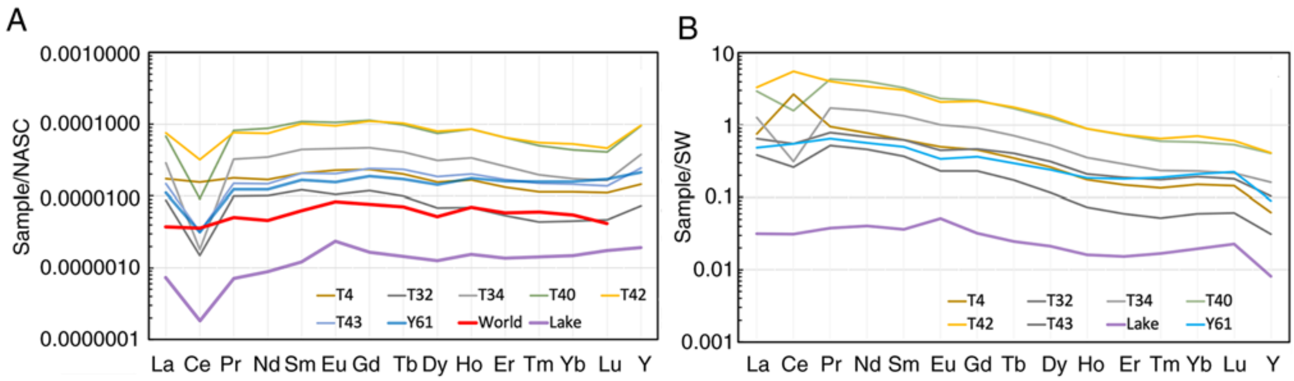

Figure 7. REE distribution profiles in water samples with the maximum REE content in the Teletsky (n=6) and Yazula (n=1) areas: (A) NASC-normalized (24); (B) normalized to seawater (please see Table I for normalization values). Of note, 'World' is the world average content (25), 'Lake' is the Teletskoye Lake (n=1). T4, 32, 34, 40, 42, 43, 61 and Y4, 32, 34, 40, 42, 43, 61 are the locations of surface and spring well water sampling in the Teletsky and Yazula areas shown in Fig. 4. REE, rare earth elements; NASC.

(0.07-6.50/1.17), and all elements of the REE group. In other elements, variations are less than an order of magnitude. The average concentrations of other trace elements are as follows: Li, 1.80; Be, 0.02; B, 16.02; P, 8.18; Sc, 0.086; Ti, 0.87; V, 0.55; Cr, 0.75; Mn, 0.88; Fe, 50.0; Co, 0.07; Ni, 0.42; Cu, 1.98; Zn, 2.23; Ga, 0.015; Ge, 0.027; As, 0.85; Se, 0. 26; Rb, 1.22; Zr, 0.16; Nb, 0.03; Ag, 0.009; Cd, 0.005; Sn, 0.01; Sb, 0.095; Cs, 0.061; Ba, 12.8; Hf, 0.004; Ta, 0.0005; W, 0.03; Tl, 0.003; Pb, 2.76; Bi, 0.001; and Th, 0.06 (data not shown).

The total concentration of dissolved forms of REE varied from 1.11 to 12.98 ppb (including Sc and Y). In all samples, the predominance of the sum of light lanthanides over heavy ones was observed with, the light rare earth elements (LREE) sums ranging from 63 to 87%.

In the Yazula area, the average concentration of HCO_3^- was 143 ppm (15.65-283), and the concentrations of other elements were as follows: sulfate ion, 11.3 (1.31-60.7); chloride ion, 0.55 (0.1-1.40); and NO_3, 1.08 mg/l (0.13-4.52). The concentrations of F and NO_2 ions were also <0.1 (the detection limit). In the composition of the main cations, Ca also was predominant, with an average of 27.3 ppm (2.77-52.3). The average content of Na was 6.03 (1.43-12.4) and that of Mg was 12.2 ppm (1.0-27.9). The content of K varied from 0.55 to 2.13 (1.54 on average). Dissolved organic carbon content ranged from 0.1 to 5.1, with an average of 2.85 ppm (data not shown).

In the composition of trace elements, significant variations (within the same order) were found for Sr (16.59 to 347 ppb with an average of 158 ppb), Mn (0.06-5.29/0.82), Th (0.0003-0.032/0.011), U (0.05-7.25/2.04) and all REE elements. For the other elements, the variations were not significant. Their average concentrations are as follows: Li-3.89, Be-0.003, B-31.12, P-8.85, Ti-0.45, V-0.95, Cr-0.81, Mn-0.82, Fe-11.53, Co-0.07, Ni-0.48, Cu-1.11, Zn-1.47, Ga-0.01, Ge-0.010, As-0.61, Se-0. 22, Rb-0.54, Zr-0.13, Nb-0.002, Ag-0.008, Cd-0.005, Sn-0.01, Sb-0.12, Cs-0.09, Ba-16.83, Hf-0.003, Ta-0.0004, W-0.09, Tl-0.0012, Pb-2.42, and Bi-0.001.

The total concentration of dissolved forms of REE varied from 0.11 to 2.21 ppb (including Sc and Y). In all samples, the predominance of the sum of light lanthanides over heavy ones was observed, with the LREE sums ranging from 62 to 82%.

As illustrated in Fig. 7A, the North-American slate (NASC)-normalized concentrations of REE and yttrium in six most REE-rich water samples from the Teletsky area and one sample from the Yazula area were compared to the average concentrations in rivers worldwide (23) and the concentration in the Teletskoye Lake. In both areas, the REE concentrations exceeded the world average values by up to 10-fold. All spectra exhibited a distinctly negative cerium anomaly (Ce/Ce*=0.08-0.53) which is typical for river waters. More detailed hydrochemical characteristics of waters with a high REE content are summarized in Tables II and III.

As shown in Fig. 7B, the REE distribution profiles in the same samples were normalized to seawater. Level '1' on the y-axis indicates that the values correspond to REE concentrations in seawater (in fact, to optimal concentrations for living organisms). In almost all but three samples, the concentrations of all elements were lower than those in seawater. The concentrations at Y were particularly low.

Mineralogy of kudurits. The sizes of the main mass of mineral particles in the kudurit samples measured on a laser particle analyzer markedly differed in the study areas (data not shown).

In the Teletsky area, the particle sizes in 11 samples of kudurits varied mainly from 0.1 to 100 μm, with their maximum number in the interval from 20 to 50 μm, which corresponds to the size of the silty or dusty fraction. The fraction of clay particles (<1 μm in size) ranged from 1 to 5%. In two samples, there were additional peaks with a quantitative maximum of ~0.2 mm.

In the Teletsky area kudurit minerals, according to the quantitative mineralogic X-ray diffraction analysis of 15 samples, quartz and feldspar crystalloclasts were predominant (41 to 73% in total), of which quartz particles contributed from 20 to 42% and plagioclase, from 21 to 34%. In other minerals, mica and chlorite were strongly predominant, namely 8 to 48% in total. As impurity minerals, kaolinite, smectite, calcite, gypsum, ankerite, zeolites, actinolite, amphiboles and rutile may be present (not exceeding 5% in total) (Table IV).

In the Yazula area, the particle sizes in 14 samples of kudurits and three samples of uneaten analogs of kudurits also varied mainly from 0.1 to 100 μm, but with quantitative maximums from 5 to 20 μm, which correspond to the fine dust

Table III. Concentrations of Y and lanthanides in water samples with the maximum REE content from the Teletsky and Yazula areas (ppb).

