

## Article

# The Main Cause of Geophagy According to Extensive Studies on Olkhon Island, Lake Baikal

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**Abstract:** From the novel results of comprehensive geological–hydrobiogeochemical studies conducted on Olkhon Island (Lake Baikal), it follows that the phenomenon of geophagy among wild and domestic ungulates on the island is caused by the deficiency of light subgroup rare earth elements (LREE) in plant food and natural waters, while not denying the possible role of other factors. This deficiency reflects the low LREE specificity of the most abundant metamorphic terrigenous carbonate rocks on the island, as well as their overlying eluvium–deluvium and soils. The resulting specificity of the landscapes may be the cause of the LREE imbalance in the nervous and hormonal systems of the body, which makes the animals regularly and periodically consume clay (kaolinite) products from weathering, enriched with the necessary nutritional elements. The identified cause of geophagy on Olkhon Island is likely to extend to a significant part of geophagy cases among animals, including humans, especially in the equatorial zone of the Earth.

**Keywords:** geophagy; ungulates; kudurs; geology; soils; surface waters; geochemistry; rare earth elements; Olkhon Island



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## 1. Introduction

The consumption of mineral soil by wild and domestic animals is common in some regions of the world. This phenomenon is referred to in the scientific literature as “geophagy”. The regular consumption of earthy substances in the same places results in the formation of specific, easily recognizable landscape complexes referred to as “salt licks” or “mineral licks”. Since these objects are not always directly related to soluble salts and licking, another term, “kudur”, borrowed from the vocabulary of Turkic shepherds, seems more appropriate [1]. The term “kudurit”, derived from kudur, refers to the mineral soil consumed by animals at kudurs. The term “lick” (“lizunets” in Russian) is used to refer to the distinct pits within kudurs as specific landscape units (complexes) formed by the active participation of herbivorous mammals.

The history of the study of geophagy spans about a hundred years, and many researchers from different disciplines have tried to find the reason why animals regularly consume earthy substances. So far, there is no generally accepted explanation for this cause. Only a number of hypotheses have been proposed, with varying degrees of justification. The most common ones will be mentioned below. Among them are the need for

sodium during periods of its lowest intake [2], the need for sodium and mineral sorbents to normalize the electrolyte balance in the digestive tract during seasonal changes in feed rations [3–5], the replenishment of some chemical elements in the organism [6–8]; the use of the bacteriostatic properties of clay minerals in the control of pathogenic microflora and intestinal parasites; the replenishment of symbiotic microorganisms or the regulation of pH in the digestive tract [9–13]; and the removal of toxic chemical elements and compounds, including organic compounds such as phenols, terpenes, tannins, alkaloids, and cyanogenic glycosides [14–18]. It has even been suggested that geophagy is not related to a physiological need, but to a sense of gustatory pleasure [6,19].

In 2015, following the analysis of published data on the geochemistry of soils eaten by animals in different regions of the world, as well as new evidence on the effects of rare earth elements (REE) in the body on the immune and hormonal spheres, most fully presented in a review by K. Redling [20], Panichev [21,22] developed the idea that one of the main causes of geophagy may be due to disturbances in the exchange of REEs in the body.

This hypothesis was partially confirmed by the studies of the authors of this article in geologically different areas of the Sikhote-Alin [23] and in the Altai Mountains [24] in 2020 and 2021. It was found that rocks and soils containing hypogenic REE minerals, which are converted to easily soluble mineral forms (REE water phosphates, carbonates, and fluorocarbonates) during weathering are common in areas where mass geophagy of wild and domestic ungulates occurs. This leads to the accumulation of REEs in all major landscape components (natural waters, soils, vegetation). This is also true for the tissues of herbivorous animals, including those of the nervous and endocrine systems. An excess of some elements of the REE group in the neuroimmunoendocrine system of the body, which is the carrier of LREEs, causes a stress response in animals, making them seek mineral sorbents capable of eliminating the REE imbalance in the body.

In 2022, to test the REE hypothesis, the authors of this article conducted the same type of system studies in the Lake Baikal region. The interest in the Baikal rift zone is not accidental. The authors have long been aware of the existence of local areas with mass manifestations of geophagy among herbivores in the regions of the East African rift belt, where volcanic rocks enriched with REEs are developed. Many researchers have drawn attention to the issue of geophagy in this part of the world [25–29].

As our studies in the area of Lake Baikal have shown, mass cases of geophagy among animals visiting dry kudurs (lithomorphic type) are observed only on the western coast, as well as on Olkhon Island. On the east coast, according to surveys of the local population, mass cases of geophagy are unknown. However, in relative proximity to the lake, especially in the valleys of the Barguzin and Turka rivers, there are occasional hydromorphic kudurs based on water sources.

This article presents the original results of the research on Olkhon Island. Among the tasks solved were the following: to assess the role of geological factors in the occurrence of the studied phenomenon according to our own observations and state geological survey materials; to conduct field sampling of various components of the natural system (natural waters; rocks, including kudurites; coprolites; soils and vegetation; and tissues of wild deer); and to perform versatile laboratory research of the collected material. Finally, on the basis of the data obtained, we aimed to draw a conclusion about the cause of ungulate geophagy in the territory of the island. If this idea of the REE hypothesis is confirmed, it would justify the idea of the main cause of geophagy, which can unite, if not all, then at least a significant part of the manifestations of this phenomenon all over the world.

