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ORIGINAL PAPER

Kudurs (mineral licks) in the Belukha Mountain area, Altai Mountains, Russia

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Abstract

Studies were carried out in the upper reaches of the Akkem River aimed at explaining why the local ungulates consume clay rocks common in the basin of the Yarlu River, a tributary of the Akkem River. Chemical composition of river and spring waters and mineral and chemical composition of clay rocks consumed by wild and domestic ungulates at kudurs were studied. The waters in the local watercourses are ultra-fresh, hydro-carbonate-calcium. Increased concentrations of rare-earth elements (REE) were observed in waters of the Yarlu River. Consumed clayey rocks (kudurits) are represented by finely dispersed quartz-plagioclase-mica-chlorite mineral associations — the products of transformation of shale rocks of the Early Paleozoic age. The comparison of the chemical composition of kudurits and coprolites of red deer showed that when the rocks pass through the digestive tract, out of all macroelements, only Na is reliably assimilated in the body in amounts from 0.1 to 0.3 g per kg of kudurit. In addition, kudurits act as sorbents, removing P, K, Mg, and sometimes Ca from the body. As part of micronutrients, they are most active in sorbing and removing REE from the body.

Keywords Kudurs · Geophagy · Ultrabasic rocks · Geochemistry · Altai Mountains

Introduction

In many regions of the world, there are known cases of clayey or powdery rocks consumption by both wild and domestic herbivorous, and sometimes omnivorous, animals. This phenomenon, known scientifically as "geophagy," has been systematically studied in relation to animals since the early 1930s. Perhaps the first scientific publication on the subject of geophagy in ungulates was an article by the Canadian researcher A. Mure (1934).

As a result of regular consumption of clay rocks by animals, easily recognized landscape complexes are formed, which are usually called salt licks or mineral licks in the research literature. Since these objects are far from being directly related to soluble salts and to licking as a form of consumption, we decided to use the term "kudur" borrowed from the vocabulary of Turkic herders (Panichev et al. 2013) to refer to them. The term "kudurit," derived from kudur, means mineral soils consumed by animals at a kudur. We also use the term "lick," but exclusively to refer to specific pits eaten out by animals within kudurs as landscape complexes.

One of the authors of this article first visited kudurs in the Belukha Mountain area in the upper reaches of the Akkem, Yarlu, and Tekelu rivers (Panichev 2011) (Fig. 1) on July 1987 together with biologist G.G. Sobansky. In those years, this area was not yet as frequently visited by tourists as it is nowadays. This made it much more densely populated with wildlife, including marals (*Cervus elaphus sibiricus*), a local subspecies of red deer, and ibex (*Capra sibirica*). The main habitats of marals were in the forest zone with movement above the

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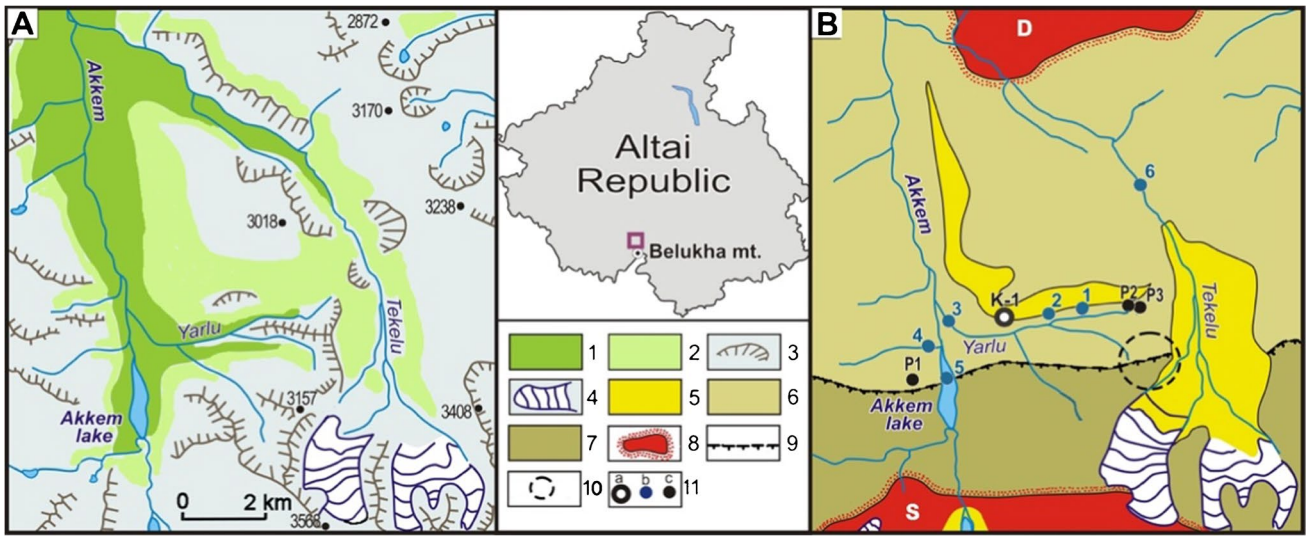


Fig. 1 The study area near Mount Belukha in the Altai Republic (**A**) and the geological map of the area (**B**): 1 – forests with the predominance of Siberian pine and larch; 2 – shrubby and meadow zone; 3 – major ridges and kars among stone deserts; 4 – mountain glaciers; 5 – glacial deposits; 6 – Ordovician terrigenous deposits (predominantly siltstone); 7 – Cambrian deposits (mainly sandstone and clay shale); 8 – Silurian granitoids with the contact metamorphism aureoles; 9 – molybdenum ore occurrence; 10 – tectonic contact; 11 – kudur (a), sampling points of water (b), and rocks (c)

forest edge in summertime, while ibex preferred to stay above the forest edge near rocky areas. We found about ten typical kudurs along the right bank of the Yarlu River valley from its middle part to the upper reaches, which were regularly visited by ungulates. The same kudurs were willingly visited by horses (about 2 dozens heads), which the local shepherds left to graze freely in the upper reaches of the Yarlu and Tekeliu rivers in the summertime. Almost all the piles of horse manure we spotted on the Yarlu slopes contained sand and pebbles typical of the local kudurits.

On August of 2019, we visited this area for the second time to study the kudurs. Over 22 years after our first visit to the area, the tourist infrastructure has grown very noticeably. Along the left shore of Akkem Lake, numerous tourist camps were built. Hiking trails appeared in the Akkem and Yarlu valleys, where hikers or horseback riders can be seen almost every day in the summertime. In the summer, a helicopter with tourists flies to Mt. Belukha often landing on a platform near the edge of the lake.

The number of marals in the area has sharply decreased, and ibex have almost completely moved to more distant habitats. As a result, most of kudurs in Yarlu have ceased to exist. In fact, there is only one kudur left (K-1), located in the forest zone, which also used to be the most visited. Currently, it is visited only by marals, hares (*Lepus timidus*) and marmots (*Marmota baibacina*).

This article presents the results of laboratory studies of the factual material collected in 1987 and 2019. Its main purpose is to introduce researchers to the results of studies of the mineral composition and geochemical features of clayey rocks eaten by ungulates in one of the hard-to-reach and unusually picturesque corners of the Altai Mountains. In the discussion of research results, we attempted to develop our own original hypothesis about the reasons of regular consumption of such rocks by animals, which, judging by our data and also by the analysis of available literature is common not only throughout the Altai Mountains but also in many mountain territories around the world, including the Caucasus and Sikhote Alin mountains (Panichev et al 2021a; b), mountains in the south of India (Ramachandran et al. 1995), western Africa (Mahaney et al. 1990; Mills and Milewski 2006), and North America (Parker and Ayotte 2004; Lavelle et al. 2014).

Materials and methods of their sampling and analysis

Factual material and sampling methods

The studied kudurs are located in the upper reaches of the Akkem River, approximately 13 km north of the Belukha Mountain, the highest peak in the Altai Republic (Fig. 1). Most of these objects in the area are concentrated along the right bank of the Yarlu River, in its middle and upper reaches. The largest kudur (K-1) is in the middle reaches of the Yarlu River (Fig. 1B). On a steep slope covered with low-growing larch (*Larix sibirica*) and Siberian pine (*Pinus sibirica*), even from a distance one can clearly see two closely spaced outcrops of light rocks that form low,

unvegetated residual ridges descending into the river valley. The upper part of the ridges is about 70 m above the floodplain. There are numerous animal tracks in the surrounding forest area. On a closer look, the rocks are composed of finely dispersed clay loam typical for glacial lakes. When wet, they are soapy in texture and bluish-greenish in color, and almost white when dry (Fig. 2A). Within the ridges, in various places and at various altitudes, we found several well-defined licks of various sizes and depths. Most of these holes appear near the roots of trees, shrubs, or grass bumps. One of such holes in the roots of a large larch is shown in Fig. 2B.

On August of 2019, 6 samples of kudurits (K-1.1, K-1.2, K-1.3, K-1.4, K-1.5, and K-1.6) were collected from licks at different outcrop elevations. In addition, one pile of maral coprolite (C-1) was collected at Lick No. 6 (sample K-1.6). Kudurit samples weighing approximately 300 g were taken from the surface and from depths of up to 10 cm and packed in polyethylene bags. Together with kudurits, three samples of loose rocks that resembled kudurits were collected. One sample was taken from deluvium of Ordovician shales on the right bank of the Akkom River and two samples in the upper reaches of the Yarlu River. Nine water samples were taken into 250-ml polyethylene bottles carefully washed beforehand in laboratory conditions. The bottles were rinsed with water three times before sampling. Figure 1B shows the water sampling locations excluding three sites. Water sample No. 7 was taken in the near-mouth part of the Akkem River (the river length is about 36 km), water sample No. 8 in the near-mouth part of the Kucherla River (this river, like Akkem, is the right tributary of the Katun River flowing to the west in parallel with Akkem), and sample No. 9 in the Katun River above the Kucherla River mouth.

In this study, we also use the data on samples from kudur K-1 collected on July 1987, published in a book earlier (Panichev 1990). These are 4 samples of kudurits and 4 samples of coprolites. In this article, the kudurits collected in 1987 from various fresh licks (from the surface and to a depth of 10 cm) are marked as 1–90, 2–90, 3–90, and 4–90, and the maral coprolites found nearby are marked as C1-90, C2-90, C3-90, and C4-90. We consider these data to be very important, maybe even unique in terms of the set of laboratory studies performed, and also because the book containing the data was published relatively long ago in Russian language only, so it is almost unknown to researchers outside of Russia.

Analytical methods

Chemical analyses of the main elements in rock samples collected in 1987 were carried out in Primorgeologiya Production Association (Vladivostok) on a SRM-20 M multichannel X-ray spectrometer. Ca and S concentrations were determined by the classic "wet" and silicate analysis methods. P, S, Ci, Mn, Ni, and Zn concentrations were analyzed using a VRA-20 X-ray fluorescence spectrometer at the Far East Geological Institute (FEGI) of the Far East Branch of the USSR Academy of Sciences (FEB USSR). Mobile silicon oxide (that can be extracted with a 5% soda solution for 2 h of shaking) was determined at FEGI. The amount of dissolved silicon oxide was determined by exotherm measurements. Absorbed cations in granular samples were determined by elution with a concentrated NH_4NO_3 solution in glass columns. The elution rate of the solution was 1 volume per hour. The completeness of the reaction was monitored by measuring the concentration of potassium ions in the eluate

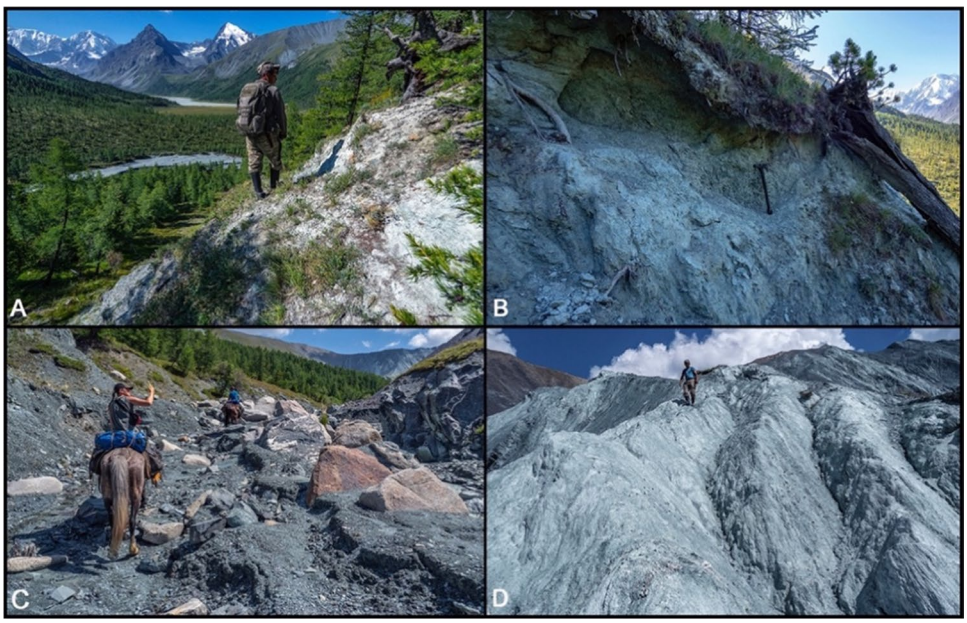


Fig. 2 **A** A fragment of kudur K-1 on lake loam at the right side of the Yarlu River (Belukha Mountain massif is visible in the background); **B** one of the largest licks in larch roots; **C** granite boulders in the middle part of the Yarlu River — the result of ice drift from the granite massif south of Belukha; **D** outcrops of Ordovician clayed rocks (argillizites) at Yarlu headwaters

(until they were completely absent). Absorbed and water-soluble cations were extracted in a specialized laboratory of the Institute of Chemistry of FEB AS USSR. Their concentrations were determined by atomic adsorption analysis.

Chemical analyses of samples collected in 2019 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. X-ray phase analysis of minerals was performed at the Department of Engineering and Environmental Geology, Faculty of Geology, Lomonosov Moscow State University (Moscow).

Upon arrival to Vladivostok, unfiltered samples were measured for pH and alkalinity in the Collective Use Center the Pacific Geographical Institute, Far East Branch of the Russian Academy of Sciences (PGI FEB RAS). For further analysis, each sample was filtered (0.45 μm) using a vacuum pump and poured into two 50-ml polypropylene tubes. A portion of the filtrate (15 ml) was used to determine the content of dissolved organic carbon (TOC-VCPH Analyzer, Shimadzu Corp., Japan). After that, water samples were analyzed in the AC FEGI FEB RAS. The water in the first test tube was treated with nitric acid (Suprapur Nitric Acid, Merck KGaA, Germany) and analyzed for the composition of 55 elements by inductively coupled plasma mass spectrometry (spectrometer Agilent 7700 × ICP-MS, Agilent Technologies Inc., USA). The second test tube was used to determine 5 macrocations by atomic emission spectrometry (spectrometer iCAP 7600 Duo, Thermo Fisher Scientific Inc., USA) and 6 anions by ion chromatography (liquid chromatograph LC-20, Shimadzu Corp., Japan). The total water salinity was determined as the sum of macrocomponents.

Rock samples were crushed and milled before the analysis. Abraded samples were put in bags and sent for chemical analysis and X-ray phase analysis of minerals. The total LOI (loss on ignition) and SiO_2 content were determined by the gravimetric method. The remaining main elements were determined by atomic emission spectrometry with inductively coupled plasma (spectrometer iCAP 7600 Duo, Thermo Fisher Scientific Inc., USA). Trace elements were determined by the same method on the same spectrometer. The samples were prepared for analysis by fusion with lithium metaborate.

The quantitative mineral composition of samples was determined by the X-ray diffraction method on an ULTIMA-IV diffractometer (Rigaku, Japan). The method is described in detail in our previous article (Panichev et al. 2021a, b).

To determine the yield of chemical elements under acidic conditions in the abomasums of ruminant mammals, 5 samples were treated with hydrochloric acid extracts with pH 1.0 and 2 samples with pH 3.0 in the Laboratory of Geochemistry of the PGI FEB RAS. A rock sample weighing 5.00 g was treated with 50 ml of HCl solution. After that, the suspension was shaken for 30 min and left for a day. The supernatant liquid was centrifuged in a plastic beaker for 30 min at 4500 rpm. The transparent supernatant was transferred to be analyzed for the studied elements. Tridistillate water and distilled extra-pure HCl were used to prepare the solution.

To reveal the ability of hydromicaceous-chlorite kudurits from kudur K-1 to sorb REE in conditions close to the ruminant's rennet environment, we carried out a laboratory experiment. To simulate the electrolyte in the abomasum, we prepared an HCl solution with pH 2.00 on tridistillate water in which we diluted La, Pr, and Sm compounds (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. Then the solution was diluted to 1 l and left to stand for 24 h. Next, 1 ml was taken from the prepared solution and diluted with a hydrochloric acid solution ($pH = 2$) to 1 l. After that, 5 g of dry kudurit powder was put into a flasks and 50 ml of REE salts solution was added. This was followed by 12 h in a shaker and 12 h settling. The liquid was separated from the minerals in a centrifuge. The analysis was performed by the ICP-MS method.

The electron microscopic study of kudurit samples was performed using a JSM-6490LV analytical scanning electron microscope (Jeol Ltd., Japan) with attachments EDS INCA Energy, X-max, and WDS INCA Wave in the laboratory of micro- and nanoresearch of FEGI FEB RAS. A loose sample was glued onto carbon tape, placed on an aluminum column, and sprayed with carbon coating. To automate the search process, we used INCAFeature software by Oxford Instruments.

Results

Geological structure of the study area and geological patterns of kudur occurrence

Data on the geological structure of the territory were taken from the materials of the state geological map of the Russian Federation in 1: 200 000 scale, sheet N-45-XXIG, 1959. The geological structure of the Akkem Lake area is presented in a scheme in Fig. 1B. According to the geological data, the kudur is confined to a lens of water-glacial deposits of pre-Holocene age embedded in primary sedimentary rocks of the Ordovician age (mainly siltstone) that occupy almost 2/3 of the studied area. Approximately 1.5 km south of the kudur, there is a latitudinal tectonic boundary (thrust) between the Ordovician and Cambrian rocks. Granitoid intrusions are mapped in the southern part of the study area, in the upper reaches of the Akkem and Tekelu rivers, as well as in the north of the area. The age of the southern massif (near the

Belukha Mountain) is estimated as Silurian, and the northern one as Devonian. The distance from the kudur to the southern edge of the intrusion, from which the loose material moved along the Tekelu and Akkem river channels, is about 4.5 km (Fig. 1B). In the Yarlu floodplain, especially in the middle and upper part, there are many granite boulders (Fig. 2C) — the result of glacial spreading of stones from the granite massif. The same boulders are found in the Akkem and Tekelu floodplains.

Especially large clusters of loose material containing a significant portion of granitoids accumulated in the form of a glacial outwash lense in the upper reaches of the Tekelu River (Fig. 1B). On these deposits, meadows with rich vegetation were formed where marals and ibex used to graze in summertime. The herds of horses often grazed there as well.

In headwaters of the Yarlu River and right tributary of the Tekelu River, there are outcrops of highly clayed Ordovician shale rocks (Fig. 2D). Their origin is associated with the discharge of hydrotherms coming from the granite igneous intrusion. Such argillizites are common throughout the entire tectonic contact zone between the Cambrian and Ordovician rocks along the edge of the granite massif. A molybdenum deposit discovered by geologists in the headwaters of the uppermost left tributaries of Yarlu and Tekelu in the 1930s is confined to the same tectonic contact (Fig. 1B). According to Sotnikov and Nikitina (1971) citing a publication of V.A. Kuznetsov from 1938, the deposit is connected to the Belukha granite massif. The ore bodies are represented by thin quartz veins and vein accompaniments of complex structure in crush zones among the host silicified and pyritized shales. The main ore mineral is molybdenite accompanied by pyrite and some scheelite.

There were no traces of animal consumption of hydrothermal argillizites in the headwaters of the Yarlu River. However, these argillizites were the main source of fine-dispersed loose deposits mapped by geologists as a glacial outwash along the right bank of the Yarlu River (Fig. 1B). They are the parent rocks of the studied kudurits.

Similar argillizites occur in the contact zone of the Cambrian and Ordovician shales in some places in the Akkem valley. These rocks are easily broken up by water streams forming a thin, poorly sedimented, milky-white suspension in the water. This makes the water in the Akkem Lake, Akkem River, and Yarlu River very muddy at all times. The mud in Akkem does not sediment up to the river mouth (for 36 km) and when mixed with clear water of Katun gives it a characteristic whitish-blue tint, which remains for hundreds of kilometers.

Near the mouth of the Akkem River, on its right side within the floodplain terraces, there are lake deposits of transported mud in the form of the finest (powder-like in size) layered almost white loam with visible thickness up to 3 m. One of the authors of this article examined them in 1987. These lake deposits also have characteristic evidence of being eaten by animals in some places.

Hydrochemistry

Table 1 contains the analysis data of the main salt components in the collected water samples. Based on the data, the water is ultra-fresh with salinity from 30 to 190 mg/l. The only water sample from a source in the Yarlu headwaters has a salinity of about 495 mg/l. The composition of the sampled water is predominantly hydrocarbonate-calcium and hydrocarbonate-calcium-magnesium (Fig. 3), with some samples having an elevated nitrate content. Na content in all water samples does not exceed 4 mg/l.

Among the trace elements in the sampled waters, the largest amounts were found for Sr from 28 to 588 ppb (average content – 151.4 ppb, median – 71.3 ppb), Fe from 5 to 200 ppb (average content – 48.6 ppb, median – 30.99), and Al from 10 to 291 ppb (average content – 72.0, median – 25.13 ppb). These are followed by Ba – 1.8 to 61 ppb (average content – 10.8, median – 3.36 ppb), Cu – 0.93 to 10 ppb (average content – 2.52 ppb, median – 1.16 ppb), P – 2 to 9 ppb (average content – 5.97 ppb, median – 5.17 ppb), B – 2 to 6 ppb (average content – 3.07 ppb,

Table 1 The content of main ions in the water samples (mg/l)

No	Sampling site	pH	HCO_3	Cl^-	SO_4^{2-}	NO_2^-	NO_3^-	Br^-	F^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
1	**Yarlu spr**	7.90	385.1	1.07	4.63	0.47	9.54	< 0.05	< 0.3	3.31	1.37	33.5	55.5	< 0.1
2	**Trib. Yarlu R**	7.02	62.54	0.49	0.81	< 0.5	0.13	< 0.05	< 0.3	4.01	0.93	10.2	4.05	< 0.1
3	**Yarlu R**	7.50	122.1	0.12	22.2	< 0.5	2.06	< 0.05	< 0.3	1.67	0.92	33.9	8.07	< 0.1
4	**Trib. Akkem R**	6.92	52.52	0.19	1.46	< 0.5	2.01	< 0.05	< 0.3	0.89	0.20	16.3	0.73	< 0.1
5	**Akkem Lk**	6.14	17.34	0.11	4.84	< 0.5	0.94	< 0.05	< 0.3	0.48	1.18	5.74	0.88	< 0.1
6	**Tekelu R**	6.73	35.57	0.11	7.51	< 0.5	0.90	< 0.05	< 0.3	0.70	0.52	11.3	1.78	< 0.1
7	**Akkem R**	6.55	25.88	0.11	4.79	< 0.5	0.91	< 0.05	< 0.3	0.71	1.32	7.69	1.16	< 0.1
8	**Kucherla R**	6.71	17.98	0.29	3.01	< 0.5	0.97	< 0.05	< 0.3	0.72	0.56	5.73	0.68	< 0.1
9	**Katun R**	6.48	57.22	0.47	2.51	< 0.5	0.90	< 0.05	< 0.3	1.50	0.44	15.2	2.05	< 0.1

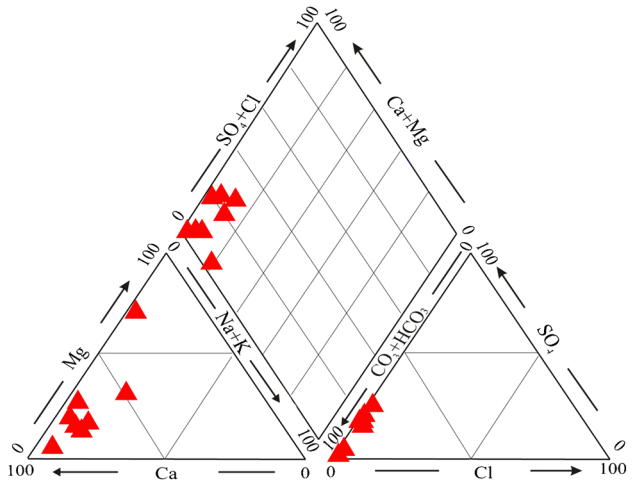


Fig. 3 The composition of the main salt components in water samples (Piper diagram)

median – 2.43 ppb), Li – 0.32 to 2.9 ppb (average content – 1.14 ppb, median – 1.12 ppb), Mn – 0.3 to 17.7 ppb (average content – 5.69 ppb, median – 1.98 ppb), and U – 0.08 to 2.3 ppb (average content – 0.67 ppb, median – 0.25 ppb). Concentrations of other trace elements do not exceed 1 ppb. In terms of average concentrations of REE, the water was close to the Teletskoye Lake water, which is clearly demonstrated by the NASC-normalized profiles in Fig. 4. The sum total of REE in the samples ranged from 0.06 to 1.23 ppb, and the LREE to HREE ratio ranged from 89/11 to 75/25%. Some waters are characterized by negative Ce and positive Eu anomalies. The most pronounced positive cerium anomaly in the source water is most likely related to the measurement error caused by high Ba concentration in the sample (Table 2).

In general, the maximum REE concentrations are typical only for the Yarlu River basin. In other watercourses, the

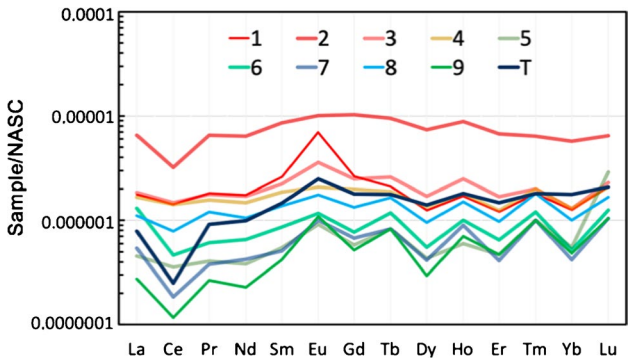


Fig. 4 Profiles of NASC-normalized REE concentrations in the studied water samples. Data for Teletskoye Lake (T) taken from Panichev et al. (2018). See Table 2 for the description of water sample numbers

concentrations of these elements were lower than in the Teletskoye Lake. (Fig. 4).

Mineralogy

Table 3 shows the results of X-ray diffraction quantitative analysis of the mineral composition indicating that kudurits consist of approximately half mica-clay minerals and chlorites, and the other half of quartz and feldspar crystals with a small admixture of calcium and magnesium carbonates (calcite, dolomite, ankerite), as well as titanium oxides (rutile, brukite). Some samples contain minor admixtures of hematite.

Geochemistry

The results of chemical analyses of the main elements in the samples collected in 2019 are presented in Table 4. The rocks were found to be closely similar to the kudurits the the Teletskoye Lake area (Panichev et al. 2018). The rocks from Yarlu, compared with those from the Teletskoye Lake, contain slightly less silicon, titanium, and calcium, and slightly more aluminum, iron, and magnesium. There are almost no differences in the composition of kudurits from glacial deposits and clayey rocks from deluvium among the Ordovician shales.

The rocks from the Yarlu area are also very similar to those from the Teletskoye Lake by the composition of trace elements (Table 5). Among trace elements, the maximum concentrations were found for Ba followed by Sr, Cr, V, Zr, Zn, Ni, Rb, Ce, Cu, Li, Co, La, Nd, Sc, Ga, and Pb. Concentrations of other trace elements do not exceed 10 ppm. Reduced concentrations of all REE (about 20%), except for Sc, are typical for all kudurits from Yarlu in comparison with the Teletskoye Lake area.

Comparing the trace element composition of the kudurits and argillizites from the Ordovician shale, a noticeable difference is observed only for REE. The argillizites contain more elements from the HREE group which is clearly seen in the diagram in Fig. 5.

Electron microscopy

According to an electron microscope study of the kudurits (K-1.1 and K-1.3) and argillizites (P3) samples, the aggregates containing REE along with often corroded magmatic phosphates (monazite and xenotime (Fig. 6D and F), and fluorocarbonates (bastnaesite) (Fig. 6A–C)) also contain easily soluble secondary fluorocarbonates similar in composition to bastnaesite (Fig. 6E). It is their presence that

Table 2 The composition of trace elements in the water samples (ppb)

Element	1 Yarlu spr	2 Trib. Yarlu R	3 Yarlu R	4 Trib. Akkem R	5 Akkem Lake	6 Tekelu R	7 Akkem R	8 Kucherla R	9 Katun R
Li	2.913	1.12	1.55	1.51	0.986	0.316	1.15	0.338	0.425
Be	0.0036	0.006	0.0031	0.0044	0.0068	0.0028	0.0076	0.0052	0.0021
B	6.512	3.93	2.44	2.47	2.32	2.08	2.13	2.17	3.59
Al	12.69	25.14	80.4	19.2	83.1	13.4	292	112	10.08
P	8.20	5.18	2.45	11.02	5.29	4.13	9.42	4.11	4.01
V	0.313	0.226	0.146	0.107	0.409	0.0720	0.691	0.336	0.228
Cr	0.301	0.254	0.350	0.196	0.251	0.224	0.649	0.344	0.229
Mn	0.303	17.7	9.57	0.235	8.33	0.414	12.4	1.99	0.289
Fe	10.92	31.0	55.0	9.60	44.0	5.07	200	76.9	5.10
Co	0.082	0.045	0.104	0.0308	0.0412	0.0220	0.141	0.0610	0.0305
Ni	1.64	0.845	0.611	0.735	0.527	0.540	0.817	0.514	0.503
Cu	10.1	4.74	1.17	2.07	0.628	1.28	0.784	0.930	0.968
Zn	0.827	2.25	0.623	3.39	1.05	2.58	1.04	1.22	2.04
Ga	0.0062	0.0079	0.0287	0.0077	0.0414	0.0157	0.084	0.0355	0.0068
Ge	0.0032	0.0059	0.0040	0.0036	0.0027	0.0018	0.0091	0.0035	0.0022
As	0.361	0.197	0.414	0.560	0.0886	0.192	0.158	0.150	0.229
Se	0.076	0.037	0.523	0.0602	0.0469	0.146	0.109	0.0656	0.0562
Rb	0.420	0.393	0.597	0.174	2.50	0.515	2.94	0.638	0.410
Sr	346	75.3	588	67.9	28.0	108	49.8	28.7	71.3
Zr	0.576	0.324	0.148	0.116	0.158	0.0386	0.0482	0.0821	0.0474
Nb	0.001	0.0022	0.0029	0.0033	0.005	0.0006	0.0183	0.0049	0.0011
Mo	0.817	0.131	4.51	2.66	0.477	1.35	0.643	0.787	0.393
Ag	0.0045	0.0022	0.0025	0.0033	0.0032	0.0035	0.0026	0.0017	0.0025
Cd	0.0073	0.0068	0.0071	0.0149	0.0071	0.0089	0.0028	0.0044	0.0073
Sn	0.045	0.0381	0.0179	0.0724	0.0499	0.0938	0.0190	0.0311	0.0788
Sb	0.234	0.212	0.239	0.2040	0.221	0.2049	0.198	0.250	0.232
Te	0.0058	0.0053	0.0028	0.0049	0.0026	0.0032	0.0034	0.0027	0.0024
Cs	0.0125	0.0068	0.0138	0.0032	0.0295	0.0051	0.0615	0.0249	0.0040
Ba	61.2	4.71	12.5	3.37	2.43	2.05	2.47	1.75	6.92
Hf	0.0107	0.0066	0.0028	0.0030	0.0035	0.0011	0.0019	0.0021	0.0013
Ta	0.0008	0.0006	0.0009	0.0005	0.0009	0.0001	0.0019	0.0022	0.0019
Tl	0.0044	0.0023	0.0024	0.0028	0.0103	0.0017	0.0098	0.0027	0.0019
Pb	0.0422	0.0600	0.0263	0.1280	0.0518	0.0663	0.0702	0.0482	0.0573
Bi	0.0026	0.0019	0.0017	0.0026	0.0031	0.0016	0.0030	0.0029	0.0018
Th	0.0195	0.0371	0.0247	0.0038	0.0222	0.0045	0.0298	0.0255	0.0039
U	2.350	0.1162	2.380	0.102	0.185	0.273	0.323	0.0844	0.252
Sc	0.0308	0.0253	0.0214	0.0161	0.0182	0.0105	0.0284	0.0256	0.0111
Y	0.0390	0.2784	0.0721	0.0195	0.0093	0.0138	0.0370	0.0297	0.0101
La	0.0561	0.2081	0.0591	0.0419	0.0145	0.0172	0.0530	0.0355	0.0088
Ce	0.1037	0.2338	0.1080	0.0339	0.0261	0.0134	0.1028	0.0576	0.0085
Pr	0.0143	0.0514	0.0140	0.0048	0.0032	0.0030	0.0124	0.0095	0.0021
Nd	0.0573	0.2113	0.0559	0.0216	0.0126	0.0140	0.0486	0.0349	0.0075
Sm	0.0149	0.0491	0.0127	0.0049	0.0031	0.0029	0.0106	0.0078	0.0024
Eu	0.0084	0.0121	0.0043	0.0014	0.0011	0.0012	0.0025	0.0021	0.0013
Gd	0.0137	0.0538	0.0130	0.0040	0.0030	0.0035	0.0103	0.0069	0.0027
Tb	0.0018	0.0081	0.0022	0.0010	0.0007	0.0007	0.0016	0.0014	0.0007
Dy	0.0072	0.0430	0.0098	0.0032	0.0025	0.0024	0.0078	0.0055	0.0017
Ho	0.0017	0.0089	0.0025	0.0010	0.0006	0.0009	0.0018	0.0015	0.0007
Er	0.0041	0.0228	0.0057	0.0022	0.0016	0.0014	0.0042	0.0033	0.0016

Table 2 (continued)

Element	1 Yarlu spr	2 Trib. Yarlu R	3 Yarlu R	4 Trib. Akkem R	5 Akkem Lake	6 Tekelu R	7 Akkem R	8 Kucherla R	9 Katun R
Tm	0.0009	0.0032	0.0010	0.0006	0.0005	0.0005	0.0010	0.0009	0.0005
Yb	0.0039	0.0178	0.0040	0.0016	0.0017	0.0013	0.0040	0.0031	0.0015
Lu	0.0010	0.0031	0.0011	0.0006	0.0014	0.0005	0.0010	0.0008	0.0005
∑REE	**0.3588**	**1.2302**	**0.3868**	**0.1583**	**0.1001**	**0.0872**	**0.327**	**0.2261**	**0.0617**
∑LREE	**0.2545**	**0.7657**	**0.2539**	**0.1086**	**0.0606**	**0.0517**	**0.2299**	**0.1474**	**0.0306**
∑HREE	**0.0342**	**0.1607**	**0.0391**	**0.0141**	**0.0121**	**0.0112**	**0.0317**	**0.0233**	**0.01**
LREE%	**88**	**83**	**87**	**89**	**83**	**82**	**88**	**86**	**75**
HREE%	**12**	**17**	**13**	**11**	**17**	**18**	**12**	**14**	**25**
Y/Ho	**22.94**	**31.28**	**28.84**	**19.50**	**15.50**	**15.33**	**20.56**	**19.80**	**14.43**
Eu/Eu*	**2.67**	**1.06**	**1.52**	**1.43**	**1.64**	**1.69**	**1.08**	**1.30**	**2.30**
Ce/Ce*	**0.80**	**0.49**	**0.82**	**0.48**	**0.83**	**0.40**	**0.87**	**0.68**	**0.43**
LaN/YbN	**1.39**	**1.13**	**1.43**	**2.54**	**0.83**	**1.28**	**1.28**	**1.11**	**0.57**
LaN/SmN	**0.67**	**0.75**	**0.83**	**1.52**	**0.83**	**1.06**	**0.89**	**0.81**	**0.65**
SmN/YbN	**2.08**	**1.50**	**1.73**	**1.67**	**0.99**	**1.21**	**1.44**	**1.37**	**0.87**
LREEN/HREEN	**1.16**	**0.67**	**0.76**	**0.71**	**0.42**	**0.53**	**0.74**	**0.67**	**0.45**

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

Table 3 Results of the quantitative X-ray diffraction analysis of the mineral composition of the studied samples (wt %)

Minerals	K-1.1	K-1.2	K-1.3	K-1.5	K-1.6	C-1	P1	P2	P3
Quartz	34.4	27.6	34.3	31.9	32.8	31.3	32.6	36.6	29.0
Plagioclase	12.9	13.1	14.1	14.0	17.3	16.3	15.7	17.6	9.7
K-feldspar	1.6	2.8	0.9	1.6	1.2	1.5	1.1	2.6	1.8
Illite + phlogopite	24.5	24.7	23.9	23.9	21.9	23.3	27.7	25.1	29.5
Chlorite	24.4	25.1	20.9	26.3	25.4	25.7	21.7	15.8	28.6
Calcite	1.4	-	1.9	1.3	0.6	< 0.5	-	-	< 0.5
Dolomite	-	-	2.8	-	-	-	-	-	-
Ankerite	-	5.4	-	-	-	< 0.5	-	< 0.5	-
Rutile	0.8	1.2	0.8	1.0	0.8	1.0	0.5	< 0.5	1.0
Brookite	-	-	-	-	-	-	-	0.8	-
Hematite	-	< 0.5	< 0.5	-	-	-	0.7	0.7	-

K-1.1…K-1.6 kudurits, *C-1* deer coprolite, *P1…P3* argillizites similar in appearance to kudurits

Table 4 The composition of the main rock-forming oxides in kudurits, a coprolite, and argillizites on Ordovician rocks (wt %)

Samples	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Σ
K-1.1	59.32	0.29	15.93	15.89	5.50	0.13	4.31	2.15	1.78	2.37	0.18	6.23	99.68
K-1.2	59.49	0.32	17.00	2.36	5.20	0.10	4.69	0.86	2.39	2.39	0.16	4.78	99.74
K-1.3	58.38	0.30	16.87	3.22	4.32	0.11	4.69	1.55	1.89	2.48	0.17	5.89	99.88
K-1.4	59.08	0.32	16.21	2.50	4.44	0.12	4.15	2.22	2.04	2.36	0.17	6.05	99.65
K-1.5	58.81	0.37	16.98	1.96	5.38	0.11	4.84	1.33	1.79	2.42	0.17	5.58	99.73
K-1.6	60.47	0.37	16.75	1.85	5.39	0.10	4.37	0.95	2.22	2.32	0.17	4.70	99.65
C-1	52.35	0.27	15.18	0.29	5.90	0.09	4.07	1.46	1.52	2.34	0.28	15.78	99.54
P 1	61.50	0.54	16.56	3.11	3.73	0.16	3.92	0.85	1.96	2.87	0.15	4.90	99.56
P 2	62.02	0.60	15.20	2.70	3.24	0.19	3.20	1.68	2.07	2.60	0.17	4.29	99.64
P 3	57.40	0.46	18.23	2.29	5.60	0.11	5.15	0.65	1.41	3.19	0.17	5.95	99.62

K-1.1…K-1.6 kudurits, *C-1* deer coprolite, *P1…P3* argillizites similar in appearance to kudurits

Table 5 The content of the main trace elements

Element	K-1.1	K-1.2	K-1.3	K-1.4	K-1.5	K-1.6	C-1	P1	P2	P3
Li	43.80	49.10	49.18	41.82	48.78	45.95	42.12	34.46	32.97	49.51
Be	1.64	1.74	1.76	1.65	1.89	1.70	1.59	1.82	1.61	2.04
V	118.4	135.8	138.0	129.6	140.4	137.4	124.2	126.7	101.3	142.5
Cr	141.0	147.7	151.0	164.8	158.0	144.3	136.2	131.4	109.2	168.4
Co	25.41	27.17	26.74	25.16	26.97	26.17	23.55	24.63	20.34	29.33
Ni	91.30	100.7	100.4	105.0	103.7	91.36	90.38	79.17	64.77	117.7
Cu	39.36	54.77	56.10	45.08	45.47	38.92	38.62	34.24	54.18	47.04
Zn	98.61	106.5	108.8	111.0	104.4	97.76	104.7	92.24	84.13	115.3
Ga	21.85	22.74	23.12	21.58	23.22	22.26	20.94	22.74	20.11	25.32
Ge	1.55	1.45	1.55	1.50	1.58	1.55	1.13	1.47	1.48	1.68
As	1.70	1.53	2.42	3.14	2.14	1.57	1.50	5.22	8.81	2.76
Rb	97.36	89.84	96.83	92.49	94.38	91.50	92.67	107.2	90.07	126.0
Sr	235.1	163.6	154.1	195.6	179.4	201.6	181.2	147.5	210.5	191.2
Zr	107.6	99.93	116.7	103.3	115.6	106.5	103.2	77.52	49.80	115.0
Nb	3.01	3.36	3.28	3.48	3.97	3.87	2.92	6.78	7.62	4.78
Mo	0.18	0.06	8.04	0.16	0.24	0.06	1.38	0.46	0.22	0.04
Cd	0.10	0.08	0.10	0.11	0.11	0.07	0.19	0.10	0.10	0.10
Sn	1.54	1.56	1.78	1.40	1.81	1.43	1.54	1.97	1.68	2.07
Sb	0.87	0.84	0.90	1.89	1.01	0.97	0.83	0.69	1.01	0.88
Cs	5.82	5.77	6.18	6.28	6.10	5.81	5.80	5.78	4.90	9.64
Ba	383.5	383.9	392.9	382.9	397.6	397.8	376.9	519.9	491.1	498.4
Hf	2.14	2.20	2.46	2.19	2.45	2.28	2.23	1.59	1.18	2.41
Ta	0.18	0.22	0.20	0.21	0.32	0.25	0.19	0.42	0.46	0.28
W	0.74	0.67	0.65	1.08	0.82	0.84	0.75	1.45	1.45	1.25
Tl	0.30	0.28	0.32	0.28	0.30	0.29	0.30	0.35	0.28	0.43
Pb	12.41	10.59	11.26	11.20	11.28	10.57	10.09	11.35	21.80	11.95
Th	5.73	6.08	6.46	5.78	6.55	5.73	5.68	6.44	7.14	6.99
U	2.87	1.82	1.75	1.39	1.88	2.13	1.83	1.26	1.45	1.85
Sc	21.91	23.60	23.30	21.80	23.10	23.30	26.13	21.29	18.77	24.70
Y	9.64	7.74	8.18	8.45	9.43	8.96	9.56	18.13	26.59	16.09
La	24.11	22.94	28.45	23.49	25.93	21.86	26.93	26.03	29.99	24.14
Ce	53.66	49.65	57.55	50.66	55.59	48.23	58.53	56.29	64.26	52.19
Pr	6.07	5.89	6.80	5.99	6.45	5.64	6.88	6.39	7.36	6.12
Nd	23.41	22.64	26.13	22.94	24.68	21.65	26.32	23.84	27.64	23.30
Sm	4.60	4.59	5.02	4.63	4.90	4.47	5.26	4.86	5.68	4.72
Eu	0.99	0.97	1.06	1.11	1.05	0.94	1.10	1.00	1.24	1.05
Gd	3.36	3.23	3.55	3.69	3.55	3.33	3.64	3.81	4.83	3.91
Tb	0.45	0.41	0.43	0.41	0.47	0.46	0.46	0.57	0.78	0.61
Dy	2.06	1.69	1.74	1.78	2.04	2.07	2.00	3.12	4.42	3.25
Ho	0.35	0.40	0.33	0.30	0.35	0.34	0.36	0.63	0.90	0.59
Er	1.05	0.87	0.99	0.95	1.04	1.00	1.11	1.84	2.60	1.62
Tm	0.16	0.14	0.16	0.15	0.17	0.16	0.18	0.26	0.34	0.25
Yb	1.25	1.14	1.31	1.21	1.37	1.26	1.45	1.71	2.17	1.73
Lu	0.20	0.18	0.23	0.20	0.23	0.21	0.24	0.25	0.27	0.27

K-1.1…K-1.6 kudurits, *C-1* deer coprolite, *P1…P3* argillizites similar in appearance to kudurits

determines the elevated REE background in the waters of the Yarlu River basin. This anomaly, most likely, is associated with hydrothermal argillizites widespread in the upper reaches of the Yarlu and Tekelu rivers. Besides REE aggregates, we also found native gold particles in argillizites.

Comparison of the chemical composition of kudurit and coprolite

As maral coprolite was found near lick No. 1 in 2019 (sample K-1.1), we compared it with this sample (Table 6). The

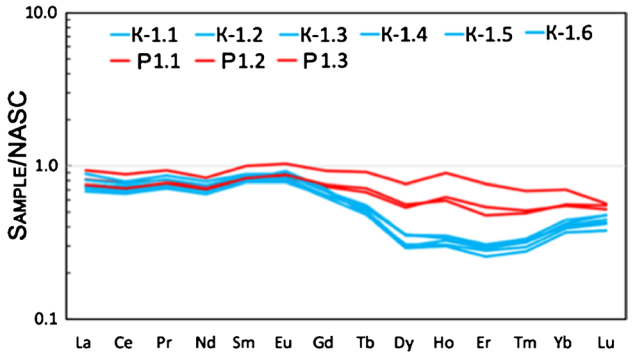


Fig. 5 NASC-normalized REE concentration profiles in kudurits and argillizites from the Ordovician shale. See note to Table 5 for sample numbers

comparison showed that there were more Si, Fe, Mn, Ca, and Na in the kudurit. The only fact that it is not subject to doubt as a result of comparing the composition of the coprolite and kudurit is the release of excess Al, ferrous Fe, K, and P from the body in the coprolite composition. Regarding the elements that are extracted from the kudurit as it passes through the digestive tract, the result is open to interpretation.

To clarify this ambiguity, we decided to compare the chemical composition of kudurits with the more numerous coprolite samples that were collected in 1987. The result is in Table 7 (according to Panichev 1990).

These data show that Na and Si yields are at least somewhat comparable to the 2019 data. Al, Ti, and Fe yields are not so clearly comparable. To clarify the extractability of certain elements from kudurits in the digestive tract, Table 8 shows the data of the analysis of the same samples from 1987, but using the X-ray fluorescence method.

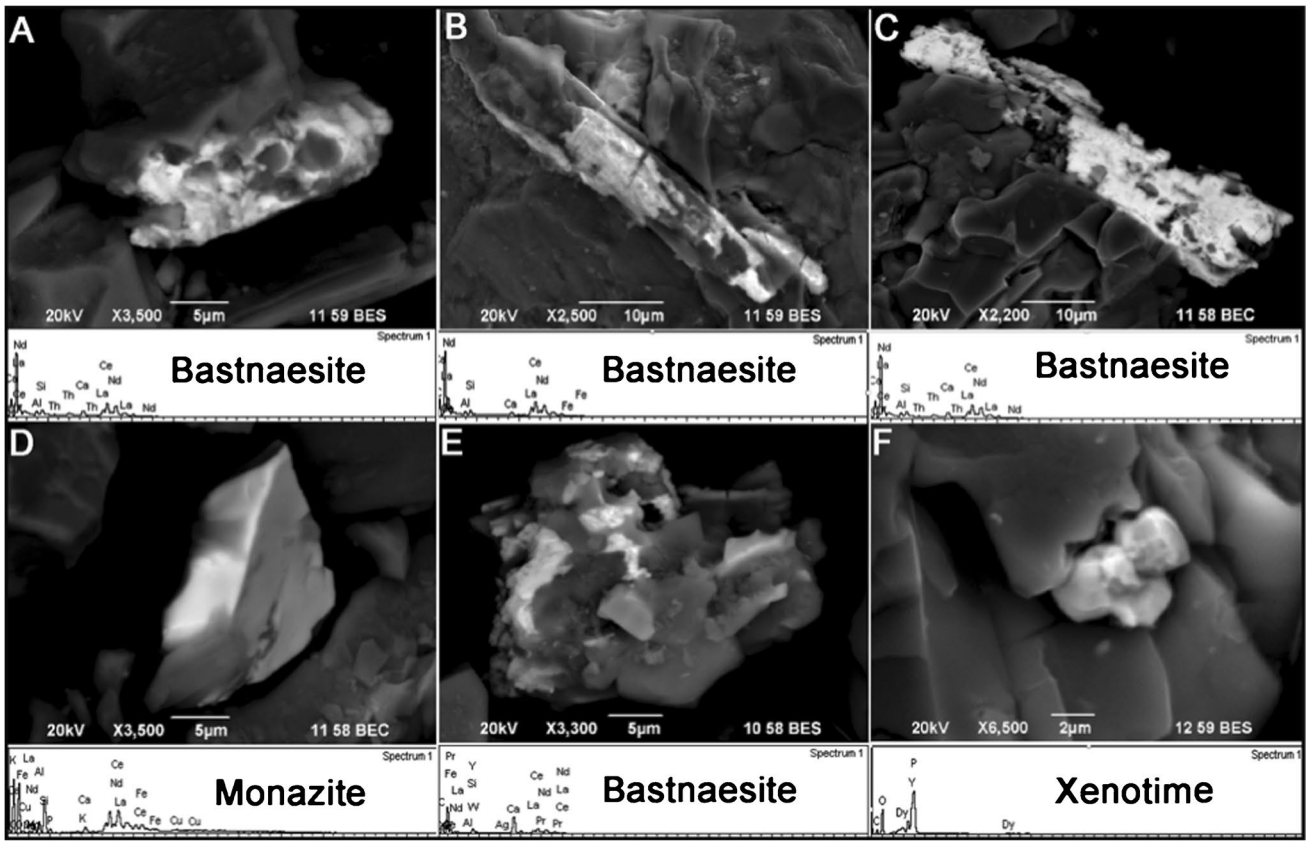


Fig. 6 Electron microscopic photo and energy dispersive spectra of rare-earth aggregates in kudurit samples from the Yarlu area

Table 6 Comparison of the chemical composition of kudurit and coprolite (2019 samples, LOI values proportionally distributed)

Sample	SiO2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
K-1.1	63.54	0.31	17.16	2.0	5.4	0.14	4.57	2.28	1.89	2.52	0.19
C-1	62.12	0.32	18.61	0.35	7.02	0.11	4.82	1.74	1.81	2.77	0.33
	− 1.42	0.01	1.45	− 1.65	1.62	− 0.03	0.25	− 0.54	− 0.08	0.25	0.14

Table 7 Comparison of the chemical composition of kudurits and coprolites collected at kudur K-1 in 1987 (according to Panichev 1990). LOI values are proportionally distributed

Semple	*SiO_2	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	K_2O	Na_2O	P_2O_5	LOI
	Kudurits											
1–90	0.07	64.26	0.83	16.44	7.94	0.09	4.31	1.17	2.50	2.30	0.16	7.36
2–90	0.94	65.20	0.77	16.07	7.71	0.11	4.10	1.36	1.96	2.52	0.20	5.04
3–90	0.82	63.30	0.94	17.14	8.11	0.1	3.88	1.54	2.57	2.25	0.17	5.98
Average 1	0.82	64.25	0.85	16.55	7.92	0.1	4.10	1.36	2.34	2.44	0.18	
	Coprolites											
C1-90	0.67	64.78	0.80	16.14	7.75	0.1	4.21	1.45	2.45	2.07	0.25	8.52
C2-90	0.92	63.32	0.84	16.32	8.38	0.11	4.32	1.32	2.75	2.06	0.58	16.13
C3-90	0.36	63.53	0.82	16.50	8.44	0.1	3.89	1.42	2.73	2.14	0.43	14.42
C4-90	0.42	62.25	0.82	16.25	8.87	0.1	4.71	1.36	2.86	2.23	0.55	15.35
Average 2	0.59	63.47	0.82	16.3	8.36	0.1	4.28	1.39	2.7	2.13	0.45	
A1-A2	−0.23	−0.78	−0.03	−0.25	0.54	0	0.18	0.03	0.36	−0.31	0.27	

**SiO2* mobile silicon oxide extracted by 5% NaOH solution

Table 8 The content of chemical elements in kudurits and coprolites collected in 1987 by X-ray fluorescence analysis (according to Panichev 1990)

Sampes	P	S	Cl	Mn	Ti	Zn
Kudurits (mg/kg)						
1–90	605	48	49	1146	5636	156
2–90	733	75	68	1026	6073	218
3–90	643	75	55	1296	4826	82
4–90	495	60	76	1226	5708	222
Average 1	619	65	62	1174	5561	170
Coprolites (mg/kg)						
C1-90	966	189	106	1061	5431	128
C2-90	2200	767	56	1092	5894	277
C3-90	1738	328	143	1017	5862	133
Average 2	1635	428	102	1057	5729	179
A1-A2	1016	363	40	−117	168	9

The data in Table 8 indicate that Ti, P, S, Cl, and Zn are removed from the body in kudurits, while Mn is taken into the body. To complete the picture, Table 9 shows the data on major cations in the same kudurits and coprolites, which are in the absorbed and water-soluble forms.

From these data, it follows that kudurits have more water-soluble forms of Mg, K, and Na than absorbed ones. Conversely, there are more absorbed forms of Ca cations than water-soluble ones. In coprolites, the ratio of water-soluble and absorbed forms of elements remains close to that in kudurits. The only element whose total amount decreases in coprolites is Na (by 0.1 g per each kilogram). The amount of other elements in kudurits increases in succession: Mg by 0.62 g/kg, K by 0.33 g/kg, and Ca by 0.08 g/kg.

Acid extracts

To provide a complete picture of the effect of acid on the kudurit in the rennet of animals, two types of acid extractions were made. One extract was made by a hydrochloric acid solution with pH of 1.0 and the other with pH of 3.0. The result of acid extraction with pH 1.0 for five samples is presented in Table 10 and that with pH 3.0 for two samples in Table 11. According to Table 10, the maximum effect of acid solution with pH 1.0 is seen in the extraction of Ca, P, and Mn. The effect of the acid solution with pH 3.0 is somewhat different. It most strongly affects the yield of Ca, P, and Na in the solution.

In the composition of trace elements, the strongly acid solution extracts the largest amount of Sr (51 to 66 ppm), Cu (14 to 27 ppm), Ba (6 to 16 ppm), Ce (4 to 15 ppm), Nd (2 to 8 ppm), La (2 to 8 ppm), Zn (2 to 5 ppm), Ni (1

Table 9 The composition of mobile (absorbed and water-soluble) cations in kudurits and coprolites collected at kudur K-1 in 1987 (according to Panichev 1990)

Sample	Cation form	Mg	Ca	K	Na	Sum	Total
Kudurits (in mg-equivalent/100 g)							
1–90	**Absorbed**	4.13	2.0	0.34	0.5	6.97	16.28
	Water-soluble	3.01	5.72	0.05	0.53	9.31	
2–90	**Absorbed**	4.91	2.19	0.68	0.58	8.36	16.07
	Water-soluble	0.83	6.44	0.05	0.39	7.71	
Average 1	**Absorbed**	4.52	2.1	0.51	0.54		16.18
Average 2	**Water-soluble**	1.92	6.08	0.05	0.46		
Coprolites (in mg-equivalent/100 g)							
C1-90	**Absorbed**	7.31	0.6	0.78	0.22	8.91	21.74
	Water-soluble	4.28	7.78	0.17	0.6	12.83	
C2-90	**Absorbed**	9.5	0.86	1.07	0.37	11.8	22.43
	Water-soluble	0.48	9.5	0.59	0.06	10.63	
C3-90	**Absorbed**	9.8	0.56	1.33	0.22	11.91	22.16
	Water-soluble	3.37	6.41	0.27	0.2	10.25	
Average 3	**Absorbed**	8.87	0.67	1.06	0.27		22.11
Average 4	**Water-soluble**	2.71	7.9	0.34	0.29		
A1-A3	**Absorbed**	4.35	−1.43	0.55	−0.27		5.93
A2-A4	**Water-soluble**	0.79	1.82	0.29	−0.17		
Total	**mg-equivalent/100 g**	5.14	0.39	0.84	−0.44		+5.93
	mg/kg	+620	+80	+330	−100		

Table 10 The yield of main elements in the acid extract (HCl, pH 1.0) in ppm and percentage of gross content

Element	K-1.1		K-1.3		K-1.4		K-1.5		P3	
	Acid extract	%	Acid extract	%	Acid extract	%	Acid extract	%	Acid extract	%
Si	250	0.09	-	-	-	-	-	-	467	0.17
Ti	0.8	0.04	< 0.1	-	< 0.1	-	< 0.1	-	0.7	0.03
Al	350	0.42	324	0.36	202	0.24	472	0.53	499	0.52
Fe	579	1.10	2533	4.8	1452	3.0	888	1.7	823	1.38
Mn	349	35.2	432	48.8	420	46	232	28	85.9	10.0
Mg	1333	5.13	2618	9.3	2042	8.2	970	3.3	431	1.39
Ca	12,750	82.9	8419	76	12,307	77	8198	86	4862	100
Na	463	3.51	287	2.04	282	1.9	42	0.32	106	1.01
K	57.6	0.29	52.8	0.26	28	0.14	70	0.35	87.6	0.33
P	481	61.2	267	36.4	125	17	530	74	714	98.7

"-" was not determined

to 2 ppm), and Li (about 1 ppm). The weakly acid solution extracts the largest amounts of Sr (3 to 7 ppm), Mo (0.04 to 3.5 ppm), and Ba (0.14 to 0.67 ppm).

Figure 7 shows the NASC-normalized REE concentration profiles in both extracts. The diagram illustrates that the extraction with pH 1.0 yields 3–4 orders of magnitude more REE than the extraction with pH 3.0. The maximum amount of extracted REE is observed in the Ordovician shale rocks.

Experiment

To determine the ability of mineral mixtures typical for the Yarlu area kudur to sorb REE in conditions close to the environment of the ruminant abomasum, a special experiment was conducted. Its procedure is described above. The result is presented in Table 12.

The experiment showed that calcite powder and quartz-plagioclase-illite-chlorite kudurits when interacting with

Table 11 The yield of main elements in the acid extract (HCl pH 3.0) in ppm and percentage of gross content

Element	K-1.3		K-1.5	
	Acid extract	%	Acid extract	%
Si	10.5	0.004	16.5	0.006
Ti	< 0.1	< 0.0055	< 0.1	< 0.0045
Al	< 0.1	< 0.0001	< 0.1	< 0.0001
Fe	< 0.1	< 0.0002	< 0.1	< 0.0002
Mn	0.2	0.019	0.2	0.018
Mg	106	0.375	169	0.58
Ca	139	1.26	137	1.44
Na	253	1.80	23.5	0.18
K	32.1	0.16	41.3	0.21
P	2.5	0.34	2.8	0.39

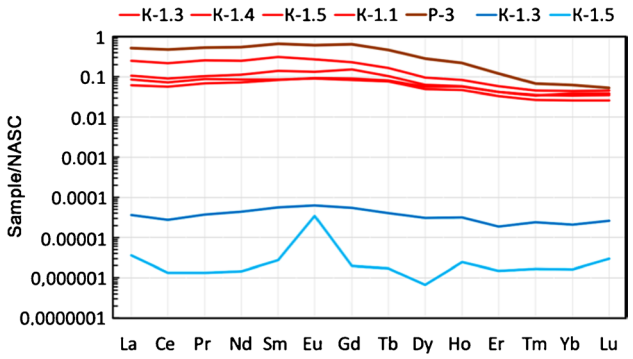


Fig. 7 NASC-normalized REE concentration profiles in acid (HCl, pH 1.0 and pH 3.0) extracts (the two lower profiles are extracts with pH 3.0)

acid REE solution sorb the elements with 60 to 99% efficiency (about 92% on average). Calcite powder was found to be the most effective sorbent with an absorption efficiency of about 99% for all elements. This result proves that quartz-plagioclase-illite-chlorite kudurits will actively sorb REE from the biological electrolyte under any pH conditions specific to the digestive tract.

The assessment of the actual REE sorption on kudurits in the animal digestive tract

This assessment is possible by comparing REE concentrations in coprolites and the corresponding kudurits. Figure 8 shows the NASC-normalized profiles of REE concentrations in the coprolite (C-1) and the corresponding in chemical and mineralogical composition kudurit (K-1.6) near which this coprolite was found. As is evident, kudurits of quartz-feldspar-illite-chlorite type most actively sorb the light REE subgroup when passing through the digestive tract. Unfortunately, there are no data on REE in the analyses made in 987 due to the absence of the necessary analytical equipment at that time.

Discussion

As a result of the conducted complex work, we found out that in the upper reaches of the Akkem river, on its right tributary Yarlu, for a long time, there have been typical kudurs actively visited by herbivorous animals, both wild species (red deer, Siberian ibex, hares, and marmots) and domestic horses when their herds were left in the upper reaches of Yarlu for free grazing. The main habitats of the animals visiting kudurs in the upper reaches of the Akkem River are the forest and steppe areas in the Akkem and Tekelu river valleys close to Yarlu, as well as the nearest mountain slopes. It is also possible that some animals may come to kudurs from a distance. It is worth noting that finely dispersed deposits similar in appearance to the kudurits in the Yarlu area are quite common in some areas of the Altai Mountains but they are by far not always sought out by animals. However, in the

Table 12 The ability of kudurits consisting of approximately 50% mica-chlorite minerals, and the calcite monomineral powder to sorb REE from an acid (HCl, pH 2.00) solution

Elements	La	Pr	Sm	Gd
Initial concentration in 0.1 N HCl solution (ppb)	**14.17**	**16.33**	**13.87**	**1.40**
After adding **calcite** (ppb)	0.12	0.12	0.11	0.02
Difference from initial concentration, ppb (%)	− 14.05 (**99%**)	− 16.21 (**99%**)	− 13.76 (**99%**)	− 1.38 (**99%**)
After adding **kudurit 1** (ppb)	1.66	1.34	1.47	0.55
Difference from initial concentration, ppb (%)	− 12.51 (**88%**)	− 14.99 (**92%**)	− 12.40 (**89%**)	− 0.85 (**61%**)
After adding **kudurit 2** (ppb)	1.23	0.56	0.51	0.23
Difference from initial concentration, ppb (%)	− 12.94 (**91%**)	− 15.77 (**97%**)	− 13.36 (**96%**)	− 1.17 (**84%**)
After adding **kudurit 3** (ppb)	0.73	0.53	0.47	0.1
Difference from initial concentration, ppb (%)	− 13.44 (**95%**)	− 15.79 (**97%**)	− 13.40 (**97%**)	− 1.30 (**93%**)

"-" a decrease in the concentration of the element in the solution

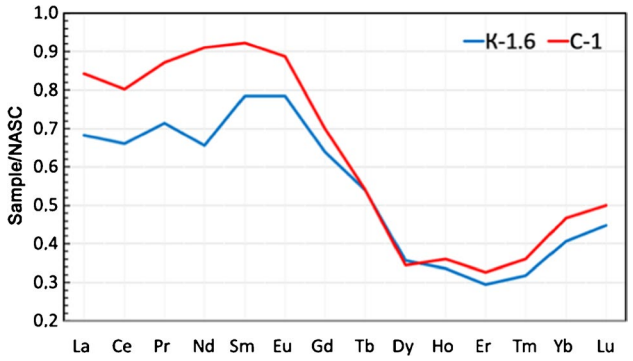


Fig. 8 NASC-normalized REE concentration profiles in a coprolite (C-1) and chemically and a mineralogically corresponding kudurit

areas of the Altai Mountains without such deposits, there are no kudurs at all.

We also found that waters of local streams and springs contain negligible amounts of salts in their elemental composition (from 0.05 to 0.5 g/l), including very little Na (0.5–4 mg/l). On the other hand, such a low level of salts and elemental composition is typical for the middle and high-mountain zone practically in the whole territory of the Altai Mountains.

The only uncommon characteristic of local waters identified by us is the increased concentration of REE in watercourses and spring in the basin of the Yarlu River. The highest concentration of REE that exceeds the level in other rivers by 10 times or more was observed in the Yarlu River itself. Among trace elements in the Yarlu River, the highest concentrations were observed for Sr (588 ppb), Al (80 ppb), Fe (55 ppb), and Mo (4.5 ppb). This hydrochemical anomaly is associated with the presence of a greisen-type molybdenum deposit in the upper Yarlu (Fig. 1B). This deposit, associated with deeply buried granites, may be a source of elevated REE concentrations in the Yarlu River basin. REE enter the local watercourses from argillizites as well. As we found out by electron microscopy, a significant portion of REE in these argillizites is in easily soluble (mobile) form. A not very significant difference in LREE and HREE concentrations in parent argillizites and in derivative kudurits can be explained by "dissolution" of some HREE minerals either at a stage when the lake existed or as a result of weathering in subaerial conditions.

The comparison of the chemical composition of kudurits and coprolites collected in different years showed that the only macronutrient that can be assimilated in the body with high probability is Na. The amount of assimilable Na in kudurits (calculated per oxide) is in the range from 0.08 to 0.31 g/kg, with about 50% of assimilable sodium as soluble salts and about the same amount as sorbed ions. Among other elements that showed a rather unstable ability to come out of kudurits after passing through the digestive tract of animals are Si, Al, Ti, Fe, Mn, and Ca. Among the elements that are most consistently sorbed on kudurits and excreted from the body are P and K in the first place, followed by Mg and sometimes Ca. We also found that rare-earth elements are actively sorbed and removed from the body when kudurite passes through the digestive tract.

The identified list and the concentrations of elements that can be metabolized on kudurits in the body are quite typical for kudurits of this mineral type, which we found by similar studies in other areas of the Altai Mountains (Panichev et al. 2018; Panichev 1990) and the Caucasus Mountains (Panichev et al. 2021a).

Next, let us try to understand if Na is exactly the element that animals seek in the studied kudurits. Assuming that Na_2O yield from the kudurit is 0.1 to 0.3 g/kg (which corresponds to 0.07–2.1 g/kg of pure element), it follows that by eating such kudurites, animals may get 20 g of pure Na (which corresponds to a tablespoon of NaCl) if they consume from 10 to 200 kg of kudurit. Apparently, it makes no sense to consume such kudurits for the sake of finding Na.

In addition to the search for Na, the "sodium" hypothesis of geophagy has a second important component. Animals can address the problem of Na deficiency in food not only by bringing the sought element in mineral substances into the body but also by greatly reducing its losses in the body. Na loss can occur, for example, in diarrheal diseases, which are widespread among herbivores, especially during seasonal changes in the diet (Kreulen 1985; Klaus Schmid 1998). Mineral sorbents are known to be quite effective in medicine and veterinary for stopping diarrhea.

During the field work in the area with kudurs on Yarlu, we found a few old (from spring) dried pellets of liquid excrement of deer, which is typical for all habitats of these animals in spring, but we did not find fresh liquid excrement in July and August. There were only fresh solid plant excrement "nuts" and stone-like coprolites of marals and ibex.

These observations, taking into account very low Na concentrations in kudurits, leave almost no chance for the "sodium" hypothesis for the territory under study. Similar facts in other territories lead researchers to consider other reasons for the consumption of such kudurits.

That is why a whole series of other hypotheses were developed along with the "sodium" one. These include the need to replenish iron deficiency in the body, replenishment of symbiont microorganisms, bacteriostatic properties of clay minerals against pathogenic microflora, parasite control, and pH regulation in the digestive tract (Abrahams 1997; Ketch et al 2001; Krishnamani and Mahaney 2002; Wilson 2003). It was also repeatedly suggested that the minerals consumed at kudurs could compensate for the corresponding losses during lactation and antler growth (Nasimovich 1938; Fraser and Reardon 1980; Moe 1993). Somewhat separate from the above, there is a hypothesis regarding the removal

of toxic organic compounds from the body with the help of mineral sorbents (Oates 1978; Kreulen 1985; Gilardi et al. 1999; Houston et al. 2001; Pebsworth et al. 2018; Ekosse et al. 2020). In relation to humans, it is most often suggested that clays can combat gastrointestinal and other diseases (Anell and Lagercrantz 1958; Vermeer and Ferrell 1985).

In recent years, we have been developing our original hypothesis, which, we believe, can unite most of the cases of regular geophagy in both animals and humans. After analyzing extensive data on the geochemistry of eaten earths in different regions of the world (our data and reports of other researchers) and taking into account the available data on the influence of rare-earth elements (REE) in the body on the immune and hormonal systems, which is particularly well described in a review by K. Redling (2006), we first had an idea that there are at least two main reasons for the desire for geophagy explaining all the cases in the world (Panichev 2015, 2016). The first one is caused by the electrolyte imbalance in the body, and the other one by the disturbance of REE metabolism in the neuroimmunoendocrine system. We assumed, in particular, that some elements from the light lanthanides group associated with nerve tissues and internal secretion gland enzymes can be replaced by heavy lanthanides, which, unlike the light ones, cannot perform the functions necessary for the body. This idea was partly tested in 2020 at two sites in the Sikhote-Alin (Panichev et al. 2021b). As a result of large-scale hydrobiogeochemical studies, we found that in areas where geophagy is common among wild ungulates, acid volcanogenic and volcano-sedimentary rocks enriched with REE are predominant. During the weathering, secondary easily soluble rare-earth minerals (water phosphates and fluorocarbonates) are formed. This leads to the accumulation of REE in all landscape components (natural water, soil, vegetation, and herbivorous animals). We concluded that an excess of REE in the neuroimmunoendocrine system of the body, which is a carrier of this group of elements, can cause a stress reaction in animals against the background of hormonal disturbances making them search for mineral sorbents that can correct the REE imbalance in the body.

Analyzing the geological map and the ungulates' habitats in the upper and lower reaches of the Akkem River, we believe that the cause of clay rocks consumption in the Yarlu and Akkem valleys is most likely an excess of REE in plant food growing in the Akkem, Yarlu, and Tekelu valleys. Increased concentrations of this group of elements may be associated with a long (at least hundreds of thousands of years) destruction of a large massif of granites in the Belukha Mountain area. Granites are rocks with almost always high or elevated concentrations of rare-earth elements. Loose sediment aprons filled with fine clastic granitoid material are constantly moving along the Akkem and Tekelu river valleys participating in the formation of floodplain soils. However, it seems more likely that the range of soils affected by mobile forms of REE is determined by the presence of hydrothermal argillizites. Their abundant outcrops are confined to the overthrust geological boundary between the Cambrian and Ordovician shales in the areas where hydrothermal activity related to the hot granite pluton occurred.

It seems that mobile forms of REE are most readily transported into vegetation as they participate in the formation of soils. Animals consuming this vegetation, as in the Sikhote-Alin (Panichev et al. 2021b), may well have hormonal disorders due to an excess of REE. The resulting stress causes them to seek out mineral sorbents that can resolve the problem in their bodies. When searching for such sorbents, animals apparently prefer to seek out and consume varieties with a higher Na content. In this case, it appears that they need this element not so much to compensate for its deficiency in the digestive cycle, but rather to relieve the stress condition. The action of Na here may be similar to that of another alkaline element — Li, whose salts are commonly used in medical practice to relieve nervous overexcitement, up to cases of manic-depressive psychosis and even schizophrenia.

There is another factor that may explain why animals, as suggested by our data, tend to eat kudurits not on primary argillizites but on their lake deposits, which are noticeably depleted in the heavy REE subgroup. It is quite possible that specific microorganisms capable of assimilating and transforming REE into forms that can be absorbed in animals may develop in such water-separated argillizites that have been in subaquatic and subaerial conditions for a long time. Such microorganisms may grow most actively in mycorrhiza of some plants, which explains why many licks are confined to the roots of trees, shrubs and some grasses. Animals may be attracted to such microorganisms as symbiont REE-converting forms permanently present in the microflora of the digestive tract because the forms necessary for the body can "degenerate" and rearrange to work incorrectly at intake of food with a "wrong" LREE to HREE ratio. In other words, if REE with a high proportion of HREE enter the digestive tract with food, then symbiont REE-converting forms of microorganisms are gradually transformed, adapting to utilize them. As a result, more and more HREE starts to enter the internal environment instead of LREE that the body needs, which, in fact, may be the cause of disorders in the neuroimmunoendocrine system. In this case, kudurits along with sorption and removal of excessive REE can also be suppliers of "correct" REE-assimilating forms of bacteria.

By now, it has been confirmed that many microorganisms assimilate REE in large quantities. In soils, for example, iron-oxidizing chemolithotrophic bacteria play an active role. Among them, the bacterium *Gallionella ferruginea* is widespread which can accumulate REE in amounts thousands of times higher than their content in rocks and millions

of times higher than in soil water (Anell and Lagercrantz 1958; Anderson and Pederson 2003). In recent years, various bacteria were successfully introduced into REE bioleaching technologies from ores, ash slag, and industrial solid waste (Barmettler et al. 2016). These include bacteria that perform well in concentrating REE at pH typical for the soil profile. For example, anaerobic microorganisms *Desulfovibrio desulfuricans* from the genus of anaerobic sulfate-reducing bacteria were used to mobilize REE from some solid materials with nearly 80% efficiency (Dudeney and Sbai 1993). According to reference books, bacteria of this genus live not only in rocks but also in the intestines of some animals and manure. Earlier, in a series of microbiological studies of kudurits in the Sikhote-Alin (Lebedeva et al. 2020), we revealed that heterotrophic aerobic and facultative anaerobic microorganisms of genera *Burkholderia* sp. and *Microvirgula aerodenitrificans* are involved in iron oxidation and sulfate reduction. This fact confirms the potential of a more in-depth study of the microbiological factor for solving the geophagy problem.

The additional microbiological factor associated with REE and the search for sodium suggests the existence of a single "rare-earth-sodium-bacterial" cause that can explain a significant number of the geophagy cases (if not all of them) in different regions of the world.

Despite the limited territory covered by this study, some facts supporting our new hypothesis have already been described by us in earlier publications (Panichev 2015; Panichev et al. 2016; 2018; 2021a, b).

Conclusions

Hydrogeochemical and geological-geochemical studies were carried out in the upper reaches of the Akkem River in the Altai Republic aimed at explaining why the local ungulates consume clay rocks common in the basin of the Yarlu River, a tributary of the Akkem River. We studied the chemical composition of river and spring waters, and mineral and chemical compositions of clay rocks consumed by wild and domestic ungulates at kudurs.

It was found that the waters in the local watercourses are ultra-fresh, hydro-carbonate-calcium. Increased concentrations of REE were observed in waters of the Yarlu River, unlike other rivers and streams. Kudurits are represented by finely dispersed quartz-plagioclase-mica-chlorite mineral associations — the products of hypergenic transformation of shale rocks of the Early Paleozoic age. The comparison of the chemical composition of kudurits and coprolites of red deer showed that when the rocks pass through the digestive tract, out of all macroelements, only Na is reliably assimilated in the body in amounts from 0.1 to 0.3 g per kg of kudurit. In addition, kudurits act as sorbents, removing P, K, Mg, and sometimes Ca from the body. As part of micronutrients, they are most active in sorbing and removing REE from the body. The concept of the toxic effect of high REE concentrations in plant food on animals was proposed as the most probable cause of geophagy, suggesting that eating finely dispersed rocks promotes detoxification of the body.

Further studies are needed to definitively prove that geophagy in the Belukha Mountain area is caused by a toxic excess of REE in plant food.

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Declarations

Conflict of interest The authors declare no competing interests.

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