	T-area							Y-area
Element	T4	T32	T34	T40	T42	T43	T26-Lake	Y61
Y	0.391	0.1991	1.0207	2.5502	2.6069	2.6069	0.0516	0.5723
La	0.5520	0.2797	0.9224	2.1568	2.4226	0.4714	0.0233	0.3520
Ce	1.1300	0.1097	0.1317	0.6676	2.3262	0.2326	0.0132	0.2309
Pr	0.1410	0.0778	0.2568	0.6446	0.6048	0.1172	0.0056	0.0969
Nd	0.5570	0.3295	1.1398	2.8689	2.4365	0.4883	0.0290	0.4061
Sm	0.1180	0.0693	0.2531	0.6185	0.5758	0.1177	0.0069	0.0948
Eu	0.0271	0.0125	0.0550	0.1276	0.1143	0.0244	0.0028	0.0186
Gd	0.1210	0.0617	0.2446	0.5915	0.5707	0.1242	0.0086	0.0972
Tb	0.0172	0.0085	0.0349	0.0831	0.0873	0.0198	0.0012	0.0145
Dy	0.0900	0.0395	0.1804	0.4291	0.4617	0.1069	0.0073	0.0830
Ho	0.0166	0.0070	0.0336	0.0850	0.0848	0.0201	0.0016	0.0176
Er	0.0449	0.0181	0.0875	0.2205	0.2214	0.0571	0.0047	0.0543
Tm	0.0057	0.0022	0.0098	0.0250	0.0275	0.0074	0.0007	0.0079
Yb	0.0352	0.0139	0.0539	0.1348	0.1639	0.0451	0.0046	0.0490
Lu	0.0053	0.0022	0.0079	0.0196	0.0222	0.0066	0.0008	0.0082
ΣREE	2.861	1.032	3.411	8.673	10.120	1.839	0.1109	1.5319
LREE	2.498	0.866	2.704	6.956	8.366	1.427	0.078	1.181
HREE	0.363	0.166	0.708	1.716	1.754	0.412	0.032	0.350
LREE%	87.31	83.95	79.26	80.21	82.67	77.62	70.72	77.12
HREE%	12.69	16.05	20.72	19.79	17.33	22.38	29.28	22.88
Y/Ho	23.55	28.44	30.38	30.00	30.74	129.70	32.25	32.52
Eu/Eu*	1.519	1.949	1.658	1.55	1.432	1.013	0.491	0.696
Ce/Ce*	1.027	0.867	1.003	0.957	0.904	0.913	1.629	0.878
La/Yb[a]	0.882	0.162	0.059	0.123	0.419	0.216	0.252	0.272
La/Sm[a]	0.833	0.719	0.649	0.621	0.749	0.713	0.602	0.661
Sm/Yb[a]	1.823	2.712	2.554	2.495	1.911	1.419	0.816	1.052
LREE/HREE[a]	0.607	0.651	0.511	0.523	0.519	0.411	0.261	0.375

Eu/Eu*=2Eu*/(Sm* + Gd*) and Ce/Ce*=2Ce*/(La* + Pr*) are formulas for calculating the europium and cerium anomalies from the NASC-normalized values; [a]the ratio of the NASC-normalized element values; ΣREE, total REE concentrations; LREE, total light REE concentrations; HREE, total heavy REE concentrations.

fraction. The clay fraction contribution was also markedly higher, sometimes up to 20%. Four samples had additional peaks in the sandy particle size range, with three samples having a 'sandy' peak in the 100-200 μm range and one sample having a peak near 1,000 μm.

In the mineral composition of 11 samples of kudurits and three similar rocks without traces of consumption by animals, crystalloclasts of quartz and feldspars (28 to 66% in total) were also predominant, of which quartz particles contributed 19 to 43%. In other minerals, mica and chlorite were also strongly predominant ranging from 20 to 69% in total. Moreover, chlorite was considerably more abundant than in kudurits from the Teletsky area. As impurity minerals, calcite, gypsum, ankerite, kaolinite, actinolite, pyrite, amphiboles, and rutile may be present (not exceeding 5% in total) (Table V). As shown the data in Table V, the mineral composition of uneaten analogs of kudurits did not differ from the composition of kudurits.

Thus, the main difference in the mineral composition of kudurits from the studied areas is in the amount of chlorite and the composition of impurity minerals. As for the sizes of mineral particles, they are noticeably smaller in the Yazula area. This may be explained by a higher contribution of aeolian particles in the upper Chulyshman glacial deposits.

Geochemistry of kudurits, gneisses and granitoids. If the eaten earths in both studied areas are formally characterize by the composition of the main oxides, they all belong to the acid and acid-medium series with low- and normal-alkaline content of alkaline elements. The SiO_2 content in 17 kudurit samples from the T-area varied from 55.2 to 70.32% with an average value of 62.76, TiO_2 from 0.54 to 0.93 (0.73), Al_2O_3 from 11.64 to 17.42 (14.15), Fe_2O_3 from 3.98 to 8.68 (6.27), MnO from 0.07 to 0.17 (0.11), MgO from 1.57 to 4.76 (3.29), CaO from 2.37 to 7.08 (4.11), Na_2O from 2.34 to 3.3 (2.75), K_2O from

Table IV. Results of quantitative mineralogic X-ray diffraction analysis of kudurit samples from the littoral zone of the Teletskoye Lake.

	Mineral fraction in samples, wt%														
	T1		T2		T3	T5	T7	T8			T9	T10	T11	T13	Koo
Minerals	1.1[a]	18-3	2.1[a]	19-1	1.1[a]	42-1	1.1[a]	1.1[a]	37-1	37-2	1[a]	1[a]	1[a]	41-1	44-1
Quartz	40.2	40.9	30.2	39.6	42.8	34.1	39.4	35.0	37.4	27.4	20.1	39.7	39.6	37.4	28.0
Plagioclase	21.7	26.8	29.0	31.1	26.6	34.7	32.0	23.3	25.1	24.4	15.0	29.8	28.6	25.4	24.5
K-f-spar	4.4	-	2.1	-	0.0	-	5.3		-	-	6.4	0.0	3.0	-	-
Micas	21.3	6.8	31.1	6.7	24.9	6.8	21.4	22.0	19.1	23.6	42.3	17.3	22.7	23.9	19.8
Chlorite	9.0	9.1	4.5	1.7	3.2	3.7	1.2	5.3	7.8	16.9	5.2	3.8	2.3	6.7	23.8
Illite-smectite	0.0	8.8	1.6	-	0.8	8.1	0.0	4.6	-	-	5.0	4.2	0.0	-	-
Kaolinite	1.0	-	0.0	-	0.0	-	1.7	0.6	-	-	1.3	0.4	1.1	-	-
Calcite	0.0	4.8	0.8	3.0	0.0	-	0.0	0.0	2.0	2.1	0.0	2.0	0.0	3.1	1.1
Gypsum	-	-	-	-	-	2.5	-	-	-	-	-	-	-	-	1.1
Ankerite	-	0,5	-	0.7	-	0.8	-	-	1.0	1.1	-	-	-	1.1	0.5
Zeolites	1.7	-	0.7	-	0.9	1.5	2.3	0.7	-	-	0.9	0.9	0.6	0.5	0.5
Actinolite	0.6	-	0.0	-	0.8	-	0.4	3.2	-	-	3.8	2.0	2.1	-	-
Amphiboles	-	1.3		17.2	-	6.9	-	-	6.0	3.5	-	-	-	2.1	
Rutile	-	0.8		-	-	-	-	-	1.0	1.0	-	-	-	-	1.5

Kudurit sample numbers correspond to the kudur numbers in Fig. 4. [a]Data are from the study by Panichev *et al* (17).

Table V. Results of quantitative mineralogic X-ray diffraction analysis of kudurits and uneaten analogs from the Yazula area.

	Mineral fraction in samples, wt%													
	Shavla River basin (Sh)				Chulyshman River basin (Ch)									
Minerals	2.2	3.1	4.0[a]	4.1	1.1	1.2	3.1	3.3	4.0[a]	6.0[a]	6.1	54	63	71
Quartz	24	27.8	19.3	22	18.5	15.3	19.2	23.6	17.6	32.6	25.3	43.1	14.8	30.5
Plagioclase	20.6	25.3	19.2	19.2	20.7	20.6	21.7	24	21.3	25.3	19.9	23.7	13.6	26.3
K-f-spar	5.7	6.4	5	5.8	6.1	5.1	5.2	9	5.4	10.8	8.3	-	-	-
Micas	30.3	22.7	34.1	29.3	29.2	31.6	31.1	22.6	32.8	14.9	26.4	10.1	46.3	19.0
Chlorite	16.3	15.1	20.1	20	21.1	20.9	18.4	15.6	18.4	8.2	15.8	10.2	23.5	19.6
Illite-smectite	-	-	-	-	-	-	-	-	-	-	-	9.0	-	-
Kaolinite	0.5	0.8	0.5	0.6	1.4	2.9	3.2	1.0	1.8	4.0	0.7	-	-	-
Calcite	0.4	0	0.3	1.5	1.3	1.3	0.2	1.9	0.6	0.8	0.6	0.9	0.5	1.9
Gypsum	1.1	0.8	0.8	0.8	0.6	1.1	0.3	0.9	0.9	1.0	1.2	0.7	-	0.6
Ankerite	-	-	-	-	-	-	-	-	-	-		0.6	0.5	0.5
Pyrite	0.3	0.1	0.1	0	0.1	0.1	0.2	0.1	0.2	0.4	0.2	-	-	-
Actinolite	0.9	1.0	0.6	1.0	1.1	1.0	0.7	1.4	0.9	2.0	1.7	-	-	-
Amphiboles	-	-	-	-	-	-	-	-	-	-	-	1.4	0.5	1.1
Rutile	-	-	-	-	-	-	-	-	-	-	-	0.5	1.2	0.8

Sample numbers correspond to the kudur numbers in Fig. 4. [a]Analogs of kudurits without traces of consumption by animals.

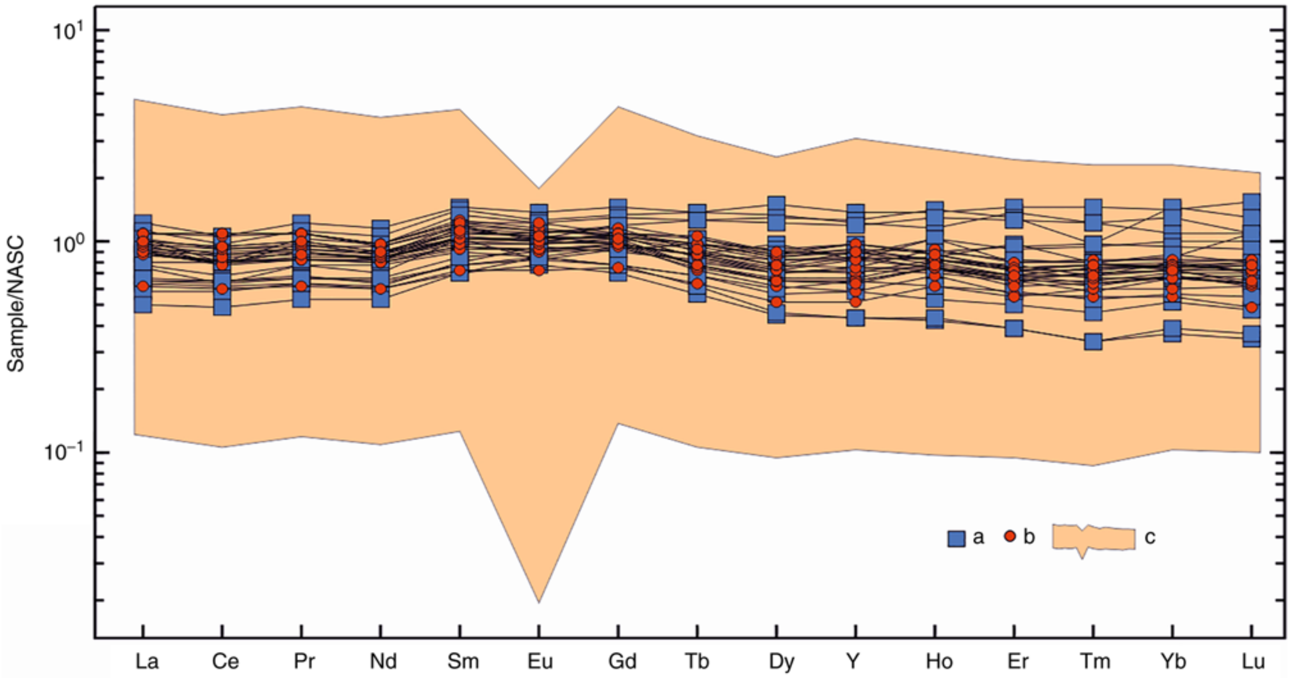

Figure 8. Distribution of chondrite-normalized (26) REE in kudurits from the (a) T-area and (b) Y-area combined with the field of REE values in kudurits from the (c) Sikhote-Alin.

1.26 to 3.70 (2.87), and P_2O_5 from 0.1 to 0.2 (0.15). The loss on ignition varied from 1.21 to 5.41%, with an average value of 3.22% (data not shown).

In the composition of 46 trace elements, the highest values were in Ba, 332 ppm on average, ranging from 189 to 590 ppm. The composition of the remaining elements was as follows in descending order: Sr, 193 (153-226); V, 126 (153-226); Cr, 123 (82-188); Zr, 84 (59-178); Rb, 68 (48-104); Zn, 59 (44-92); Ni, 56 (42-80); Ce, 50 (36-65); Cu, 49 (29-105); Li, 28 (22-41); Nd, 23 (18-29); La, 23 (16-30); Y, 18 (12-25); Sc, 16.31 (11-21); Co, 16 (1-22); and Ga, 12.24 (11-18). These are followed by concentrations <10 ppm in descending order: Pb, As, Nb, Th, Pr, Sm, Gd, Dy, Cs, W, Er, Yb, Hf, U, Sn, Ge, Mo, Be and Eu; and <1 ppm-Sb, Ho, Tb, Ta, Tm, Lu, Tl, Se, Bi, Cd, Ag and Te (data not shown).

The sum of REE in kudurits from the T-area (including yttrium and scandium) ranged from 128 to 202 ppm, with an average of 155 ppm.

The granitoids of the T-area were characterized in five samples. They had the following composition of the main oxides: SiO_2 from 63.26 to 72.68%, with an average of 68.09, TiO_2 from 0.18 to 0.98 (0.59), Al_2O_3 from 14.09 to 15.63 (14.54), Fe_2O_3 from 1.79 to 6.23 (4.15), MnO from 0.03 to 0.11 (0.08), MgO from 0.51 to 2.46 (1.56), CaO from 1.32 to 4.57 (2.86), Na_2O from 3.07 to 4.27 (3.59), K_2O from 1.84 to 5.46 (3.45), and P_2O_5 from 0.15 to 0.26 (0.21). The loss on ignition ranges from 0.07 to 1.21% with an average of 0.53%. The sum of REE (including yttrium and scandium) ranges from 102 to 174 ppm, with an average of 135 ppm (data not shown).

The SiO_2 content in 20 kudurit samples from the Y-area ranged from 47.56 to 66.06%, with an average of 55.83, TiO_2 from 0.39 to 0.94 (0.71), Al_2O_3 from 13.70 to 20.95 (17.62), Fe_2O_3 from 5.79 to 10.47 (7.95), MnO from 0.10 to 0.18 (0.14), MgO from 2.81 to 5.11 (4.16), CaO from 1.01 to 6.9 (2.22), Na_2O from 1.32 to 2.92 (2.25), K_2O from 2.03 to 4.06 (2.91), and P_2O_5 from 0.11 to 0.25 (0.18). The loss on ignition ranged from 2.13 to 10.32%, with an average of 5.1% (data not shown).

In the composition of trace elements, the highest values were: Ba, 578 ppm, on average, ranging from 356 to 857 ppm. The following are presented in descending order: Sr, 204 (115-320); Cr, 164 (102-299); V, 142 (99-218); Rb, 126 (75-167); Zn, 115 (77-163); Ni, 110 (78-187); Zr, 93 (42-125); Ce, 68 (43-91); Li, 54 (37-76); Cu, 49 (29-105); La, 32 (20-40); Nd, 29.49 (14-35); Co, 24 (15-30); Y, 23 (14-35); Ga, 22 (14-28); Sc, 22 (14-30); and Pb, 17 (13-23). These are followed by concentrations <10 ppm in descending order: Th, Cs, Nb, As, Pr, Sm, Gd, Dy, Sn, U, Er, Yb, Hf, Be, W, Ge, Eu and Sb; and <1 ppm: Ho, Tb, Ta, Tl, Mo, Tm, Lu, Ag, Se, Cd and Te. The sum of REE in kudurits in the Y-area (including yttrium and scandium) varied from 141 to 271 ppm, with an average of 206 ppm (data not shown).

The granitoids of the T-area were characterized in five samples. They had the following composition of the main oxides: SiO_2 from 61.65 to 74.53% with an average of 66.58, TiO_2 from 0.30 to 1.17 (0.67), Al_2O_3 from 12.70 to 17.04 (15.19), Fe_2O_3 from 2.18 to 6.41 (4.56), MnO from 0.03 to 0.12 (0.08); MgO from 0.38 to 4.08 (1.61), CaO from 1.22 to 3.17 (2.48), Na_2O from 3.09 to 5.36 (4.20), K_2O from 1.32 to 4.91 (3.21), P_2O_5 from 0.06 to 0.37 (0.21). LOI varies from 0.09 to 1.85% with an average of 0.77%. The sum of REE varies from 131 to 240 ppm with an average of 183 ppm.

Fig. 8 shows profiles of the chondrite-normalized REE in kudurits from the Teletsky and Yazula areas on the field of values for kudurits from two areas in the Sikhote-Alin (15). Apparently, the kudurits from geographically and geologically different regions are comparable in REE concentration.

Table VI. Results of the automated search on an electron microscope with an analytical attachment for aggregates containing REE in kudurit samples.

			No. of phases containing an element in significant quantities														
Sample	S, mm^2	No. of particles	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
The Teletsky area																	
T 18	95	4514	553	616	8	583	-	1	15	-	33	-	8	-	4	-	85
T 37	108	5122	131	157	-	138	1	-	5	4	11	-	4	-	4	-	17
T 38	95	5655	258	285	23	271	16	1	44	6	52	-	49	-	31	-	86
T 44	109	7259	233	304	12	254	8	2	12	-	22	-	16	-	8	-	49
SUM	407	22,550	1,175	1,362	43	1,246	25	4	76	10	118	-	77	-	47	-	237
The Yazula area																	
Ch 49	112	2,453	45	48	3	45	-	-	5	2	9	-	9	-	5	-	9
Ch 59	106	1,832	154	168	6	161	2	-	14	-	27	-	16	-	9	-	32
Ch 62	116	7,087	378	418	23	404	19	8	29	27	34	-	22	-	16	-	75
Ch 71	78	2,122	82	90	1	90	1	-	3	3	7	-	2	-	-	-	17
SUM	411	13,494	659	724	33	700	22	8	51	32	77	-	49	-	30	-	133

S, the surface area with the glued layer of kudurit on an aluminum column; the '-' indicates levels below the detection limit.

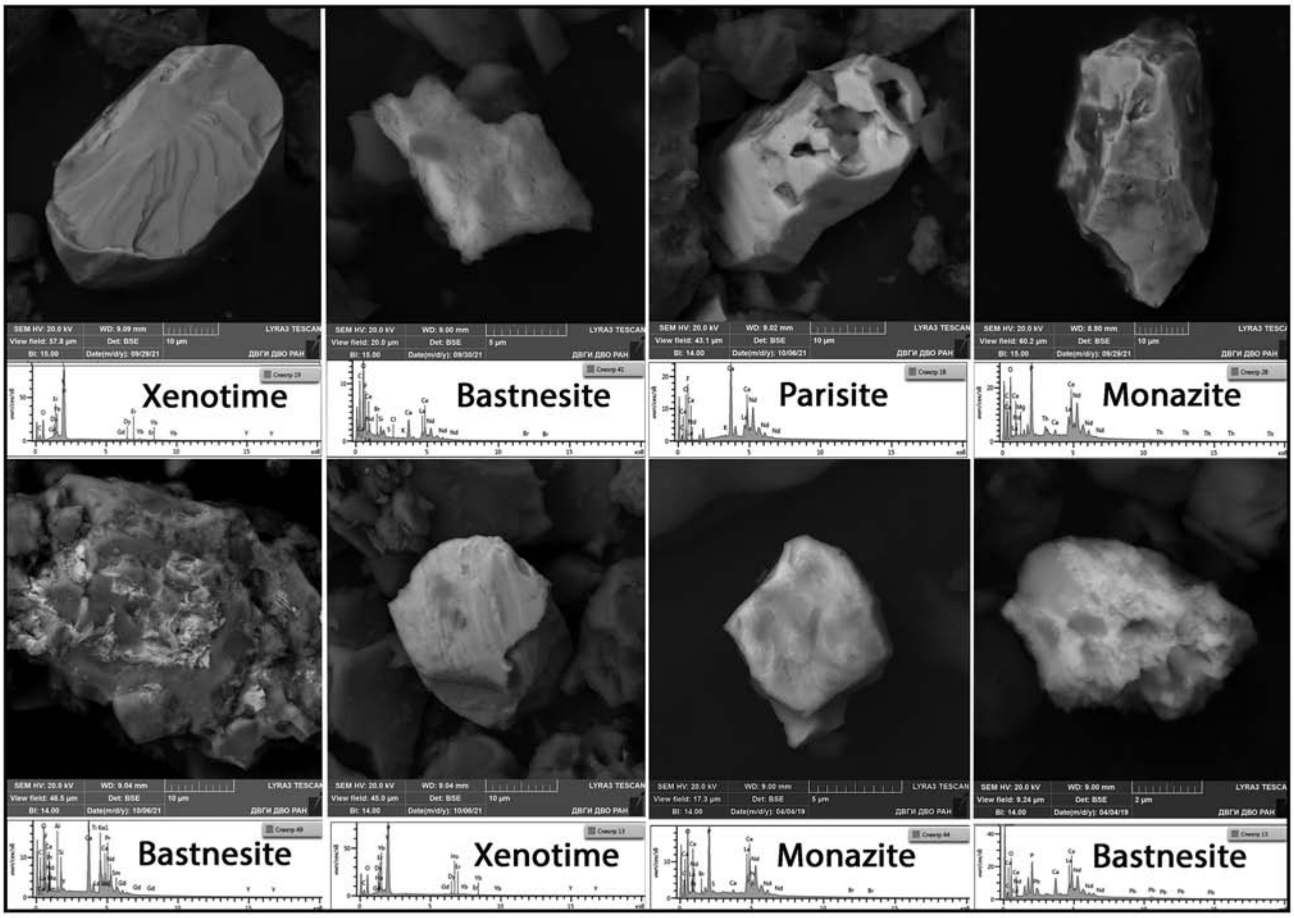

Figure 9. Images and micromineral spectra of rare-earth aggregates in the kudurit samples from the Teletsky (upper panels) and Yazula (lower panels) areas. Electron microscope images are shown.

Electron microscopy. Four samples each from both areas were selected for the automated quantitative determination of mineral aggregates of REE in kudurits on an electron microscope. The results are summarized in Table VI. It is evident that at almost the same scanning surface, the abundance of REE aggregates in kudurits in the Teletsky area is almost twice as high as in the Yazula area. In terms of individual elements, the maximum amount of REE aggregates in the T-area is for Ce, followed by Nd, La, Dy, Er, Gd, Yb, Pr, Sm, Tb and Eu. In the Y-area, the succession is somewhat different: Ce, Nd, La, Dy, Gd, Er, Pr, Yb, Tb, Sm and Eu. All the detected fluorine-containing REE aggregates were identified as the REE fluorocarbonates parizite and bastnaesite. The remaining REE aggregates were phosphates (xenotime, monazite, and rhabdophane). The most representative of the identified REE aggregates are presented in Fig. 9.

Acid extracts. The indicators of the most notable macrocations (Na and Ca) coming out into the hydrochloric solution from the kudurits indicate a significant variation of the content of the Na forms soluble in the acidic environment: from 50 to 3,472 ppm, or from 0.4 to 19.7% from the gross content (Table VII). The content of the soluble forms of Na in the earthly substances not consumed by animals was lower in total than in the consumed ones. However, there are the kudurit samples, in which there is less Na available for animals than in the unconsumed earths. In comparison with the kudurits of the of the Teletsky area, the kudurits from the Yazula area contained more Na and substantially less Ca (tens and hundreds of times) available for animals. The yield of the element in the extract from different samples also proved to be highly variable, clearly indicating that animal interest in Fe is not related to geophagy.

Among trace elements in the extracts from Teletsky kudurits, the highest concentrations were in Ba, with a range of values from 20 to 119 ppm, Sr (5-27), V (0. 09-7.39), Cu (0.31-7.00), Zn (0.01-5.00), Ni (0.42-4.06), Co (0.16-3.96), Cr (0.06-3.31), Ce (0.04-8.43), Nd (0.05-4.48), Y (0.12-5.25), Gd (0.01-1.10) and Pb (0.004-1.66). The concentrations of other trace elements was <1 ppm.

In the Yazula area kudurits, the situation with trace elements in extracts differed substantially. The data obtained after statistical processing (arithmetic mean ± error of the mean) indicated that the highest average concentrations in the extracts (downward) were in Sr, 24.52±3.22 ppm; and Ba, 18.64±5.76 ppm. A group of five elements had a yield of 5 to 12 ppm, including Ce, 11.17±0.50 ppm; Y, 5.40±0.25 ppm; Cu, 8.53±1.16 ppm; Nd, 5.79±0.28 ppm; and La, 5.58±0.32 ppm. A group of 11 elements had a yield of 1 to 4 ppm, including Pb, 4.06±0.64 ppm; Zn, 3.94±0.53 ppm; Ni, 3.16±0.34 ppm; V, 2.00±0.46 ppm; Cr, 1.76±0.30 ppm; Co, 1.63±0.0.18 ppm; Gd, 1.39±0.05 ppm; Li, 1.33±0.12

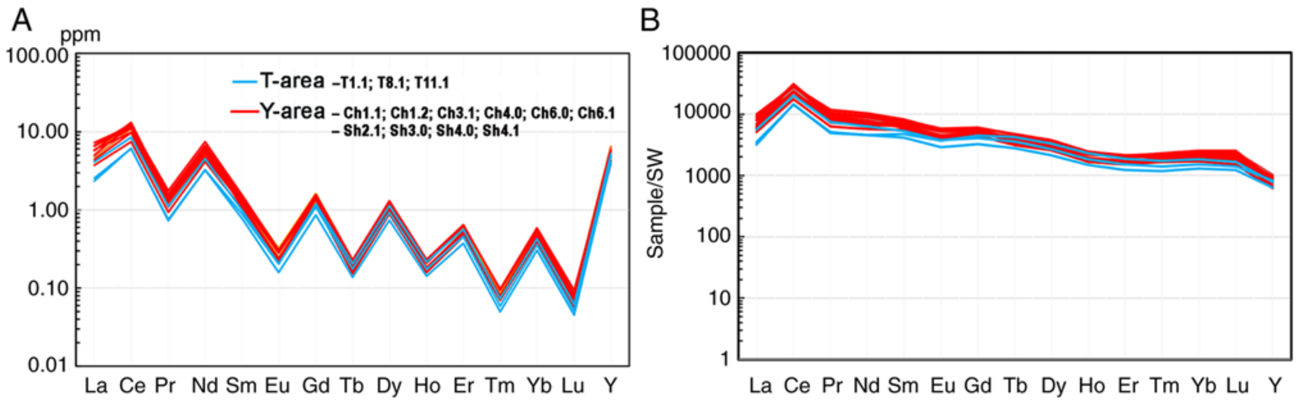

Figure 10. (A) Concentration profiles of acid-soluble forms of rare earth elements in kudurits from the Teletsky area (n=3) and kudurits and uneaten earths from the Yazula area (n=10) (Chulyshman and Shavla rivers); (B) a summary profile normalized to seawater.

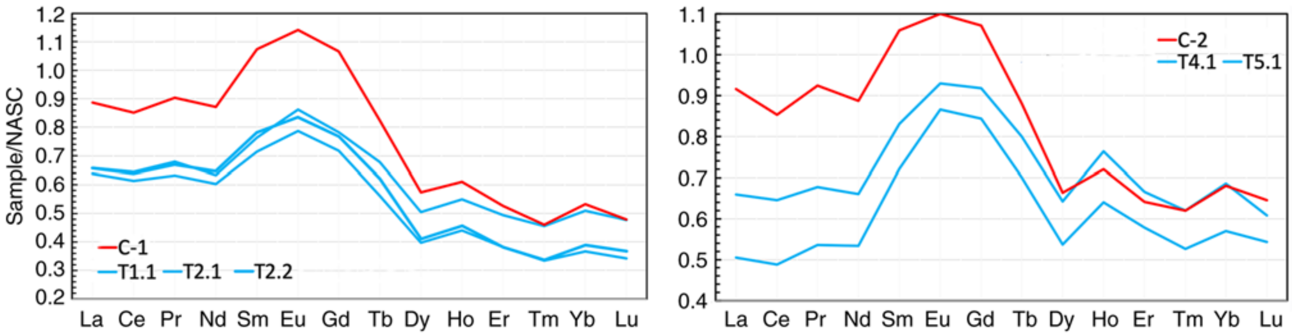

Figure 11. NASC-normalized of rare earth element concentration profiles in coprolites (C-1 and C-2) and their corresponding kudurits from the Teletskoye lake shore. NASC North-American slate.

ppm; Sm, 1.32±0.05 ppm; Dy, 1.10±0.04 ppm; and U, 1.01±0.22 ppm. The yield of other elements in the solution was <1 ppm.

The REE distribution spectra in the acid extracts from the Teletsky and Yazula areas kudurits (Fig. 10) indicated that the quantitative yield of REE from the rocks of both sites was almost identical (P=0.96). When normalized to seawater, it becomes evident that the distribution of REE in the extracts relative to the living matter is relatively uniform with a slight deficit in Y and La and a slight excess in Ce, while the concentration of LREE elements is four orders of magnitude higher and heavy rare earth elements (HREE) is three orders of magnitude higher than in seawater.

Experiment. For the purpose of revealing the ability of some minerals to sorb REE in conditions close to the environment of abomasum and intestine of ruminants, a specific experiment was conducted. The experimental method was described above. The results are presented in Tables VIII and IX.

The experiment revealed that pure mineral powders of quartz and plagioclase (albite) were unable to sorb REE from acid solution (Table IX). Moreover, when they were treated with an acidic solution, the additional leaching of REE occurred, resulting in an increase in their concentration in the solution. In alkaline solution (pH>8.60), quartz and albite sorb REE well due to the formation of silica gels, capturing >80% of dissolved elements from the solution (Table IX).

It was found that chalcedony, calcite and smectite powders, as well as quartz-plagioclase-illite-chlorite kudurits during interaction with acidic REE solution sorb REE with efficiency from 60 to 99% (~92% on average). Calcite powder turned out to be the most effective sorbent with a sorption efficiency of about 99% for all elements. This result effectively demonstrated that quartz-plagioclase-illite-chlorite kudurits are actively sorbing REE from the biological liquid in any pH range in the conditions of the digestive tract.

Assessment of the real ability of kudurits to sorb REE in the digestive tract of animals. The actual assessment of the ability of kudurits to sorb REE in the digestive tract of animals is possible by comparing REE concentrations in coprolites and corresponding kudurits. The NASC-normalized profiles (24) of REE concentrations in coprolites (C-1 and C-2) and chemically corresponding kudurits near which the coprolites were found are shown in Fig. 11. It can be seen that kudurits of quartz-feldspar-illite-chlorite composition most actively sorb the light REE subgroup in the digestive tract, and the nature of the curves in the kudurit-coprolite analogs remote from each other has quite an obvious similarity.

Biogeochemistry. A high REE background within the investigated areas is most pronounced in vegetation, particularly in ferns. For example, the sums of lanthanides with scandium and yttrium in 15 fern samples collected in the Teletsky area

Table VII. Yield of macrocations in the acid solution (HCl, pH 1.0) from the eaten and uneaten soils from the Yazula and Teletsky areas.

		Na		Ca		Fe	
Area	Sample	ppm	%	ppm	%	ppm	%
Teletskoye Lake shore	T1.1	585	6.4	6428	28	-	-
	T2.1	1,080	9.8	14,400	46	-	-
	T3.1	495	5.7	5,207	19	-	-
	T7.1	155	1.3	2,196	11	-	-
	T8.1	780	5.1	7,892	33	-	-
	T9.1	510	5.6	5,919	24	-	-
	T10.1	145	1.7	18,876	37	-	-
	T11.1	50	0.4	1993	41	-	-
Yazula, Chulymshan River	Ch1.1	972	6.1	121	0.7	0.31	0.0005
	Ch3.1	842	5.5	305	2.6	4.07	0.0067
	Ch3.3	1,154	6.7	110	0.9	0.98	0.0018
	Ch4.0[a]	321	2.2	188	1.5	0.82	0.0013
	Ch6.0[a]	181	1.1	352	1.5	<0.01	<0.0001
	Ch6.1	2,499	13.4	232	1.8	<0.01	<0.0001
Yazula, Shavla River	Sh1.1	130	1.5	15,600	32	<0.01	<0.0001
	Sh2.1	3,472	19.7	188	1.5	0.17	0.0003
	Sh3.0[a]	9	0.1	105	1.0	2.23	0.0043
	Sh4.0[a]	101	0.7	291	2.4	<0.01	<0.0001
	Sh4.1	67	0.5	147	0.8	0.85	0.0016

Data for the Teletsky area were obtained from the study by Panichev *et al* (17). [a]Analogs of kudurits from outcrops without traces of consumption by animals; '-', not determined.

varied from 0.294 to 139.5 ppm per dry matter (mean, 22.95; median, 7.85). No ferns are growing in the Yazula area.

In 14 sagebrush samples from the T-area, the REE sums ranged from 0.051 to 7.183 ppm (mean, 0.991; median, 0.12), and in 15 samples from the Y-area they ranged from 0.139 to 4.56 (arithmetic mean, 1.28; median, 0.74). In 34 sedge samples from the T-area, the REE amounts varied from 0.051 to 2.32 ppm (mean, 0.459; median, 0.21), and in 13 sedge samples from the Y-area, they varied from 0.055 to 2.61 (mean, 0.96; median, 0.79). The values of REE concentrations in plants were almost similar to those we found when studying areas with active geophagy in the Sikhote-Alin (15).

The maximum concentrations of REE in plants were found on granites and gneisses enriched in these elements. Minimum concentrations are common in loose deposits remote from their primary sources, gneisses and granitoids. In glacial deposits located in relative proximity to granitoids, the REE concentration is usually at a medium level. This pattern is evident in Fig. 12, where the diagram on the left panel demonstrates the profiles of the maximum, minimum, mean and median REE concentrations normalized to seawater in ferns from the T-area, and the diagram on the right panel demonstrates the same in sedges from the T-area and Y-area.