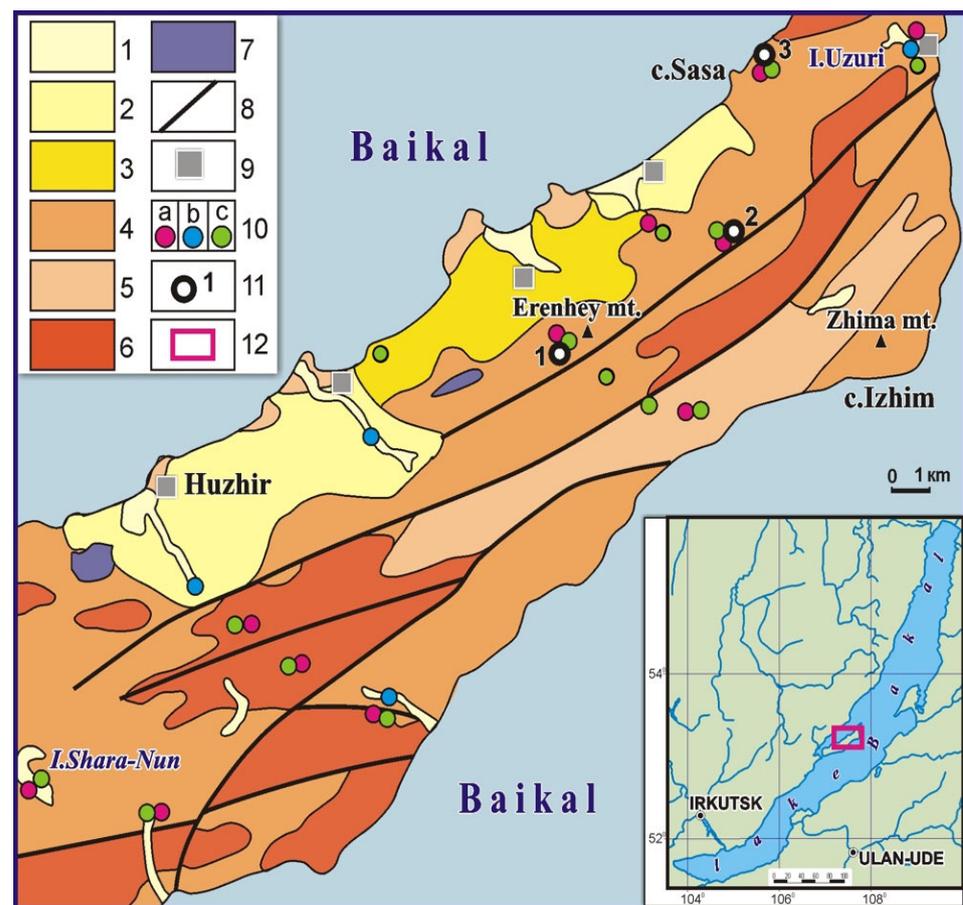
## 2. Brief Description of the Study Areas and Research Objects

Olkhon is the largest island in Lake Baikal and one of the three largest islands in the world. It is 71.5 km long and 20.8 km wide at its widest point. The southeastern part of the island is mountainous and covered with pine (*Pinus sylvestris*), larch (*Larix sibirica*), and spruce (*Picea obovata*) forests. Here is the highest point of the island—Mount Zhima (absolute altitude 1276 m; 818 m above the level of Lake Baikal). The shores of this part

of the island are rocky and steep. The western and northwestern parts of the island are dominated by steppes with sparse pine forests. The relief is low and peneplain, and the shores are mostly steep, but not high.

The minimum air temperature on the island reaches  $-50\text{ }^{\circ}\text{C}$ , the maximum—up to  $+40\text{ }^{\circ}\text{C}$ . The frost-free period lasts about 4.5 months. Most of the territory of the island is characterized by insufficient humidity, and the annual rainfall does not exceed 300 mm. Most of it falls during the summer months. Winters on the island are very dry.

There are few rivers and streams on the island due to the high dryness of the climate. In the summer, many streams and small drainless lakes, including the only saline lake, Shara-Nur (Figure 1), usually dry up.



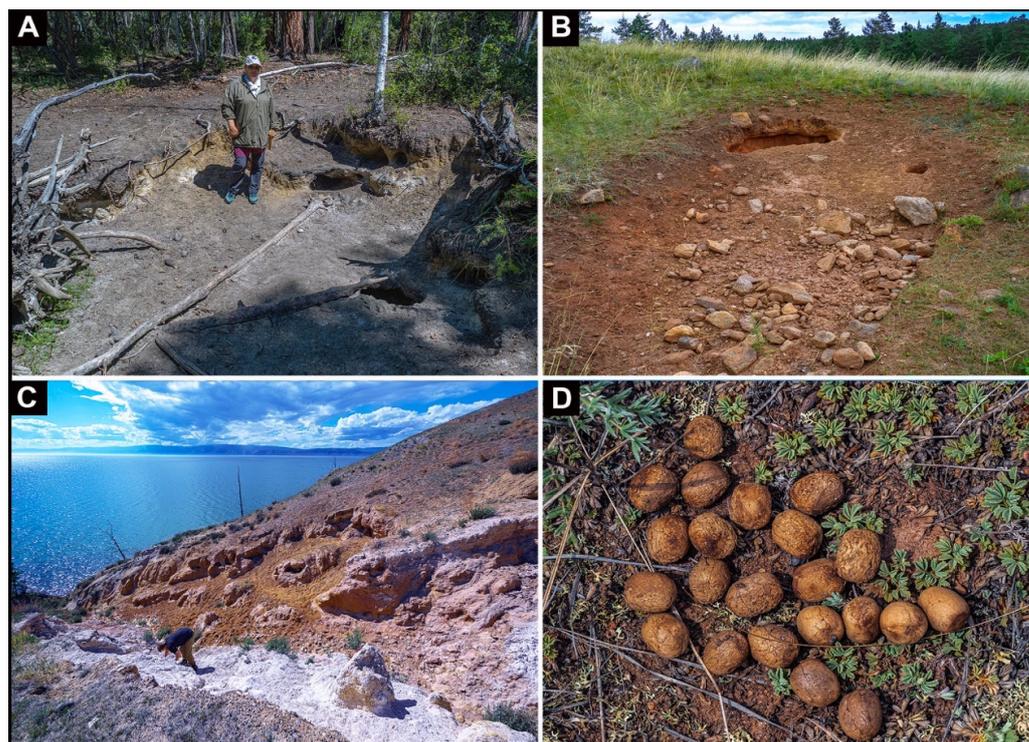
**Figure 1.** Geological structure of the study area on Olkhon Island according to the geological map of the Russian Federation (2006) at the scale of 1:1,000,000 with additions by the authors: (1)—modern river alluvium (pebbles, sandy loam, and clay); (2)—Quaternary (Upper Pleistocene-Holocene) lake shore deposits, alluvial and glacial deposits (mostly sand and clay); (3)—Neogene deposits of the Khalagai Formation (alternation of sand, loam, and clay, lignite interlayers); 4, 5—Proterozoic metamorphic rocks, including (4) Chernorudskaya Formation (mainly amphibolite with marble and gneiss interlayers) and (5) Izhimei Formation (crystalline limestone with graphite, micaceous quartzite, gneiss, and amphibolite interlayers); (6)—Proterozoic granitoid of the Olkhon migmatite-granite complex; (7)—Proterozoic peridotite, hornblendite, and gabbro-dolerite of the Erenheic complex; (8)—Tectonic disturbances; (9)—Settlement areas; (10)—Rock (a), water (b), soil and vegetation (c) sampling sites; (11)—Kudurs; (12)—Outline of the working area in the inset.

The most widespread parent rock on the island (about 75%) is strongly metamorphosed metasedimentary rock of Proterozoic age, represented by interbedded crystalline schists, amphibolites, gneisses, and marbles, including metabasite and ultrametabasite bodies. About 15% of the territory of the island is occupied by single-age migmatites of the granitoid

series. About 10% of the territory is covered by loose sedimentary deposits of Neogene and Quaternary age. Neogene sediments are concentrated mainly on the northwestern coast in the central part of the island and are represented mainly by sands, loams, and clays (Figure 1). Quaternary (Upper Pleistocene–Holocene) deposits form low Baikal terraces up to 10–12 m high, as well as glacial, alluvial, eluvial–deluvial–proluvial, and colluvial formations. Modern river alluvium is fragmentarily developed in the valleys of a few rivers and streams (Figure 1).

Ancient (Cretaceous–Paleogene) weathering crusts occur in several places on the island, especially in its northwestern part on many capes, including Cape Sasa, as well as on the slopes of Mount Erenhei. Their formation is related to the selective weathering of rocks along the most exposed strata and tectonic fault zones. The strongest linear weathering crusts on the western shore of Lake Baikal, formed along tectonic faults, reach depths of 100–150 m [30].

There are relatively few kudurs on Olkhon compared to, for example, the coastal area in the southeastern part of Teletskoye Lake in the Altai Mountains. All of them are exclusively dry. Most of them are insignificant in terms of area and the amount of soil eaten by animals. Outwardly, kudurs look like rare localities on leveled surfaces and flat mountain tops, sometimes on the site of former lakes, with depressions gnawed and licked out by animals in subsoil clay horizons or in the weathering crust of rocks. One such small but well-defined kudur (No. 2, Figure 1) appeared in a small lake basin on the top of the mountain. Its general view is shown in the photograph (Figure 2A).



**Figure 2.** (A)—One of the small-sized kudurs (No. 2) in the lake basin on the summit of an unnamed mountain. (B)—One of the sites of kudur No. 1 in the near-summit part of Mt. Erenhei. (C)—A fragment of kudur No. 3 near Cape Sasa. (D)—A pile of clayey excrement (coprolites) of a deer at the same site.

One of the two largest kudurs on the island (No. 1, Figure 1) is located in the near summit part of Mount Erenhei. It combines two sites about 100 m apart. The size of both is about one hundred square meters. One of them has several well-eaten licks; the other has only one large lick (Figure 2B). The animals eat stiff clay of yellow and red color. Not far from the kudur (50 m to the north) is an outcrop of flesh-colored migmatites (sample G-5).

The kudur areas are scattered with unrounded fragments of similar rocks and slightly rounded amphibolite schists and quartzites.

The other largest kudur in terms of area and amount of soil eaten (No. 3, Figure 1) is located in the lakeshore area, one kilometer northeast of Cape Sasa. It is an east–west striking ravine about 100 m long that descends to the lake (Figure 2C). In its upper part, a bed of strongly weathered carbonate rocks of white, sometimes white-pink hues, is exposed. In the lower part of the ravine, strongly clayed rocks appear, sometimes with remnants of primary foliation characteristic of crystalline schists. Among the rocks eroded by weathering, there are variations with large (up to 1 cm and more) flattened crystals of light mica (muscovite). Animals eat mainly clay and clay–carbonate varieties. The clays eaten are yellow and reddish to intense red. The preference for clays over carbonates is evidenced by the fact that most of the licks are formed in clays and by the fact that none of the dozen coprolite piles (Figure 2D) found nearby had a significantly elevated carbonate content.

About one hundred meters southeast of kudur No. 3, there are several small outcrops of amphibolite schist. The fact that bedrock outcrops are relatively close to kudurs No. 2 and 3 indicates that the clay rocks that attract animals are limited to linear weathering crusts that mark tectonic disturbances.

Red deer (*Cervus elaphus xanthopygus*) dominate among the animals that visit Olkhon's kudurs; Siberian roe deer (*Capreolus pygargus*) and hare (*Lepus timidus*) also come to the kudurs. According to the expert estimates of biologists T.V. Desyatova and V.N. Mitin (researchers of Pribaikalsky National Park), the number of deer on the island is about 100–150 individuals. According to their observations, the main peak of kudur visits is from April to July. Some increase in activity also occurs in the fall, in September–November. The kudurs in the Cape Sasa area are also visited by domestic animals, such as cattle and sheep. It should be noted that about two-thirds of all deer encounters on Olkhon, both in winter and in summer, were recorded by biologists in the area of the Shara-Nur salt lake (see Figure 1). Another interesting observation made by the same biologists: on the island, among the antlers dropped by deer, there are often found not completely hardened antlers, partially or completely covered with a thick layer of skin, which is not at all typical for the red deer species. Similar facts have been noted on the western shore of Lake Baikal in the area from the mouth of the Goloustnaya River to Srednye Khomuty, where mass cases of geophagy among hoofed animals have also been reported. These observations will be discussed in more detail in Section 5.

### 3. Materials, Sampling, and Analysis

#### 3.1. Factual Material and Sampling Methods

Fieldwork on Olkhon Island was conducted from 4 to 7 July 2022, using a car. Sampling sites were added to a 1:100,000 scale topographic base and 1:200,000 scale geological maps of the area using GPS receivers.

In April 2022, a male deer drowned near Cape Kharantsy. Its carcass was transported to Irkutsk, where a full set of biochemical samples was collected during its autopsy. In this article, the results of the analysis of its tail gland are presented. This gland was chosen for the study because it is one of the largest exocrine glands. It is also convenient for research.

Water was sampled in 250 mL polyethylene containers that were stored in an automobile refrigerator during fieldwork. Samples of rock material (both rocky and earthy) and soil weighing at least 200 g were placed in sturdy polyethylene bags. Kudurits were collected from depressions gnawed and licked by animals at the surface and to a depth of 10 cm. Soil and plants were sampled at the same locations. Aboveground plant parts were sampled at one point within a 10 m radius. Each sample of 3–10 individual plants was placed in a paper bag. Herbaceous plants in this case are generally characterized only by sedges as the most common herbaceous forage for animals. The species composition of sedges included *Carex supina*, *C. pediformis*, *C. caryophyllea*, and *C. globularis*, all of which are widely distributed in Eastern Siberia.

### 3.2. Analytical Methods

The elemental composition of water, rock, vegetation samples, and animal tissues was determined by plasma spectrometry (ICP-AES and ICP-MS) at the Analytical Center of the Far East Geological Institute, Far East Branch of the Russian Academy of Sciences (FEGI FEB RAS, Vladivostok, Russia). Electron microscopic studies using X-ray spectral microanalysis of micrograins of rare earth minerals on the analytical scanning electron microscope (SEM-EDS) were also carried out there. Mineralogical X-ray analyses were performed at the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry of the Russian Academy of Sciences (IGEM RAS, Moscow, Russia).

The chemical composition of soils was determined by ICP-AES and ICP-MS methods in the laboratory of Tomsk Polytechnic Institute (TPU, Tomsk, Russia).

Deer tail gland samples were prepared for analysis in several steps. First, samples (0.50 g) were soaked in a solution of 5 mL concentrated high purity HNO<sub>3</sub> and 25 µL concentrated high-purity HF. The mixtures were then incubated for 18 h in HP500 Mars 5 autoclaves (Cem Corporation, Matthews, NC, USA). Then, 5 mL of deionized water was added to the mixtures, and the autoclaves were exposed to microwave radiation (magnetron power 1200 W, pressure 165 psi (sensor ESP-1500 Plus, Cem Corporation, Matthews, NC, USA), temperature 200 °C (sensor RTP-300 Plus, Cem Corporation, Matthews, NC, USA)). The decomposed samples were transferred to polypropylene tubes (50 mL).

The other methods of sample preparation and analysis, as well as the instrumentation used, have been described by Panichev et al. [23].

In order to determine quantitative indices of the yield of chemical elements from soils under acidic conditions in ruminant rennet, 12 samples were subjected to hydrochloric acid extractions at the Analytical Center of FEGI FEB RAS. A 1 g weight of dried and kneaded soil was treated with 50 mL of HCl solution at pH 1 (close to that of cattle rennet). The resulting suspension was then placed in a shaker for 12 h and left for 12 h. The supernatant was centrifuged in plastic cups at 4500 rpm. The transparent supernatant was transferred for elemental analysis. Deionized water (18.2 MΩ × cm) and distilled ultrapure acid were used to prepare the HCl solution. Analysis was performed by ICP-MS method.

To optimize the presentation of REE concentration profiles from aquatic and biological samples, the original seawater (SW) normalization standard introduced earlier by Panichev et al. [24] was used. The essence is that the optimal REE concentration in the upper, permeable, 40 m layer of seawater should correspond to locations with the highest nekton productivity, since it is the marine environment that is the source of REEs for fish.

Mathematical processing of the results of numerical data was carried out using Excel and STATISTICA software, which are part of the licensed software package of Tomsk Polytechnic University.

## 4. Results

### 4.1. Hydrochemistry

Due to the unusually dry climate on Olkhon and the long period of no rain, most of the small streams and lakes were dry during the sampling period. Only three samples were collected from streams (their locations are shown in Figure 1) and one sample from a lake at the mouth of a dried stream near the settlement of Uzury (the settlement shown in the gray square in Figure 1 in the northeastern part of the island). Due to the small number of water samples, the full set of their analyses is given in the article (Tables 1 and 2).

As for the degree of mineralization, the waters are fresh, with a salinity of 0.3 to 0.5 g/L; as for the chemical composition of the waters, it is sulphate–hydrocarbonate–magnesium–calcium; as for the pH value (7.65 to 8.11), the waters are slightly alkaline. According to the content of most microelements (Table 2), the waters are very similar. Maximum differences (within one order) are observed only for P, Mo, and V. For the other elements, the range of concentration fluctuations is less than one order. The total concentration of dissolved forms of REEs is insignificant and varies (including Sc and Y) from 0.12 to 0.16 ppb. In all

samples, there is a predominance of the sum of light lanthanides over the heavy ones, with a range of LREE sums from 79 to 83%.

**Table 1.** Concentration of major ions in water samples from Olkhon Island.

Sample	pH	Ion Concentration, mg/L (ppm)											
		HCO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	Si
O-13	8.11	232.5	38.2	0.44	<0.05	1.05	<0.3	10.0	3.38	47.5	22.5	<0.1	8.77
O-48	7.65	125.2	34.4	1.26	<0.05	0.24	<0.3	5.84	1.40	55.1	12.5	<0.1	7.35
O-49	7.90	224.6	95.9	0.61	<0.05	<0.1	<0.3	6.52	2.25	69.9	21.0	<0.1	9.63
O-61	7.70	203.2	66.5	0.8	<0.05	1.68	<0.3	7.00	3.35	67.3	20.9	<0.1	9.05

**Table 2.** Concentration of trace elements in water samples from Olkhon Island (ppb).

Element	Sample Number				Element	Sample Number			
	O-13	O-48	O-49	O-61		O-13	O-48	O-49	O-61
Li	2.776	1.035	4.643	2.617	Ta	≤0.001	≤0.001	≤0.001	≤0.001
Be	0.001	0.002	0.001	0.001	W	0.084	0.011	0.015	0.015
B	23.25	10.39	15.64	18.22	Tl	0.001	0.001	0.001	0.001
Al	2.541	2.430	5.913	2.940	Pb	1.166	2.235	1.844	1.844
P	59.23	6.102	52.85	22.62	Bi	0.001	0.001	0.002	0.002
Ti	0.406	0.372	0.460	0.392	Th	0.001	0.002	0.002	0.002
V	1.603	0.600	5.375	0.737	U	6.857	2.095	9.572	9.572
Cr	0.853	0.611	0.487	0.394	Sc	0.073	0.065	0.092	0.070
Mn	0.085	0.334	0.418	0.161	Y	0.017	0.035	0.017	0.020
Fe	2.159	12.71	8.204	7.505	La	0.007	0.014	0.007	0.007
Co	0.102	0.136	0.146	0.155	Ce	0.013	0.014	0.008	0.011
Ni	0.728	0.797	0.819	1.906	Pr	0.001	0.003	0.001	0.002
Cu	1.156	0.680	1.108	0.831	Nd	0.005	0.013	0.006	0.008
Zn	2.516	1.120	2.630	1.592	Sm	0.002	0.003	0.002	0.003
Ga	≤0.002	0.003	0.003	≤0.002	Eu	0.003	0.004	0.004	0.003
Ge	0.011	0.007	0.009	0.006	Gd	0.002	0.004	0.002	0.003
As	0.229	0.095	0.444	0.093	Tb	≤0.001	0.001	≤0.001	≤0.001
Se	0.919	0.212	2.202	1.757	Dy	0.001	0.003	0.001	0.002
Rb	0.571	0.339	0.240	0.345	Ho	≤0.001	0.001	≤0.001	0.001
Sr	329.0	241.9	571.8	305.5	Er	0.001	0.002	0.001	0.002
Zr	0.045	0.065	0.063	0.065	Tm	≤0.001	≤0.001	≤0.001	≤0.001
Nb	0.001	0.002	0.002	0.002	Yb	0.001	0.003	0.001	0.002
Mo	11.47	1.743	26.85	7.315	Lu	≤0.001	0.001	≤0.001	≤0.001
Ag	0.009	0.008	0.013	0.032	Σ REE	0.038	0.065	0.034	0.043
Cd	0.044	0.004	0.021	0.019	Σ LREE	0.032	0.051	0.028	0.034
Sn	0.020	0.011	0.022	0.013	Σ HREE	0.006	0.014	0.007	0.009
Sb	0.093	0.080	0.081	0.071	LREE, %	83	79	81	79

Table 2. Cont.

Element	Sample Number				Element	Sample Number			
	O-13	O-48	O-49	O-61		O-13	O-48	O-49	O-61
Te	0.003	0.007	0.004	≤0.002	HREE, %	17	21	19	21
Cs	0.004	0.001	0.001	0.001	Ce/Ce *	0.99	0.49	0.70	0.69
Ba	25.84	33.16	37.41	28.40	Eu/Eu *	7.81	4.84	11.21	6.16
Hf	0.002	0.002	0.002	0.002	La */Yb *	0.64	0.51	0.51	0.45

Note. Σ—sums of concentrations of corresponding groups of elements; Ce \*—element normalized to NASC.

Figure 3A shows the profiles of NASC-normalized concentrations of lanthanides in Olkhon water samples in comparison with the averages for world rivers according to [31]. REE concentrations in Olkhon water samples are an order of magnitude lower than the world average. Lower concentrations of light lanthanides in Olkhon water compared to North American shale should be noted.

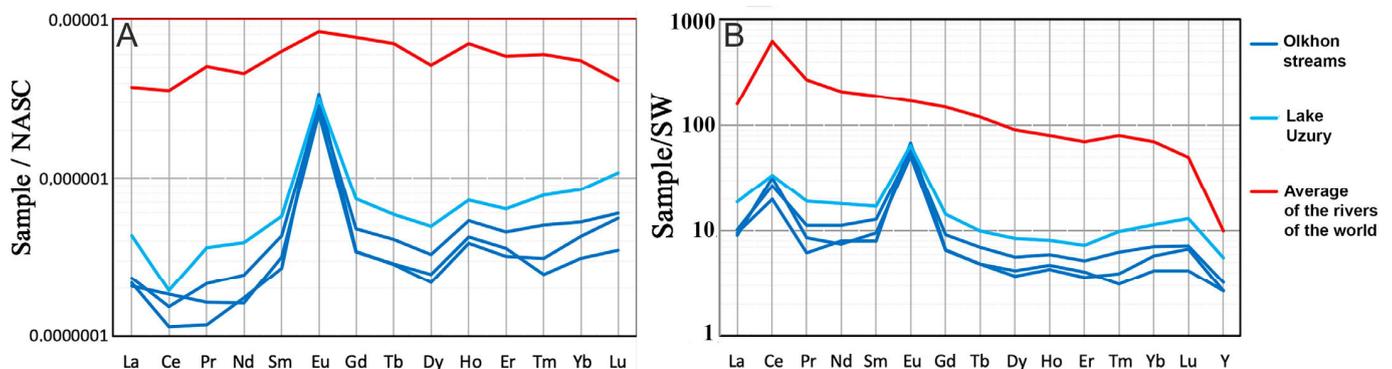


Figure 3. Distribution of REEs in water samples from Olkhon compared to the average values for rivers of the world according to [31]: (A)—normalized to the North American shale composite (NASC) according to [32]; (B)—normalized to seawater according to [24].

Figure 3B shows the distribution profiles of REE values in the same samples normalized to seawater according to [24]. The value “1.00” on the ordinate axis means that the values correspond to REE concentrations in seawater.

Numerical hydrochemical characteristics of Olkhon waters are presented in Tables 1 and 2.

#### 4.2. Mineralogy of Kudurits

According to the quantitative X-ray diffraction analysis of seven samples (Table 3), clay minerals (mainly kaolinite from 59 to 95%) predominate among the minerals in Olkhon kudurits. The main impurity minerals are quartz (up to 6%) and iron oxides (up to 10%), and the minor minerals are amphiboles and zircons.

Table 3. Results of X-ray diffraction quantitative mineralogical analysis of kudurits, carbonate rocks, and bottom sediments of the Shara-Nur salt lake from Olkhon Island.

Mineral	Sample of Kudur No. 1				Sample of Kudur No. 3				Shara-Nur
	1–6	1–8	1–10	1–11	C-18	3–19	3–20	3–22	OZ
Kaolinite	91.7	94.5	83.9	79.5	-	78.4	76.7	58.8	-
Mica	-	-	-	-	1.4	11.2 *	4.0 **	-	14.8
Smectite	-	-	-	12.3	-	-	6.4	28.4	4.3
Quartz	0.7	3.1	6.2	1.2	3.5	3.8	2.0	5.5	2.9

Table 3. Cont.

Mineral	Sample of Kudur No. 1				Sample of Kudur No. 3				Shara-Nur
	1–6	1–8	1–10	1–11	C-18	3–19	3–20	3–22	OZ
Plagioclase (Albite)	-	-	-	0.5	-	-	-	-	2.5
Kalishpat	-	-	-	1.4	-	6.6	6.4	7.3	2.8
Goethite	-	-	6.0	3.1	-	-	-	-	-
Hematite	6.0	2.4	3.9	1.3	-	-	-	-	-
Calcite	-	-	-	-	93.3	-	-	-	10.8
Dolomite	1.6	-	-	-	-	-	-	-	-
Ankerite	-	-	-	-	-	-	2.4	-	57.6
Amphiboles	-	-	-	-	-	-	1.1	-	1.4
Celestine	-	-	-	-	1.8	-	-	-	-
Zircon	-	-	-	0.7	-	-	-	-	-
Thenardite	-	-	-	-	-	-	-	-	2.9

Note. \*—true mica (muscovite, biotite) and illite; \*\*—true mica (muscovite, biotite), illite, and mixed-layer minerals of the illite–smectite series. C-18—a sample of carbonate crystalline schist from the upper part of kudur No. 3.

In a sample of mud sediments of Lake Shara-Nur not eaten by animals (taken for comparison with kudurits), carbonates (ankerite—58%; calcite—11%) and micaceous minerals (about 15%) predominate. Impurity minerals include smectite (about 4%), quartz and feldspars (about 12% in total), sodium sulfates (tenardite, about 3%), and amphiboles (about 1.5%).

#### 4.3. Petrogeochemistry of Kudurits, Rocks of Terrigenous–Carbonate Metamorphic Formation and Granitoid Migmatites

The macroelement compositions of the kudurits, coprolites, and background rocks from Olkhon Island are shown in Table 4. It can be seen that the background rocks (samples A-n and C-n, Table 4) belong to the high-carbonate, low-alkaline series. In terms of silica content, most of them correspond to rocks of medium and basic composition. Granitoid migmatites (samples G-n) are characterized by elevated potassium contents. Clayey rocks of the weathering crust (kudurits) are significantly depleted in silica, alkaline, and alkaline-earth elements and partially in manganese compared to the parent rocks, but enriched in Ti, Al, Fe, and P (see samples n-N, Table 4). In the bottom sediments of the Shara-Nur salt lake (sample OZ), more than half of the mass fraction is composed of Ca and Mg carbonates, with a rather significant fraction of Na and simultaneously low content of Al and Fe and especially K. The characteristics of the chemical composition of coprolites (samples n-NK) should be evaluated in comparison with kudurits only taking into account the proportional variation in hygroscopic water (H<sub>2</sub>O) and loss on ignition (LOI) values. This will be carried out in the Discussion section.

Table 4. Composition of kudurits, coprolites, and the most common rocks on Olkhon Island in percent of elemental oxides.

Sample	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O <sup>-</sup>	LOI	Σ
1–6	34.81	2.15	24.83	18.76	0.078	0.37	1.51	0.36	0.11	0.41	2.01	14.20	99.59
1–7	35.03	2.42	26.50	17.14	0.06	0.53	1.56	0.65	0.07	0.56	1.27	13.98	99.76
1–9	34.88	2.53	26.61	18.26	0.09	0.36	1.30	0.41	0.12	0.37	1.03	13.84	99.79
1–11	36.30	1.48	26.24	18.03	0.03	0.54	1.08	0.42	0.18	0.30	2.64	12.25	99.51

Table 4. Cont.

Sample	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O <sup>-</sup>	LOI	Σ
1-12	36.34	1.42	26.71	18.23	0.027	0.39	0.85	0.41	0.16	0.30	2.31	12.64	99.78
2-17	50.00	0.77	13.77	6.77	0.03	1.22	9.15	0.36	0.46	0.06	3.81	13.14	99.54
3-22	47.42	1.06	20.03	11.65	0.02	1.02	0.39	0.40	3.05	0.09	6.39	8.29	99.79
1-2K	36.50	1.35	18.36	11.85	0.213	0.81	2.03	0.27	0.99	0.42	0.10	26.88	99.77
1-3K	25.13	1.58	19.10	13.30	0.049	0.25	1.23	0.05	0.22	0.52	3.43	34.70	99.55
1-14K	33.11	1.20	20.96	12.95	0.043	0.44	2.99	0.13	0.34	0.55	2.83	24.12	99.66
1-15K	23.67	1.27	16.47	10.04	0.05	0.50	3.14	0.11	0.48	1.01	4.96	38.07	99.78
3-24K	33.52	0.94	17.72	10.61	0.12	1.31	1.84	0.12	1.24	0.30	4.26	27.62	99.61
G-3	62.45	0.32	19.58	3.82	0.03	0.91	0.36	0.21	4.01	0.07	1.94	5.82	99.52
G-4	69.75	0.59	13.24	4.73	0.053	0.50	2.23	2.63	5.07	0.15	0.15	0.45	99.55
G-5	75.65	0.08	15.81	0.34	0.02	0.04	0.03	0.14	3.36	0.01	0.23	4.06	99.78
A-O	52.15	1.49	14.43	11.24	0.17	5.48	10.59	2.71	0.71	0.14	0.01	0.64	99.76
A-1	49.02	0.18	14.86	7.31	0.122	11.34	15.27	0.95	0.08	0.02	0.19	0.48	99.82
A-16	49.15	0.97	19.76	12.52	0.21	3.74	8.88	2.93	1.15	0.20	0.16	0.06	99.74
A-26	62.76	0.71	14.26	6.07	0.08	3.41	7.69	1.85	0.56	0.28	0.38	1.71	99.76
C-4a	1.34	0.01	0.09	0.09	0.003	0.14	54.62	0.01	0.01	0.01	0.10	43.09	99.51
C-18	3.45	0.02	0.61	0.52	0.03	0.48	52.44	0.14	0.13	0.04	0.23	40.94	99.03
OZ	14.72	0.18	3.02	2.22	0.093	13.38	18.03	4.02	1.95	0.17	4.52	37.31	99.61

Note. The kudurits and coprolites include only the samples used for the subsequent comparison with each other (see Table 5). n-N—kudurits from kudurs Nos. 1, 2, and 3; n-NK—coprolites from the corresponding kudurs (highlighted in gray); G-3, G-4—granitoid migmatites from kudur No. 1; G-5—granitoid migmatites from the area away from kudurs; A-N—amphibolite crystalline schists; C-N—carbonate crystalline schists; OZ—bottom sediments of Lake Shara-Nur.

Table 5. Comparison of the composition of kudurits and coprolites from Olkhon Island in percent of elemental oxides without H<sub>2</sub>O and LOI.

Sample	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Σ
1-6	41.74	2.58	29.79	22.5	0.09	0.44	1.81	0.43	0.13	0.49	100.00
1-3K	40.90	2.57	31.10	21.65	0.08	0.41	2.00	0.08	0.36	0.85	100.00
	0.84	0.01	1.31	0.85	0.01	0.03	0.19	0.35	0.23	0.36	2.09–2.09
1-6	41.74	2.58	29.79	22.5	0.09	0.44	1.81	0.43	0.13	0.49	100.00
1-14K	45.53	1.65	28.83	17.81	0.06	0.61	4.11	0.18	0.47	0.76	100.00
	3.79	0.93	0.96	4.69	0.03	0.17	2.30	0.25	0.34	0.27	6.87–6.87
1-6	41.75	2.58	29.79	22.5	0.09	0.44	1.80	0.43	0.13	0.49	100.00
1-15K	41.75	2.23	29.03	17.69	0.09	0.88	5.52	0.19	0.84	1.78	100.00
	0	0.35	0.76	4.81	0	0.44	3.72	0.24	0.71	1.29	6.16–6.16
1-9	41.07	2.98	31.34	21.5	0.11	0.42	1.53	0.48	0.14	0.43	100.00
1-3K	40.9	2.57	31.1	21.65	0.08	0.41	2	0.08	0.36	0.85	100.00
	0.17	0.41	0.24	0.15	0.03	0.01	0.47	0.40	0.22	0.42	1.26–1.26
1-9	41.07	2.98	31.34	21.5	0.11	0.42	1.53	0.48	0.14	0.43	100.00

Table 5. Cont.

Sample	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Σ
1–22K	42.01	2.34	31.73	20.41	0.08	0.41	1.88	0.11	0.35	0.68	100.00
	0.94	0.64	0.39	1.09	0.03	0.01	0.35	0.37	0.21	0.25	2.14–2.14
1–12	42.84	1.67	31.49	21.49	0.03	0.46	1.00	0.48	0.19	0.35	100.00
1–3K	41.00	2.56	31.10	21.65	0.08	0.41	2.00	0.08	0.36	0.85	100.00
	1.84	0.89	0.39	0.16	0.05	0.05	1.00	0.40	0.17	0.50	2.72–2.72

Note. Blue color indicates increase in an element in coprolite; red indicates a decrease.

Among the trace elements in the samples of kudurits ( $n = 11$ ), the highest values (in ppm) are in Ba (average—311; range—57–692). Then, in descending order: V, 209 (3–315); Sr, 124 (57–336); Zn, 97 (13–186); Cr, 70 (8–141); Zr, 56 (9–89); Cu, 55 (4–123); Ce, 52 (11–141); Rb, 41 (2–178); Ni, 38 (12–61); Sc, 30 (1–48); Nd, 25 (3–74); Ga, 24 (17–29); Li, 21 (8–41); La, 20 (3–60); Y, 14 (2–37); Pb, 12 (5–16); and U, 11 (1–20). Next, in concentrations less than 10 ppm in descending order: Nb, Co, Pr, Sm, Gd, Th, Dy, Mo, As, Hf, Er, Yb, Sn, Be, Ge, Eu, and Cs; in concentrations less than 1 ppm: Tb, Ho, W, Ta, Sb, Lu, Tm, Tl, Se, Cd, Bi, Ag, and Te. The amount of REEs (including Y and Sc) varies from 24 to 420 ppm, with an average of 167 and a median of 134.

Coprolite samples ( $n = 9$ ) also have the highest Ba values, with an average of 240, ranging from 77 to 624. Other elements in descending order: V, 164 (119–222); Sr, 129 (68–180); Zn, 91 (67–130); Cr, 52 (13–151); Cu, 44 (29–84); Zr, 38 (26–59); Rb, 33 (3–163); Ni, 31 (10–96); Ce, 28 (12–58); Sc, 27 (17–49); Ga, 16 (11–20); Li, 13 (6–27); and Nd, 11 (4–23). Then, in concentrations less than 10 ppm in descending order: Pb, Y, La, Co, U, Nb, Mo, Pr, Sm, Th, Gd, Dy, As, Be, Hf, Yb, Sn, Er, and Cs; in concentrations less than 1 ppm: Ge, Eu, W, Ho, Tb, Cd, Ta, Tl, Sb, Lu, Tm, Se, Bi, Ag, and Te. The amount of REEs ranges from 64 to 141, with an average of 97 and a median of 90.

In two samples of granitoid migmatites at kudur No. 1, the highest values are again in Ba, with an average of 842 ppm, ranging from 772 to 911. Next, in descending order: Sr, 196 (143–248); Ce, 135 (10–260); La, 127 (50–204); Rb, 114 (67–160); Nd, 64 (24–105); Zn, 40 (12–69); V, 32 (5–60); Cr, 25 (3–46); Zr, 24 (23–24); Th, 23 (2–45); Ga, 21. 2 (20–22); Pr, 20.8 (7–35); Pb, 19.2 (9–29); Li, 18.9 (10–28); Y, 17.7 (17–18); Ni, 17.2 (15–19); Cu, 16 (8–25). Then, in descending order, in concentrations less than 10 ppm: Gd, Sm, Sc, U, Nb, Dy, As, Cs, Er, Co, Yb, Ge, Eu, and Be; in concentrations less than 1 ppm: Tl, Tb, Mo, Hf, Ho, Sn, W, Se, Tm, Lu, Sb, Ta, Bi, Cd, Ag, and Te. The amount of REEs ranges from 128 to 666, with an average content of 397.

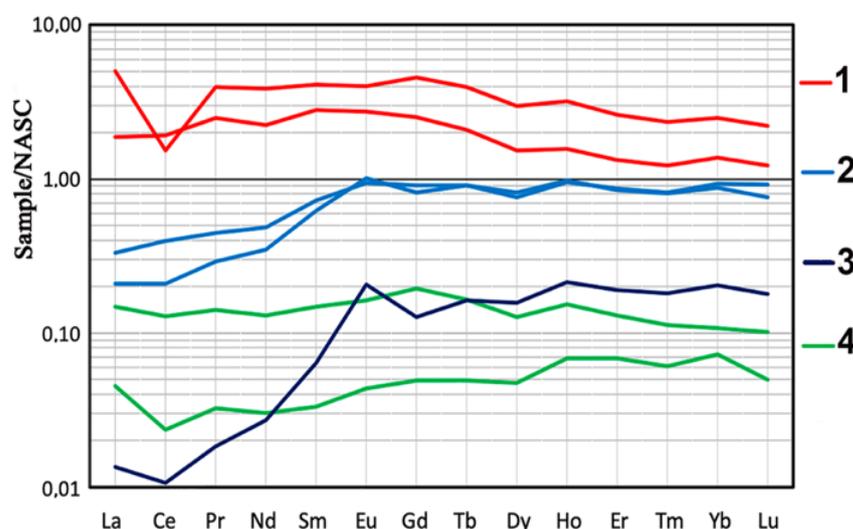
Rocks of the amphibolite crystalline schist type ( $n = 5$ ) are characterized by the highest Sr values (average—253 ppm; range 79–450). Accordingly, in descending order: Cr, 253 (9–592); V, 162 (42–261); Ba, 150 (46–298); Ni, 101 (1–182); Zn, 65 (27–97); Cu, 34 (5–60); Co, 32 (18–47); Sc, 29 (15–45); Zr, 21 (5–46); Y, 21 (5–32); Ce, 21 (1–43); