Kudurs (mineral licks) on ultrabasic rocks in the Altai Mountains, Russia

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Abstract. In the present study, the mineral and chemical compositions of kudurits consumed by wild ungulates and the chemical composition of forage vegetation near the water-divide of the Abakan Range, Mountain Altai, Russia, were studied. It was found that the kudurits are represented by smectite-vermiculite mineral associations with chlorite-the products of hydrothermal transformation of metamorphosed ultrabasic rocks (serpentinites) following the intrusion of neighboring gabbroid dikes. Acid extracts (hydrogen chloride, pH 1.0) from kudurits most actively extract Ca, K, Mg, Fe and Na. In the composition of trace elements, Ba, Sr, Ni, Cu, Cr, Co, V, Zn and Li are most mobile. The comparison of the chemical composition of a kudurit and coprolite of red deer indicates that when mineral earth materials pass through the digestive tract out of all trace elements only about 0.4 g/kg of Na is reliably assimilated in the body, while kudurits simultaneously sorb and remove P, K, Mg and Ca. Chemical analyses of vegetation in places from which animals most often come to kudurs revealed high concentrations of rare earth elements. A rare-earth-sodium hypothesis of the cause of geophagy is developed, which may explain the majority of cases of regular consumption of earthy substances by animals and humans.

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Introduction

The phenomenon of the animal consumption of mineral earth material, termed 'geophagy', has been studied for approximately one hundred years. Possibly, the first scientific publication on the subject of geophagy among ungulates was the article of the Canadian researcher, A. Mure (1). Approximately a thousand articles and several tens of monographs have been published on this topic; however, scientific interest in geophagy has not weakened due to the fact that the cause of the phenomenon is not yet fully known.

Easily identifiable landscape complexes, which are developed as a result of the regular consumption of mineral earth material by animals, are commonly referred to as salt licks or mineral licks in the Western scientific literature. These objects, however, are not necessarily associated directly with the consumption of soluble salts and with licking; thus, it was decided to use the term 'kudur' to refer to these. This term is borrowed from the vocabulary of Turkic shepherds (2). The derived term 'kudurit' is used by the authors to denote mineral soils consumed by animals at kudurs. The present study uses the term 'lick' exclusively to denote specific depressions eaten out by animals within kudurs.

The majority of articles on geophagy in animals are focused on the study of the chemical composition of kudurits, as well as on ecological aspects. There are not many articles dealing with the mineralogical aspects of kudurits. The mosts well-known ones are the articles by Mahaney *et al* (3-9), as well as other researchers (10,11). In previous studies by the authors, ample attention was paid to the mineralogy of kudurits; the mineral composition of the studied kudurits was most fully discussed in monographs (12,13). Thus far, the geological features of kudurit formation have received the most thorough attention in the articles written almost exclusively by the present group of authors (2,14-17).

The cited literature describes a number of mineralogical types of kudurits, which can be divided into mainly silica,

carbonate, zeolite-clay and pure clay (smectite, kaolinite, hydrosludite-chlorite and hydrosludite-chlorite). By the dispersion level, they most often belong to the clay and clay-siltstone varieties. Kudurits are formed on the parent rocks which can be sedimentary, magmatic and metamorphic varieties. In terms of the silicic acid content, the vast majority of such parent rocks are in the interval from acidic to basic varieties. Much less frequently, animals eat soil mainly from the lower horizons of the soil profile. In terms of mineral composition, it does not differ from the mineralogical types aforementioned, the only difference being that they contain considerably more organic matter.

The present study demonstrates the results of geological-mineralogical and chemical analyses of three kudurs with a rare mineralogical type of clay kudurits formed on ultrabasic rocks on the Abakan Ridge, in the border part of the Altai State Nature Biosphere Reserve. Based on these analyses, the authors present a hypothesis of the reasons why animals regularly consume kudurits of this type.

The studied kudurs are located in the border part of the Altai State Nature Biosphere Reserve near the water-divide of the Abakan Ridge separating the Teletskoye Lake from the Bolshoy Abakan River (Fig. 1A). One of the kudurs (A-1) is located in the upper reaches of the Yerinat River, a tributary of the Bolshoy Abakan (coordinates: 51.35599; 88.27132, abs. alt. - 2328 m). The kudur originated on the southeastern slope of a small detached hill (~40 m high) in the central part of the nival kar (nival hollow) surrounded by lakes on three sides. On the entire southeastern slope of the hill within a 50x30 m area trampled by animals, particularly in its upper part, there are licks in bleached bluish-greenish mineral earth materials. A fragment of kudur A-1 with licks in the form of a water-filled pit in the upper part of the slope is illustrated in Fig. 2A.

The second kudur (A-2; Fig. 1) is located in the upper reaches of the Uzun-Karasu River (coordinates: 51.33991; 88.33788, abs. alt. -2386 m). It is located on the saddle of the ridge, covering its northwestern slope. The trampled area with animal licks is ~25x50 m.

The third kudur (A-3; Fig. 1) is located in the head of the Tyurgensu River, a tributary of the Bolshoy Abakan River (coordinates: 51.30938; 88.49099, abs. alt. -2132 m). It is located within the saddle of the spur at the northern slope of the main ridge (Fig. 2B and C). The area of mineral earth material with traces of animal licks is ~60x20 m with westward exposure.

All kudurs are above the forest edge, which in these areas, is located at heights of 1,800 to 2,000 m, as well as above alpine meadows, that is, practically in the stone deserts zone. In late summer, vegetation in the form of sparse sedges and grasses can be found only around the kudurs A-2 and A-3.

The author AMP first noted the kudurs on the Abakan Ridge in 1986 during fieldwork. Since 2014, the kudurs on the Abakan Ridge were regularly visited by the author and biologist, YNK, a researcher of the Altai Reserve, who studied the ecology of ungulates. A trail camera was deployed at the furthest kudur (A-3). Judging by the information collected at kudurs in the 7 years, maral, a local subspecies of red deer (*Cervus elaphus sibiricus*), and Siberian ibex (*Capra sibirica*) were predominant among the animals visiting all three kudurs. The main peak of animal visits to kudurs occurs between May to July with gradual fading by September.

Materials and methods

Factual material and sampling methods. In September 1986, two samples of kudurits, one sample of clayey mineral earth material without traces of animal consumption, and one sample from a neighboring gabbroid dike were collected at kudur A-1. In addition, several samples of clayey excrements (coprolites) of reindeer were collected. A geological and structural scheme of the kudur was also created at that time (Fig. 3). The results of the analyses of the collected factual material have been previously published (18). In the present study, previously obtained results are also presented to compare these with the new data.