In the REE profiles for all grasses in both studied areas, there was an increase in the concentration of Eu, as well as a chaotic distribution of elements of the HREE subgroup from medium to low concentrations, which is particularly common in glacial deposits. (This effect may be due to the inaccuracy of determinations at low concentrations). As an example, Fig. 13 shows diagrams of seawater-normalized REE concentrations in sedges collected along a 500-m-long profile near kudur no. 8 (Fig. 4, T-area).

The analysis of REE content in the tail (supracaudal) gland of red deer (*Cervus elaphus sibiricus*) killed by wolves near the Bele cordon on Teletskoye Lake in December, 2022 demonstrated almost complete similarity of concentration profiles in iron and in sedges growing on dealluvium granites (Fig. 14). Comparing it to the REE concentration profile in iron normalized to seawater (Fig. 14B), the unusually high cerium content in it becomes evident.

Discussion

As a result of the present study, first of all, it was found that surface and ground waters in areas where geophagy among wild and domestic animals is common, contain markedly less dissolved forms of REE compared to waters in similar areas of the Sikhote-Alin. However, their increased concentrations (≥10-fold) were found in some streams and springs with the lowest pH values. Typically, such waters are confined to REE-enriched metamorphic and magmatic rocks and the associated glacial deposits. Significantly lower concentrations of REE in the waters of the Altai Mountains compared to the Sikhote-Alin are caused by higher pH values in the Altai

Table VIII. The ability of grinded monominerals, as well as the Teletsky and Yazula kudurits to sorb REE from an acid solution (HCl, pH 2.00).

Elements	La	Pr	Sm	Gd
Initial concentration in 0.1 N HCl solution (ppb)	14.17	16.33	13.87	1.40
Following addition of quartz	15.90	16.82	15.09	1.78
Difference from initial concentration (%)	+1.73 (12%)	+0.49 (3%)	+1.22 (9%)	+0.38 (27%)
Following addition of albite	24.22	17.35	15.82	4.23
Difference from initial concentration (%)	+10.05 (71%)	+1.02 (6%)	+1.95 (14%)	+2.83 (202%)
Following addition of chalcedony	1.86	1.06	0.75	0.14
Difference from initial concentration (%)	-12.31 (87%)	-15.27 (94%)	-12.92 (93%)	-1.26 (90%)
Following addition of calcite	0.12	0.12	0.11	0.02
Difference from initial concentration (%)	-14.05 (99%)	-16.21 (99%)	-13.76 (99%)	-1.38 (99%)
Following addition of smectite	0.86	0.57	0.54	0.11
Difference from initial concentration (%)	-13.37 (94%)	-15.76 (97%)	-13.33 (96%)	-1.29 (92%)
Following addition of No. T10.1	1.66	1.34	1.47	0.55
Difference from initial concentration (%)	-12.51 (88%)	-14.99 (92%)	-12.40 (89%)	-0.85 (61%)
Following addition of No. Ch4.0	1.23	0.56	0.51	0.23
Difference from initial concentration (%)	-12.94 (91%)	-15.77 (97%)	-13.36 (96%)	-1.17 (84%)
Following addition of No. Ch1.2	0.73	0.53	0.47	0.1
Difference from initial concentration (%)	-13.44 (95%)	-15.79 (97%)	-13.40 (97%)	-1.30 (93%)

'+', an increase in the concentration of the element in the solution; '-', a decrease in the concentration of the element in the solution.

Table IX. The ability of grinded monominerals (quartz and albite) to sorb HREE from an alkaline solution (pH 8.60).

Elements	Eu	Gd	Tb	Dy	Lu
Initial concentration in pH 8.60 solution (ppb)	2.49	1.94	2.56	2.59	1.49
Following addition of quartz	0.30	0.22	0.30	0.29	0.22
Difference from initial concentration (%)	2.19 (88%)	-1.72 (89%)	-2.26 (88%)	-2.30 (89%)	-1.27 (85%)
Following addition of albite	0.37	0.27	0.34	0.35	0.26
Difference from initial concentration (%)	2.12 (85%)	-1.67 (86%)	-2.22 (87%)	-2.24 (86%)	-1.23 (83%)

waters, which is associated with the abundance of calcium and magnesium carbonates in the rocks. The climate in the Altai Mountains is also somewhat relevant, as it is drier and colder there.

Secondly, it was found that the vast majority of kudurs in the Chulyshman river valley and the littoral zone of the Teletskoye Lake are formed on fine-grained glacial deposits in relative proximity to outcrops of granite-gneisses and REE-enriched granitoids. Deluvium on such parent rocks, as well as glacial deposits, too are enriched in REE minerals, both phosphates and carbonates of magmatic genesis (monazite, xenotime, orthite, parisite, etc.), and secondary phosphates and fluorocarbonates (parisite and rhabdophane).

Thirdly, the vegetation on such glacial deposits, particularly directly on REE-enriched weathering crust gneisses and granitoids, also accumulates significant concentrations of these elements. Not only ferns, the natural REE concentrators (19), but also sedges and artemisia, which are food plants for ungulates, accumulate these elements. Fig. 15 shows the profiles of maximum and minimum REE concentrations in the sedges from the three regions studied by the authors thus far. These data well illustrate the fact that sedges on REE-enriched rocks are capable of accumulating these elements up to ≥100-fold than those on ordinary widespread rocks with an average REE content. Notably, the REE concentration profile of a potato tuber sample from a vegetable garden in the Bele settlement on the Teletskoye Lake shore differs from the profiles of grasses demonstrating a relatively sharp enrichment in the HREE group of elements. This fact can be directly related to the health of people in the area. Further on, we will discuss this issue in more detail.

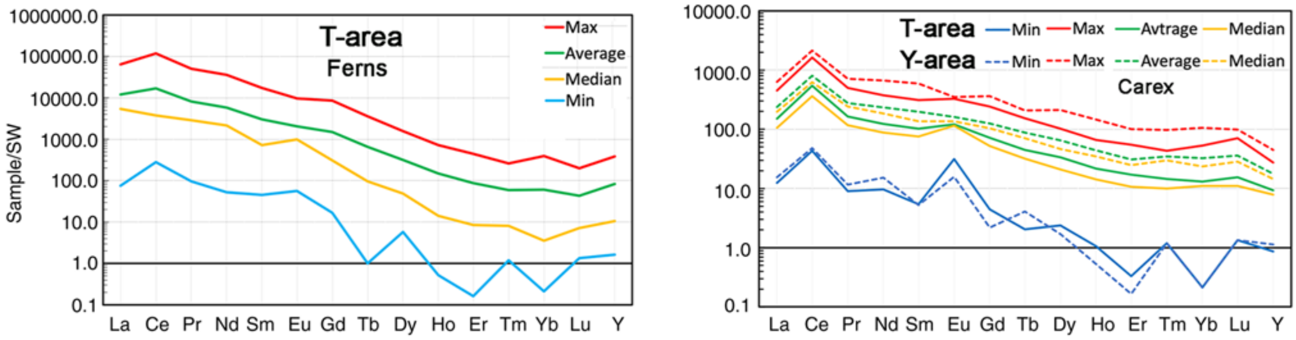

Figure 12. Profiles of seawater-normalized maximum, minimum, mean and median rare earth element concentrations in ferns from the T-area (n=9) and sedges (Carex) from the T-area and Y-area (n=26).

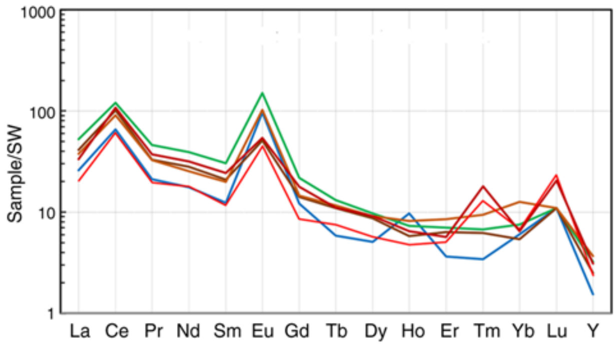

Figure 13. Profiles of seawater-normalized rare earth element concentrations in sedges (Carex) (n=6) growing on aqueoglacial deposits near the Bele settlement (T-area).

According to the observations of ungulates in the southern part of the lake, which have been conducted for several years by the nature reserve employee Dr Yu. N. Kalinkin, the main habitats of these animals are the slopes and the near-to-summit parts of the mountain ridge on the right bank, where REE-enriched plants are most widespread. In spring and summer, animals periodically go down to the kudurs where they consume mineral sorbents, which, as we found out, can remove excessive REE from the body.

However, the question of how far animals can travel to kudurs in the Altai Mountains has not been specifically studied (25,26). The only reliable data on animal travel to kudurs are for ibex and bighorn sheep on the American continent. For example, Rice (27), using the radio tracking method, found that animals living in a relative vicinity of kudurs (4-5 km) visit them most often. Occasionally, animals come from afar (up to 29 km) and may stay near kudurs sometimes for up to a month or more. According to the study by Sobansky (18), red deer come to the kudurs on the Teletskoye Lake shore even from the Abakan Ridge spurs covering distances up to 15 km. These data suggest that the kudurs in the Altai Mountains may be visited by animals not only from nearby territories but also from relatively distant ones.

The mineral composition of the Altai kudurits is fundamentally different from the kudurits in the Sikhote-Alin. The main mineral sorbents in the Altai Mountains are quartz-plagioclase-illite-chlorite mineral mixtures with minor additions of calcium carbonates and clay minerals (mainly kaolinite). A similar mineral composition of kudurits was discovered by the authors as early as 1988 in another geophagy area in the Chulyshman River basin, along the Bashkaus tributary (28). The geological structure of the kudur areas along the Bashkaus River demonstrates a perfect analogy with the geological structure of the area near the Yazula settlement. The Altai type sorbents, in contrast to the smectite-zeolite ones in the Sikhote-Alin, have a much lower absorption capacity for such macrocations as Na and Ca (3), at the same time being able to absorb REE from the biological electrolyte in the pH range from 4.0 to 8.6 no less effectively.

Special attention should be paid to some varieties with an admixture of calcium carbonates among the Altai kudurits. The matter is that in the tropics, the main sorbents in the mineral composition of kudurits most often are clay minerals of either kaolinite or smectite groups. Varieties with an admixture of calcium carbonates are also present there (8,29). The mineral composition of 'edible earths' consumed by humans contains the same mineral assemblage and, again, varieties with calcium and magnesium carbonates (8,30,31). The literature describes even predominantly carbonate varieties of soil eaten by humans, such as 'hydromagnocalcite' by Gebel (32), consisting of redeposited earthy magnesium and calcium carbonates with an admixture of sulfates, which was bought at one of the markets in Central Asia. The present study demonstrated the unusually high sorption capacity of calcium carbonates in relation to REE (particularly HREE), and the interest of animals and humans in the consumption of this mineral becomes more understandable. It is possible that the dietary interest of pregnant women in scribe chalk is related not only, and maybe not so much to the lack of Ca in the body, but rather to the instinctive impulse to regulate the REE imbalance in the body as REE is the most important components in the hormonal system, which determines the activation of mineralization and demineralization of the skeleton. This ability of lanthanides is pointed out, in particular, in the review by Redling (33), who refers to the works of several researchers.

As regards sodium, in the present study, it was once again verified that the only biologically available macronutrient found in kudurits in increased concentrations is Na. However, the obtained data also indicate that the desire to find this element cannot explain the cause of geophagy. To demonstrated the validity of this statement, some calculations are

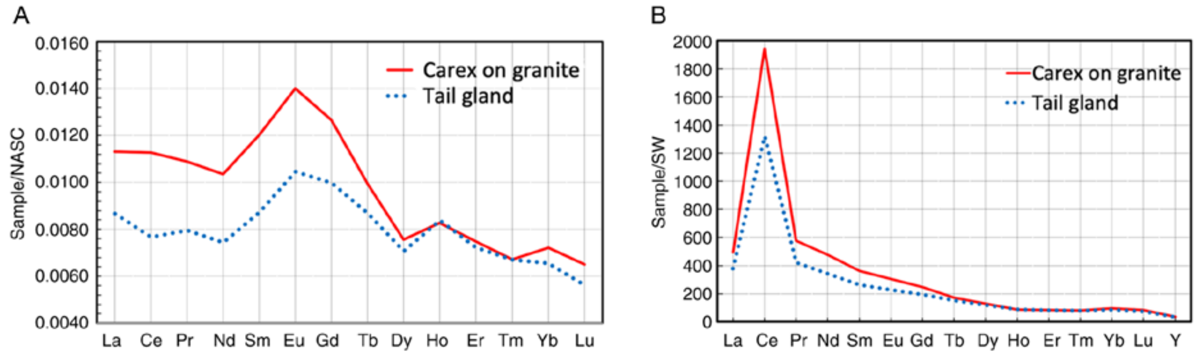

Figure 14. Profiles of NASC-normalized (A) and seawater-normalized (B) rare earth element concentrations in sedges (Carex) along granite deluvium in the T-area (n=7) and in red deer tail gland. NASC North-American slate.

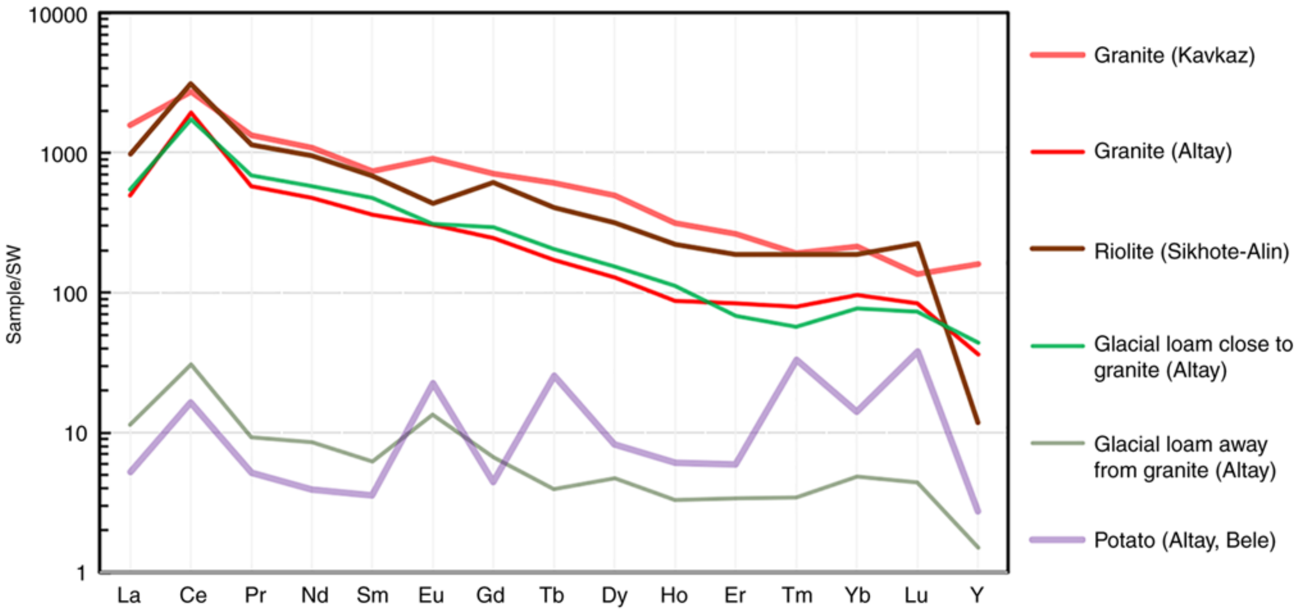

Figure 15. The profiles of maximum and minimum rare earth element concentrations in sedges (Carex) in the areas of active geophagy in the Altai (n=1), Sikhote-Alin (n=1) [according to (15), and the Caucasus mountains (n=1) (26)], and in a potato tuber (n=1) from a vegetable garden in the Bele settlement (Teletskoye Lake shore).

made. To extract 20 g of pure Na (the weight of the element in 50 g or a tablespoon of NaCl) from the most Na-enriched kudurit in Table VII (3.5 g/kg Na, sample No. Sh2.1) one needs to consume at least 6 kg of soil. This is assuming that the concentration of the sought element is uniform in all the volume of the eaten soil. If one should consume the kudurit with the minimum Na content (0.05 g/kg, sample No. T11.1), then the weight of soil for getting the same dose of Na increases to 400 kg. From this reasoning it becomes clear that animals consume kudurits not for the sake of Na, at least, not only and not so much for the sake of getting exactly this element. It is appropriate to note the long-proven fact: Even the most severe Na deficiency in the diet is not fatal for animals (34).

The variations of Na (as well as Ca) concentrations in kudurits (Table VII) are most likely related to the fact that sodium and calcium salts are concentrated on outcrops close to the day surface due to capillary rise of saline groundwater in hot summer conditions. Here animals find them using their taste buds and eat them instead of similar, but less Na-enriched earths. The typical compaction of initially loose kudurits in the studied areas is caused precisely by their saturation with sulfates and calcium carbonates brought in as part of groundwater and pore water.

Thus, it was confirmed that the search for Na cannot explain the animals' desire for geophagy, as kudurits contain too few biologically available forms of this element. It is worth noting that animals can address the Na deficiency issue also by greatly reducing the losses of the deficient element in the body. Na loss can occur, for example, in diarrheal diseases, particularly during seasonal changes in the diet (2,4). Mineral sorbents including those based on clays and silica gels are known to be effective in medicine and veterinary for stopping diarrhea.

The desire to stop diarrhea, undoubtedly, may be a reason for consuming kudurits. However, one cannot recognize it as the main reason that can unite the majority of geophagy cases worldwide. The findings obtained do not point to the only possible connection between the desire of ungulates for geophagy and diarrhea, although individual facts of such a connection in the spring period have long been noted by a number of researchers, including those in the Altai Mountains, for example by Shaposhnikov (35). The observations of humans and great apes are particularly illustrative in this respect. The mineral soils consumed by these groups of geophages contain practically no available Na and are most often used without obvious signs of digestive disorders (36-38).

Concluding the discussion of sodium in connection with geophagy, an interesting fact can be noted indicating the existing connection between Na, Ca and REE in the body. Powis *et al* (39), in experiments on cell cultures, found that La^{3+} can independently transport itself into chromaffin cells of bovine adrenal glands by exchange through sodium-calcium channels and trigger the release of the catecholamine hormones. It is worth noting here that REE involvement in the regulation of catecholamines is not their most critical role in hormone function. There are data on their participation in the regulation of several hormones and enzymes, including growth hormones (pituitary gland), thyroid hormones, sex hormones, insulin, etc., which can be found in many references to studies in the review by Redling (33).

As regards the trace elements, in the present study, Sr, Ba, Y and LREE demonstrated the highest concentrations among the trace elements in acid extracts. Assuming that the first two elements can hardly be attributed to those that animals seek at kudurs, it is Y and LREE that are the most likely trace elements to be looked for, judging by the amount and stability of yield into the acid solution. It is considered that the other trace elements as less likely candidates, since all of them both in this and in similar studies on other types of kudurits and other regions worldwide (16), show highly unstable results. However, the appearance of any trace elements (other than REE) in the digestive tract can undoubtedly influence the symbiont microflora. Some of these elements can even be absorbed in the body, but it is also hardly appropriate to consider them as candidates for the main cause of geophagy (the one that unites this phenomenon throughout the world).

Having found relatively high concentrations of easily soluble forms of LREE in kudurits of the Sikhote-Alin, Altai Mountains and Caucasus (16,26,40) and the fact of unusually high gross concentrations of REE in African and Indonesian kudurits described in the publications of several authors (35,37,41-43), it was first suggested that animals consume kudurits to compensate the lack of some elements from the LREE group in the body. The aforementioned series of articles was devoted to proving this hypothesis. However, following a thorough investigation in two areas of the Sikhote-Alin in 2021 (15), it became evident that the cause of geophagy may be connected not only with REE deficiency in food and drinking water, but also with their excess. The excessive content in the plant food negatively influencing animal health appears to be more frequent. The evidence that the positive effects of REE on the animal body, be it the stimulation of growth, an increase of immunity, influence on cell proliferation and others, can dissipate, and turn into opposite effects as the REE concentration increases, is supported by ample data, which can be found in the most complete form in the review by Redling (33).

The cases of LREE deficiency are probably most common in humid tropical forests where elements are actively transported from soils by acidic solutions, and also in areas where biogenic carbonate rocks are widespread as biogenic carbonate accumulates negligible amounts of REE (44). Animals may also need LREE if there is a sharp imbalance in feed and drinking water in favor of HREE at the expense of the lighter counterparts, or if there is a toxic element present in large amounts that blocks the ingestion of LREE.

There is evidence of high concentrations of mobile forms of REE in kudurits, which were found both in the Sikhote-Alin and the Altai Mountains. These findings are not quite consistent with the explanation of the cause of geophagy by an excess of REE in food plants and the desire to consume minerals capable of sorbing these elements. There could be two possible explanations. The first one is that animals have no other suitable sorbents. The second possibility (which appears more credible) is that specific microorganisms may develop in such rocks, that can assimilate REE converting them into forms suitable for digestion in animals. It is to be expected that these microorganisms may actively grow in the mycorrhiza of some plants, explaining why a number of animal licks appear near the roots of trees, shrubs and some species of grass. Animals may be attracted to such microorganisms as symbiont REE-converting forms in the digestive tract microflora as the forms required by the organism can 'degenerate 'at the intake of food enriched in REE with a 'wrong' LREE to HREE ratio.

Concluding the discussion of the results obtained, a brief focus is made on the possible negative effects of excess REE content in landscape components on humans. The situation of unusually high concentrations of LREE (particularly cerium) in vegetation and the tail gland of deer (Fig. 14B) that we found in the Altai Mountains, coupled with the published data on specific human pathologies, such as the endomyocardial Leffler fibrosis (EFL) which has a direct link with the excess of cerium in the plant diet of humans in India (45,46) and Africa (47), strongly suggest that geophagy both in herbivores and humans is associated with an impaired REE exchange in the body. Within the considered aspect, the connection of human consumption of earthy substances with the disease described in South America as Cachexia Africana (48) also does not appear coincidental. Previous studies on geophagy in humans have demonstrated that the urge for geophagy develops against a background of specific pathologies accompanied by signs of mineral metabolism disorders (49-52).

It is important to note that geophagy in animals is also common in the southern states of India that are not affected by EFL disease in humans. Such cases have been reported, in particular, in the Chinnar Nature Park (53) in Kerala, India and the neighboring state of Tamiland in the Marakkanam Reserved Forest, India (54). The Chinnar Park is located on a mountain plateau with heights up to 2,500 m. Similar to the plateau in the upper Chulyshman River, it is composed of metamorphic rocks of the Precambrian age, mainly crystalline schists and gneisses, including the Charnockite series, where the major part of REE is concentrated in monazite (55). Biogeochemical endemic diseases in humans associated with an excess of REE in monazite-bearing sands were revealed along the banks and in the estuarine parts of rivers running precisely from this plateau. Similar rocks are very widespread not only in the south but also in the eastern parts of India, i.e., exactly where geophagy among humans was widespread at the beginning of the XX century, according to Laufer (56).

As a development of this topic, there was an interesting fact that was found in 2021 in Yazula, when residents were interviewed (data not shown). Some of the interviewees assured us that there were individuals in the village who periodically ate the most finely dispersed varieties of kudurits. This leads to the hypotheses that one should also expect mineral metabolism disorders and other endemic pathologies associated with an excess of REE in people living in the areas we studied in the Chulyshman River basin, namely in the Balykcha, Koo and Yazula settlements. However, specific medical research is required for this to be determined.

In conclusion, geological and hydrobiogeochemical analyses conducted in two areas in the Teletskoye Lake basin in the Altai Mountains suggest that geophagy among wild and domestic herbivores in the studied areas develops in mountain-taiga with steppe landscapes on Proterozoic metamorphic rocks near outcrops of Paleozoic granitoids with high concentrations of magmatogenic REE minerals. This circumstance is the reason for high concentrations of REE in loose diluvial deposits and glacial deposits adjacent to granitoids, as well as in derivative soils and vegetation. This geochemical specificity of the landscape with a high probability can lead to an excess of REE in the neuroimmunoendocrine system of the body, a carrier of this group of elements, which can cause a stress reaction in animals. This condition most likely causes animals to compensate for the resulting problems in the body by using mineral sorbents capable of removing the excess of REE from the body. When choosing these, the animals tend to find Na-enriched varieties if possible. The obtained results justify the need to continue testing the validity of the REE-hypothesis in other regions of the world, including the sites of geophagy among humans.

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Authors' contributions

All authors (AMP, NVB, IVS, IYC, EAV, YVK, TNL, NYP, AVR, DSO, EVE, AVV, OVP, RAM and YAM, ASK, DAS, AT and KSG) contributed to the conception and design of the study. Material preparation, data collection and analysis were performed by AMP, NVB, IVS, IYC, EAV, YVK, TNL, NYP, AVR, DSO, EVE, AVV, OVP, RAM and YAM. The first draft of the manuscript was written by AMP and all authors commented on previous versions of the manuscript. AMP and KSG confirm the authenticity of all the raw data. All authors have read and approved the final manuscript.

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Not applicable.

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Not applicable.

Competing interests

DAS is the Managing Editor of the journal, but had no personal involvement in the reviewing process, or any influence in terms of adjudicating on the final decision, for this article. AT is an Editorial Advisor of the journal, but had no personal involvement in the reviewing process, or any influence in terms of adjudicating on the final decision, for this article. The other authors declare that they have no competing interests.

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