In June 2021, the biologist, YNK visited the kudurits on the Abakan Ridge again and at our request obtained kudurit samples (A-1.1, A-2.1, A-2.2, A-3.1 and A-3.2) from fresh licks at three kudurs. Kudurit samples weighing up to 300 g were collected from the surface to a depth of 10 cm and packed in polyethylene bags. In addition, three samples of vegetation (*Carex*) were collected, including sample T-1, on deluvium within granitoids; T-2, within Proterozoic shales; and T-3, within Paleozoic shales. The sampling sites are marked in Fig. 1B. Leaves of sedges were selected from several plants at a radius of not >10 m and stored in paper bags in ventilated areas.

Analytical methods. Chemical analyses of the main elements in mineral earth material samples collected in 1986 were performed at the Primorgeologiya Production Association (Vladivostok, Russia) on a SRM-20M multichannel X-ray spectrometer. The Ca and S concentrations were determined using the classic 'wet' and silicate analysis methods.

Chemical analyses of mineral earth material and vegetation samples collected in 2021 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. The quantitative X-ray phase analysis of minerals was carried out at the Department of Engineering and Environmental Geology, Faculty of Geology, Lomonosov Moscow State University (Moscow, Russia).

Crushed and milled mineral earth material samples were sent for chemical analysis and X-ray phase analysis of minerals. The analytical methods are described in detail in a previous study by the authors (17).

The quantitative mineral composition was determined using the X-ray diffraction method on an ULTIMA-IV diffractometer (Rigaku Corporation). The operating mode was 40 kV-40 mA, copper radiation, nickel filter, the measuring range was 3-65° 2θ, scanning angle step -0.02° 2θ, and a fixed system of focusing slots. To speed up the analysis and improve the quality of the experimental data, a new generation semiconductor detector (DTex/Ultra) was used, with a scanning speed of 10° 2θ per minute. The mineral composition was analyzed by comparing the experimental and reference spectra from the PDF-2 database in the Jade 6.5 software package from MDI. For the clay fraction, a comparative analysis of oriented samples in the air-dry state and following saturation with ethylene glycol was carried out. Quantitative diagnostic analysis was performed using the PDXL software package from Rigaku Corporation (analyst Dr V.V. Krupskaya,

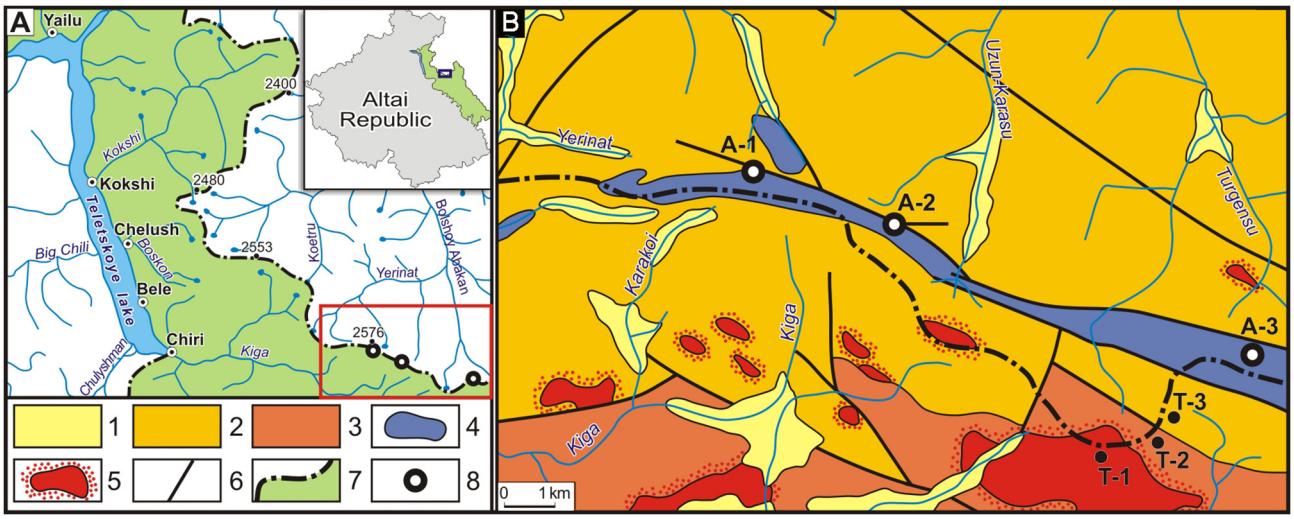

Figure 1. The study area on the (A) Abakan Ridge and within the Altai Republic and (B) the geological map of the study area: 1, Quaternary deposits including modern alluvium and glacial boulder gravel, sand and sandy loam; 2, Early Paleozoic terrigenous deposits (mainly metamorphosed flyschoid strata); 3, -Proterozoic metamorphic rocks (crystalline schists and gneisses); 4, Early Paleozoic ultrabasic magmatic rocks (serpentinite); 5, Silurian granitoids with the contact metamorphism aureoles; 6, tectonic faults; 7, the border of the Reserve along the Abakan Ridge; 8, kudurs A-1, A-2, and A-3; T-1, T-2 and T-3 - vegetation (*Carex*) sampling points.

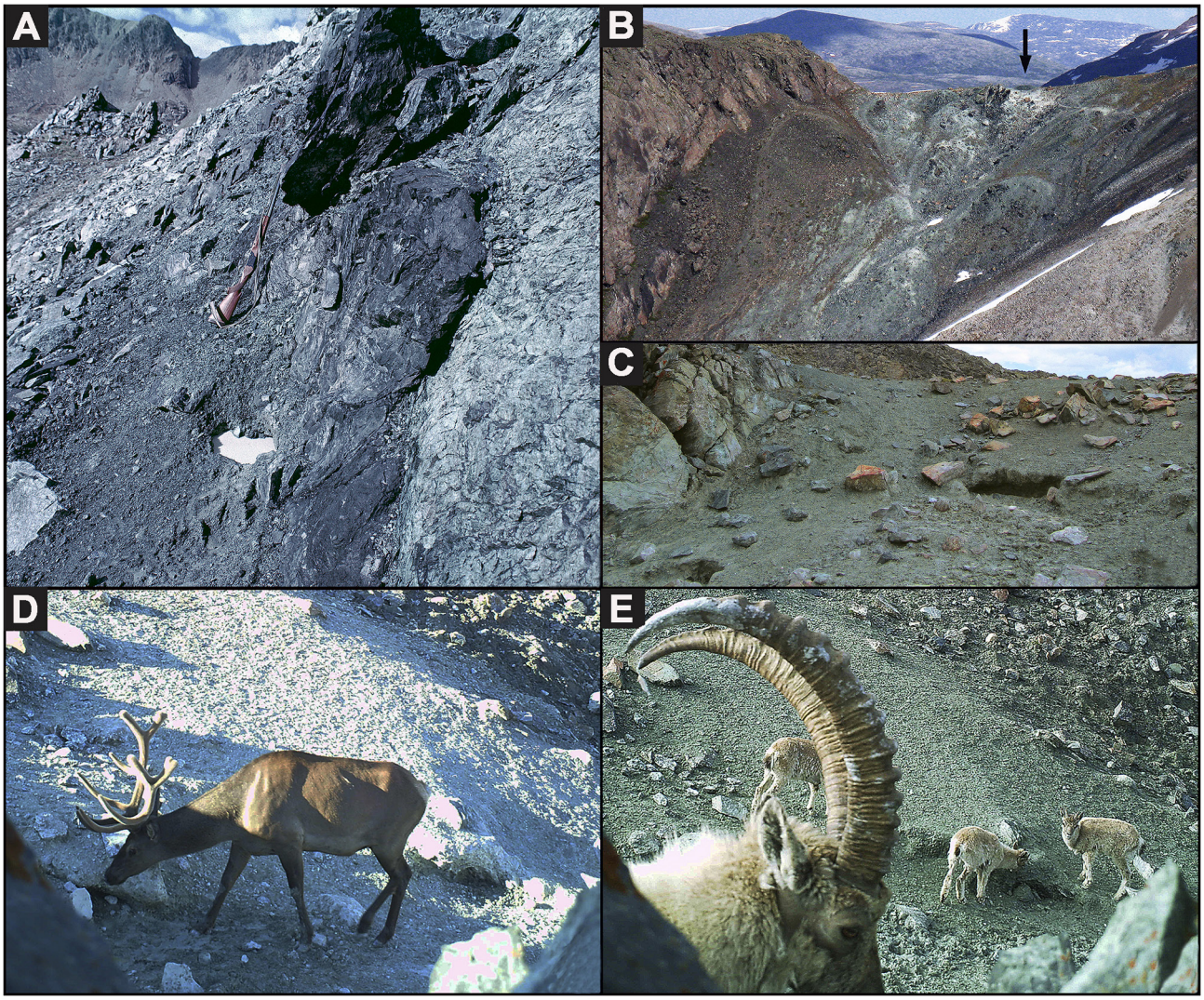

Figure 2. (A) A fragment of kudur A-1 on clayed serpentinites in the head of the Yerinat River with a white rainwater-filled lick; (B) a view of kudur A-3 (arrow) in the head of the Tyurgensu River at the saddle between the main ridge and the northern spur; (C) a close-up fragment of kudur A-3 with licks; (D) red deer *(Cervus elaphus sibiricus*) and Siberian ibex (*Capra sibirica*) (E) at kudur A-3.

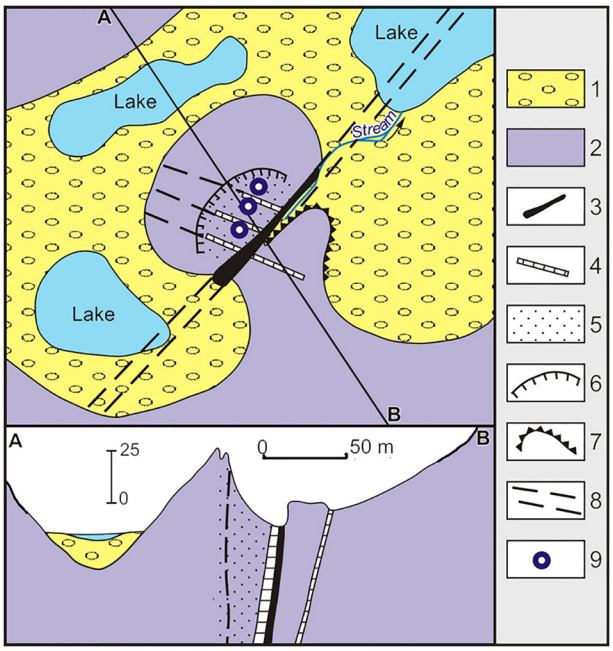

Figure 3. Geological and structural position of kudur A-1: 1, loose deposits within the nival kar (nival hollow); 2, serpentinites; 3, alkaline gabbroids dike; 4, quartz veins; 5, mineral earth material in the area of hydrothermal impact; 6, solifluction pit; 7, rock cliffs; 8, fractures and fracture zones; 9, licks.

Institute of Geology of Ore Deposits of the Russian Academy of Sciences, Moscow). The calculation was performed using BGMN software (www.bgmn.de) according to the Rietveld method. The error in the quantitative identification of minerals depends on a number of factors and varies from 0.5 to 2%. The sizes of mineral particles in the kudurit samples were determined using an Analysette 22 NanoTech plus laser particle analyzer (Fritsch GmbH).

To determine the ability to extract chemical elements from kudurit in an acid medium comparable to the medium in the abomasums of ruminant mammals, one sample (A-1.1) was subjected to acid extraction in the geochemistry laboratory of Pacific Geographical Institute of the Far Eastern Branch of the Russian Academy of Sciences. A kudurit powder sample weighing 5.00 g was treated with 50 ml of HCl solution with a pH of 1.0 (normality 0.1), then the suspension was shaken for 30 min and left for 24 h. The supernatant was separated in a centrifuge for 30 min at 4,500 rpm (3,5 x g) at 22˚C and then sent for the analysis of the studied elements.

To determine the ability of smectite kudurit to sorb rare earth elements (REE) in the environment of the abomasum, a special laboratory experiment was carried out. A hydrogen chloride (HCl) solution with pH 2.00 on tridistilled water was prepared as a model of electrolytes in the abomasum, in which La, Pr and Sm compounds (one of them appeared to have an admixture of Gd) were diluted. $La_2(CO_3)_3$ salt (0.1648 g), PrO_2 (0.1129 g) and SmO (0.1106 g) oxides were dissolved in 3.3 ml of 10% HCl. The solution was then diluted to 1 liter and allowed to stand for 24 h. Subsequently, 1 ml was taken from the prepared solution and diluted with a HCl solution (pH 2) to 1 L. 5 g of dry smectite powder (A-3) were put into flasks and 50 ml of REE salts solution was added. The suspension was left in a shaker for 12 h and then allowed to settle for a further 12 h. The liquid was separated from the mineral powder in a centrifuge (for 30 min at 4,500 rpm (3,5 x g) at 22˚C) and then sent for the inductively coupled plasma mass spectrometry analysis. 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

Geological structure of the objects and the study area. The geological structure of the territory around kudurs on the Abakan Ridge is schematically presented in Fig. 1B (based on the state geological map of the Russian Federation in 1:200,000 scale, sheet N-45-IV, 1959). All kudurs were confined to an extended massif (>15 km long and from the first hundred meters to 1 km wide) of metamorphosed magmatic ultrabasic rocks dated to the Middle Cambrian, transformed into serpentinites. The serpentinite massif is surrounded by metasedimentary and magmatic rocks of the Early Cambrian age. To the south, at a distance of 1 to 5 km from the serpentinite massif, the Cambrian rocks border (often on the tectonic boundaries) with metamorphic Proterozoic rocks (crystalline schists and gneisses) and with numerous intrusions of granitoids of the Silurian age (Fig. 2B).

All kudurs have an obvious connection with fault tectonics. The mineral earth material within all the kudurs shows evidence of hydrothermal genesis through changes of parent rocks in the younger magmatic body intrusion zones. The geological and structural situation with an alkaline gabbroids dike, as well as quartz veins (up to 1 m thick) and cracks that filled the flanking, orthogonal to the gabbroids and fractures, is shown in the scheme of the geological and structural position of kudur A-1, compiled in field conditions by AMP (Fig. 3).

Mineralogy. The diagrams presented in Fig. 4 show the dimensions spectra of mineral particles in kudurits sampled from licks at kudurs A-1 and A-3.

According to the obtained results, the particle sizes in sample A-1.1 range from ~0.1 to 100 μm, with the maximum number of particles having the size of 40 μm. In sample A-3.1, the particle sizes range from 0.1 to 500 μm (with the maximum number of particles having the size of 70 μm). In both samples, the sizes of the majority of particles correspond to siltstones. The fraction of clayey particles (2 μm and smaller) varies from 10 to 20 %.

A summary of the results of quantitative XRD mineralogical analysis, demonstrating that kudurits consist of 70-90% of smectite, smectite-vermiculite, mica-clay minerals and chlorites, is presented in Table I. Only one sample had 25% of clay minerals with a predominance of the serpentinite (antigorite) base and dolomite. Feldspars, zeolites, actinolite, calcite and dolomite were present as impurities. X-ray diffraction patterns on the example of sample A-3.2, including the bulk composition, as well as oriented preparations of the fraction <1 μm in the air-dry state and following saturation with ethylene glycol are illustrated in Fig. 5.

A relatively high content of smectite with a fraction of zeolites in the mineral earth material indicates the hydrothermal nature of the argillization zone, which was formed after the intrusion of the alkaline gabbroid dike.

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

Minerals	A-1.1	A-2.1	A-2.2	A-3.1	A-3.2
Smectite	0.0	21.2	0.0	0.0	41.8
Smectite-vermiculite	38.2	28.1	19.5	34.9	0.0
Illite	3.8	14.7	0.0	16.1	10.0
Phlogopite	1.8	8.9	0.0	11.0	3.1
Kaolinite	0.6	5.1	0.0	1.6	6.7
Chlorite	47.6[a]	9.8[a]	7.1	9.5	19.8[a]
Quartz	0.0	0.0	0.0	0.2	0.0
Plagioclases	0.5	4.0	0.0	3.3	3.4
Potassium feldspar	1.3	4.3	0.0	2.7	3.8
Clinoptilolite	0.0	0.0	0.0	1.0	5.8
Heilandite	0.6	0.0	0.0	5.0	3.3
Amphiboles	5.6	0.0	2.3	14.8	2.4
Calcite	0	3.4	0.0	0	0
Dolomite	0.0	0.5	17.8	0.0	0.0
Antigorite	0.0	0.0	53.3	0.0	0.0

A-1.1, kudurit from the upper Yerinat River; A-2.1 and A-2.2, kudurits from the upper Uzun-Karasu River; A-3.1 and A-3.2, kudurits from the upper Tyurgensu River; [a]interstratified minerals (chlorite-smectite-vermiculite).

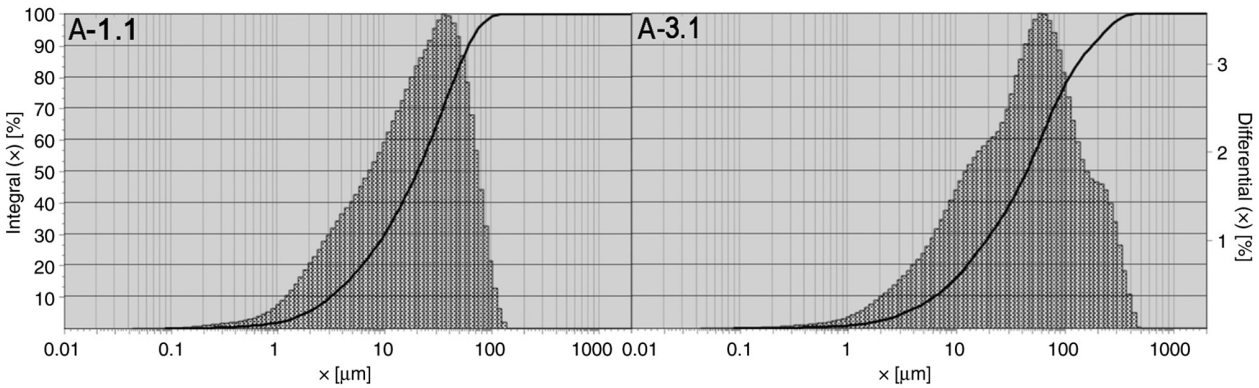

Figure 4. Particle size distribution of kudurits A-1.1 and A-3.1, as determined using a laser particle analyzer.

Geochemistry. The results of the chemical analyses of major elements in the samples collected in 1986 [published in 1988 (18)] at the kudur A-1 and in samples from 2021 at three kudurs are presented in Table II. Although in 1986, the analyses were carried out on an X-ray multi-channel spectrometer SRM-20M and partly using the 'wet' method, the correlation of the results is quite satisfactory. It is necessary to include the results from 1986 as they clearly demonstrated that the mineral earth material from the gabbroid dike differs from the rest of the samples in sharply increased concentrations of Ti, Al, Fe and Na, and a sharply reduced content of Mg and LOI indicators. Due to a relatively high Na content in this earth material and considering the general chemical composition, this material was conditionally termed an alkaline gabbroid. In the 1986 data, the analysis of coprolite compared with the data on kudurits is also quite informative. A more detailed comparison of kudurit and coprolite is presented below in the Discussion section.

The trace element composition of kudurits in 2021 (in 1986, no analytical tools were available to determine trace elements) is presented in Table III. There is a noticeably good association of almost all indicators for all three kudurits. The maximal concentrations in trace elements are for Cr and Ni (thousands ppm), followed by V, Ba, Co, Cu, Sr, Zn, Zr, Sc, Y and Rb (two orders of magnitude less), then As, Pb, Ga, Ce, Nd, Cs, La, Dy, Yb, and Er (from several units to tens ppm). The concentrations of other trace elements do not exceed 1 ppm. All kudurits are characterized by relatively low concentrations of REE, apart from Sc and Y. In general, such concentrations of trace elements are quite typical for ultrabasic rocks.

Acid extracts. The acid extract from the sample A-1.1 (Table IV) demonstrated that the following macroelements were most actively coming out into the HCL acid solution with pH-1.0 (in descending order): Ca, K, Mg, Fe, Na, Al, P and Ti. In the trace elements (Table V), the most mobile (in

Table II. Gross concentrations of the main rock-forming oxides in kudurits from the Abakan Ridge (wt %).

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Σ
1-86	44.63	1.74	10.52	20.34[a]	-	0.30	7.55	9.07	4.93	0.05	0.05	0.82	100.00
2-86	42.80	0.22	3.79	7.41[a]	-	0.14	31.56	1.36	0.74	0.07	0.06	11.85	100.00
3-86	37.67	0.30	6.01	7.69[a]	-	0.11	22.81	6.21	1.13	0.13	0.03	18.00	100.00
4-86	42.54	0.52	5.72	9.18[a]	-	0.17	27.04	3.57	1.43	0.27	0.07	9.56	100.00
C1-86	39.17	0.27	5.05	7.34[a]	-	0.10	23.81	6.61	0.81	0.48	0.24	16.12	100.00
A-1.1	40.54	0.24	6.29	3.09	3.97	0.10	29.13	4.28	1.01	0.68	0.05	9.92	99.73
A-2.1	41.70	0.15	3.92	2.92	3.9	0.10	30.39	3.43	1.22	0.41	0.00	10.80	99.82
A-3.1	41.80	0.63	7.19	6.36	3.84	0.13	23.87	4.67	0.97	0.33	0.05	8.49	99.61

x-86, samples obtaomed in 1986 at the kudur A-1: 1-86, alkaline gabbroid dike; 2-86, clay without traces of animal consumption; 3-86, from lick-1; 4-86, from lick-2; C1-86, deer coprolites; X[a], the sum of ferric and ferrous iron; A-1.1 to A-3.1, kudurit samples from 2021: A-1.1, from the kudur in the upper Yerinat River; A-2.1, in the upper Uzun-Karasu River; A-3.1 , in the upper Tyurgensu River.

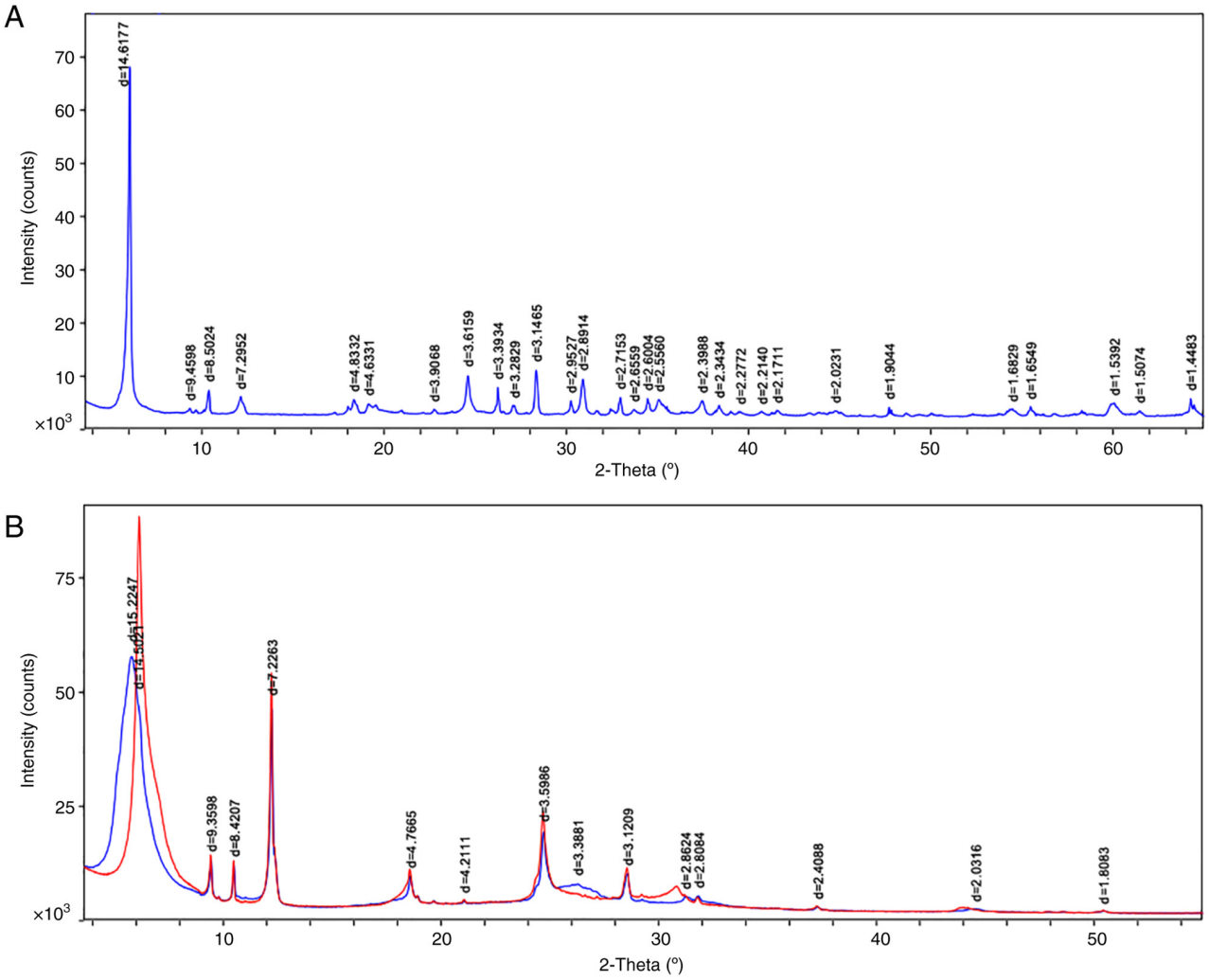

Figure 5. (A) X-ray diffraction patterns of bulk sample A-3.2 and oriented preparations from sample A-3.2 of fraction <1 μm, where blue color illustrates the result for the air-dry preparation, and (B) red color those for the preparation saturated with ethylene glycol.

descending order) were Ba, Sr, Ni, Cu, Cr, Co, V, Zn and Li. The yield of REE elements in the extract produced a result two orders of magnitude lower than the bulk values, with a slightly higher extraction of elements of the middle subgroup (Fig. 6).

Biogeochemistry. The REE concentration profiles in the samples of sedges are demonstrated in Fig. 7. Plants on granites accumulate at least 10-fold more elements of this group than those growing within the lower Paleozoic shales. This specific

Table III. Concentrations of trace elements in kudurits from the Abakan Ridge (ppm).

El	A-1.1	A-2.1	A-3.1	El	A-1.1	A-2.1	A-3.1	El	A-1.1	A-2.1	A-3.1
Be	0.22	0.12	0.18	Nb	0.71	0.32	0.96	Dy	1.98	0.81	2.34
Sc	16.2	15.4	25.8	Mo	0.25	0.33	0.35	Ho	0.42	0.20	0.50
V	90.75	60.65	163.2	Cd	0.48	0.00	0.00	Er	1.26	0.62	1.46
Cr	1931	2038	1267	Sn	0.21	0.52	0.17	Tm	0.18	0.13	0.21
Co	73.92	67.77	55.92	Cs	1.75	1.33	3.54	Yb	1.17	0.54	1.46
Ni	1335	1300	742	Ba	79.0	51.0	269	Lu	0.19	0.18	0.24
Cu	40.95	17.46	21.62	La	1.51	1.20	2.04	Hf	0.76	1.04	1.63
Zn	52.9	45.2	62.1	Ce	3.00	1.88	4.97	Ta	0.15	0.04	0.18
Ga	4.92	3.86	4.77	Pr	0.51	0.26	0.73	W	0.27	0.12	0.37
As	5.11	13.09	1.10	Nd	2.41	1.38	4.84	Pb	5.00	7.96	4.79
Rb	16.43	8.65	10.58	Sm	0.74	0.38	1.52	Th	0.23	0.13	0.14
Sr	58.0	36.0	67.0	Eu	0.22	0.22	0.50	U	0.12	0.05	0.15
Y	13.19	4.24	12.15	Gd	0.97	0.81	1.99				
Zr	17.3	27.8	43.6	Tb	0.21	0.09	0.35				

Please see Table II for the explanation of the samples. El, element.

Table IV. The yield of macroelements in the acid (HCl pH 1) extract (ppm).

Sample	Al	Ti	Fe	Mn	Mg	Ca	K	Na	P
A-1.1	3.47	0.002	11.09	0.51	17.06	78.32	54.98	4.15	1.05

Table V. The yield of trace elements in the acid (HCl pH 1) extract (ppb).

Element	A-1.1	Element	A-1.1	Element	A-1.1
Li	0.572	Zr	0.002	Tb	0.015
Be	0.001	Nb	0.0001	Dy	0.104
Sc	0.154	Mo	0.044	Ho	0.024
V	1.094	Cd	0.018	Er	0.0639
Cr	4.544	Sn	0.001	Tm	0.0076
Co	2.820	Sb	0.002	Yb	0.0374
Ni	48.331	Cs	0.297	Lu	0.0045
Cu	24.887	Ba	63.700	Hf	0.0004
Zn	0.993	La	0.043	Ta	0.0001
Ga	0.006	Ce	0.130	W	0.0003
Ge	0.002	Pr	0.019	Tl	0.072
As	0.925	Nd	0.095	Pb	0.222
Rb	14.359	Sm	0.031	Th	0.0001
Sr	46.300	Eu	0.015	U	0.006
Y	0.630	Gd	0.065		

Please see Table II for the explanation of the samples.

feature of REE distribution in food plants eaten by ungulates will prove useful below when discussing the results of the study.

Experiment. The result of the experiment to determine the ability of smectite to sorb REE is presented in Table VI, from which it is clear that in a medium with pH close to that of the ruminant rennet, dissolved REE in concentrations from single units to tens ppb will be sorbed with efficiency from 92 to 97%.

Discussion

Following a number of analyses, it was found that kudurits on magmatic ultrabasic rocks were formed in areas of a specific impact of hot alkaline solutions on the parent rock during the intrusion of gabbroid dikes. As a result, the zones of hydrothermal argillization with the formation of high-iron smectite, vermiculite and mixed smectite-vermiculite-chlorite mineral mixtures, sometimes with zeolites, were formed around the dikes. The absorbing complex of such mineral mixtures includes a significant proportion of sodium. Surface outcrops of such sodium-containing mineral earth materials located in the habitat of ungulates can be found and regularly consumed by them. In these cases, typical kudurs are formed, which can be maintained by animals for an indefinite period of time (sometimes millennia).

The smectite-vermiculite-chlorite mineral composition of kudurits on ultrabasic rocks is fundamentally different from the composition of kudurits most common in the South Siberian mountains, where the main mineral components are finely-dispersed quartz-plagioclase-illite-chlorite mineral mixtures with minor additions of calcium carbonates and clay

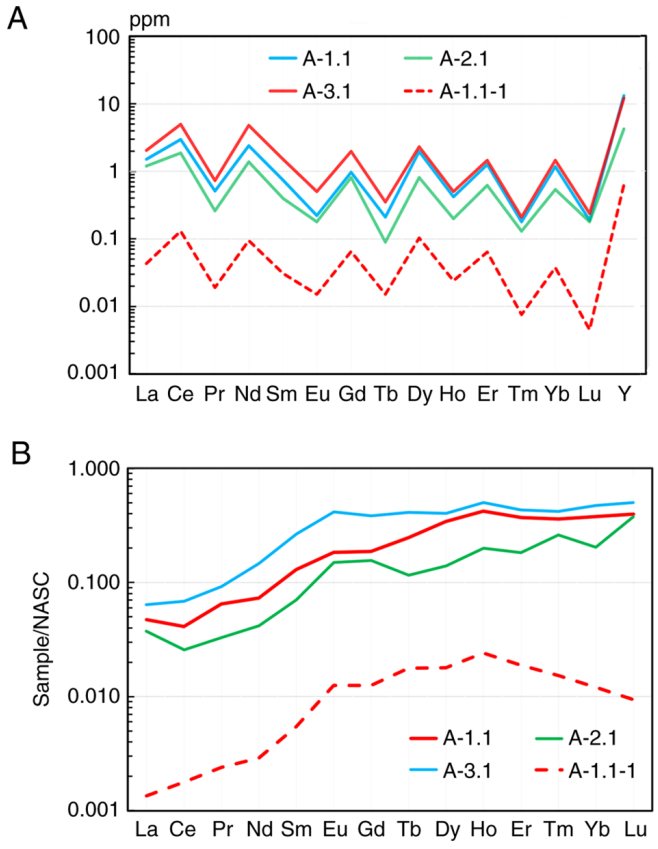

Figure 6. (A) Bulk rare earth element concentration in kudurits and acid (HCl, pH 1.0) extract from the sample A-1.1; (B) the same in the NASC-normalized form (19). NASC, North American shale composite.

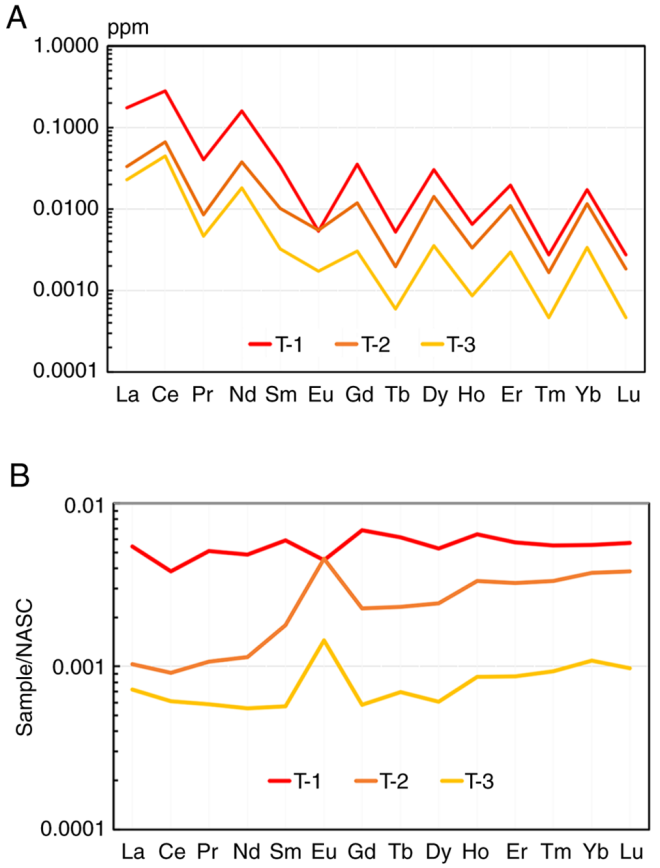

Figure 7. (A) Rare earth element concentration profiles in sedges (*Carex*) collected on the deluvium of Silurian granitoids (sample T-1), Proterozoic shales (sample T-2) and Lower Paleozoic shales (sample T-3); (B) the same in the NASC-normalized form. NASC, North American shale composite.

minerals, usually with the predominance of kaolinite (16). By the high smectite content, the kudurits on ultrabasic rocks are more similar to kudurits of young volcanic areas, particularly common in the Sikhote-Alin, which have been studied quite thoroughly (17).

As regards sodium, the authors aimed to determine whether Na is exactly the element that the animals are searching for in the studied kudurits. A comparison of the main rock-forming oxides in kudurit 3-86 and coprolite C1-86 (please see Table II) from kudur A-1 [the data of the analyses from 1986; after the proportional distribution of losses during ignition is presented in Table VII. As shown in Table VII, the results revealed that the elements that are excreted from the kudurites and remain inside the bodies of animals are Al, Na, Fe and Ti, in descending order. Assuming that the Na_2O yield of ~5 g per 1 kg of kudurit (amounting to 3,7 g/kg of pure Na) more or less corresponds to the reality, it follows that animals eating similar kudurits may receive 20 g of pure Na (corresponding to a tablespoon of NaCl) if they consume 5 to 6 kg kudurit. Considering that animals eat ~0.5 kg of kudurit at a time on average, they would receive a spoonful of salt in 10-15 visits to a kudur. Considering that an average-sized deer can consume up to 5 kg of soil at a time (12), replenishing the Na-deficiency in the body with this type of kudurit appears to be feasible.

Furthermore, it is noteworthy to remember that animals can solve the Na deficiency in feed by reducing losses of the element in the body. The loss of sodium is typical, for example, in diarrheal diseases widespread among herbivores during seasonal changes in the diet (20,21). In medicine and veterinary medicine, mineral sorbents, including those based on clay, have been widely used in recent years to combat diarrhea.

Thus, the conducted studies of the possible effects of kudurits on the body from a formal point of view at least do not contradict the 'sodium' hypothesis of geophagy. However, it is possible that this is a complete answer to the question about the reason for the consumption of the studied earthy substances.

The sodium hypothesis of geophagy, which assumes the replenishment of Na-deficiency, as well as the desire to combat the loss of the element through diarrhea, can certainly be the reason for the consumption of clay kudurits. For the temperate zone, this hypothesis has been addressed in a number of studies, for example (12,20-23) and for the tropical conditions during the change of diet at the transition between drought and the rainy season, this has been addressed in the studeis by Kreulen (20) and Moe (10). However, it is hardly possible to recognize this hypothesis as a comprehensive one, the one that can unite the majority of geophagy cases worldwide. 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 (8,9,24). The research data presented herein also do not show the only possible connection between the desire

Table VI. The ability of smectite to sorb rare earth elements from an acid solution (HCl, pH 2.00).

Elements	La	Pr	Sm	Gd
The initial concentration in 0.1 N HCl solution (ppb)	14.17	16.33	13.87	1.40
Following the addition of 10 g of Abakan kudurit in 50 ml of initial solution	0.86	0.57	0.54	0.11
Difference from the initial concentration (%)	-13.37 (94%)	-15.76 (97%)	-13.33 (96%)	-1.29 (92%)

Table VII. Comparison of the main rock-forming oxides in the kudurit and coprolite from kudur A-1 (according to analyses from 1986), wt %.

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_3
3-86	45.82	0.36	7.33	9.38	0.13	27.83	7.57	1.38	0.16	0.03
C1-86	46.14	0.32	6.02	8.99	0.13	28.44	7.88	0.97	0.57	0.29
Diff.	+0.32	-0.04	-1.33	-0.39	0	+0.61	+0.31	-0.41	+0.41	+0.26

Losses on ignition (LOI) are proportionally distributed. 3-86, earthy substance from the kudur; C1-86, maral coprolites; Diff, the difference of content in the kudurit and coprolite; '-', a decrease after the mineral earth material was in the digestive tract; '+' - an increase after the mineral earth material was in the digestive tract.

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 (25).

It may noted here that other hypotheses about the causes of geophagy have been proposed along with the 'sodium' one. These include 'replacing iron deficiency in the body'; replenishing symbiotic and suppressing pathogenic forms of microorganisms; cleansing from parasites; regulating acidity in the digestive tract (26-29). It has also been suggested that the consumption of minerals at kudurs can compensate their losses during lactation and antler growth (10,30,31). There is a hypothesis regarding the 'removal of toxic organic compounds from the body' (20,32-36). In relation to humans, it has been suggested that clays can help in case of gastrointestinal and other diseases (24,37).

Judging by the results presented in Table VII, it appears feasible to focus on the 'replenishment of iron deficiency in the body' from the aforementioned hypotheses. This hypothesis was expressed, in particular, by Mahaney (3,38,39) when studying geophagy in African buffaloes inhabiting Kenya in the altitude belt of ~3,000 m. He justified his hypothesis by the fact that the concentration of oxygen in the atmosphere decreases with altitude, which should increase the need for iron hemoglobin in the body of mammals. Citing Robbins (40), he pointed out that consumed clay minerals can be both a source of iron and a factor contributing to anemia, depending on the prevalence of either the iron forms available to the body, or the iron binding (chelating) ability.

The accumulated experience of chemical investigations of coprolites and their corresponding kudurits, which is presented in detail in the monograph (12), testifies that the behavior of iron during the passage of kudurits of any mineral variety through the digestive tract is rather unstable. At the same time, it appears that the possibility of iron regulation by geophagy in the body is not entirely impossible. However, it can be considered only as not the main (rather, side) effect of the biological action of kudurits.

Over the past 10 years, the authors have been developing their hypothesis of the cause of geophagy. This may be a universal one, uniting most cases of regular geophagy in both animals and humans. After reviewing the materials on the geochemistry of the eaten rocks in different regions of the world, taking into account the data on the effect of REE on the immune and hormonal spheres in the body, which is well shown in the literature review by Redling (41), it was first assumed that there may be only two main reasons for the desire for geophagy (42,43). The first one is caused by the electrolyte imbalance in the body and the other, and the other by the disturbance of REE metabolism in the neuroimmunoendocrine system. The authors proceeded on the assumption that some elements from the light REE group associated with internal secretion gland enzymes and nerve tissues can be replaced by heavy analogues, which are not able to perform the necessary functions. This hypothesis was tested in the Sikhote-Alin on two objects (17). It was found that in the areas known for geophagy, acid volcanogenic and volcano-sedimentary rocks enriched with REE were predominant. During their weathering, secondary easily soluble water phosphates and fluorocarbonates of REE are formed. This results in the concentration of REE in natural water, soil, vegetation and herbivorous animals. In fact, the landscape REE-abnormalities are developed. As a result of the study by Redling (41), a conclusion was reached, that an excess of REE in the neuroimmunoendocrine system of the body, which is the main carrier of this group of elements, can cause hormonal disturbances and a stress reaction in animals. In this situation, animals are forced to search for mineral sorbents that can eliminate the REE imbalance in the body.

Finally, after studying the work of Powis *et al* (44), pointing to the connection between Na, Ca and REE in the body, it was

considered that the 'sodium' and 'REE' hypotheses could be combined and named, for example, the 'rare-earth-sodium' hypothesis. Powis *et al* (44) in experiments on cell cultures found that La^{3+} could independently transport itself into chromaffin cells of bovine adrenal glands by exchange through sodium-calcium channels and trigger the release of the catecholamine hormones. In other words, it turns out that some elements from the REE group (in this case, the experiment was with La) together with Na and Ca operate as triggers of hormone release from the adrenal glands.

It should be noted here that this is only a part of REE functions in the regulation of the body's hormonal sphere. 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 several references to studies in the review by Redling (41). From this it may follow that regular geophagy (not including the occasional consumption of minerals, as well as cases of artificial salt deposition) is always an urge of the body, in the first place, to normalize its more or less disturbed hormonal sphere, which is responsible for the metabolism (particularly for mineral exchange), primarily by balancing the ratio and concentration of REE in the body, as the major components of the neuroimmunoendocrine system, and also by consuming Na and Li as the most crucial elements that can reduce the hormonal stress.

There are no reliable (scientifically proven) cases of such neuroimmunoendocrine disorders in animals yet. However, they are known in humans. In humans, the extreme cases of REE imbalance in the hormonal sphere are various endemic diseases of geochemical etiology. For instance, a number of studies focusing on geophagy in humans have reported that the urge for geophagy develops against a background of specific pathologies accompanied by signs of mineral metabolism abnormalities (45-48). Endomyocardial Leffler fibrosis (EFL) appears to be among the most severe pathologies of this type, having a direct connection with the excess of REE in the plant-based diets of individuals in India (49) and Africa (50). Within the considered aspect, the connection of human consumption of earthy substances with the disease described in South America as cacchexia afrikana (51) also does not seem coincidental.

Finally, the subject of the chemical composition of forage vegetation was approached (more precisely, the subject of REE concentrations in it) in the areas from which red deer most often come to kudur A-3. The detected increased concentrations of REE (although very conventionally in individual samples) in forage vegetation growing within granite massifs where animals may spend a part of their life, may well be the cause of disturbances in the ratio and concentration of REE in the neuroimmunoendocrine system of the animals' bodies. Feeling anxiety and the need for motion activity in a state of hormonal stress, animals may seek out and consume mineral sorbents capable of eliminating excess REE in the body and simultaneously providing Na and Li, which can relieve the hormonal stress-response state. It is possible that in this case, Li and Na function like a well-known lithium chloride medication that is prescribed to individuals in a state of nervous overexcitement (to the point of having schizophrenic episodes).

It is considered believe that our 'rare-earth-sodium hypothesis' on the causes of geophagy requires substantial testing involving additional objects and research methods.

In conclusion, the present study examined the mineral and chemical composition of clayey kudurits formed on ultrabasic rocks consumed by wild ungulates near the water-divide of the Abakan Ridge in the border part of the Altai State Nature Biosphere Reserve (Altai Republic, Russia). It was found that the kudurits are represented by the smectite-vermiculite mineral associations with chlorite-the products of hydrothermal transformation of magmatic ultrabasic rocks (serpentinites) at the stage of alkaline gabbroid dikes intrusion. Acid extracts (HCl, pH 1.0) from kudurits most actively extract Ca, K, Mg, Fe, and Na. The most extractable trace elements are Ba, Sr, Ni, Cu, Cr, Co, V, Zn and Li. The comparison of the chemical composition of a kudurit and coprolite of red deer indicates that from the composition of macroelements in kudurit only Na is reliably assimilated in the body, while K, P, Mg, and Ca are simultaneously sorbed and removed. Chemical analyses of vegetation in areas from which animals most often come to kudurs revealed high concentrations of REE. Through chemical analyses, it was demonstrated that smectite-vermiculite kudurits actively sorb REE in the animal digestive tract. A 'rare-earth-sodium' hypothesis was proposed as the cause of geophagy, which, may explain the majority of cases of regular consumption of earthy substances by animals and humans. The reason for kudurit consumption by animals on the Abakan Ridge may be connected, on the one hand, with the desire of animals to remove from the body the excess of REE taken with food and, on the other hand, to add sodium and possibly lithium, which can relieve the nervous overexcitement associated with the REE exchange disorders in the neuroimmunoendocrine system of the body.

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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, IYC, YNK, 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, IYC and YNK. AMP and KSG confirm the authenticity of all the raw data. The first draft of the manuscript was written by AMP and all authors commented on previous versions of the manuscript. All authors have read and approved the final manuscript.

Ethics approval and consent to participate

Not applicable.

Patient consent for publication

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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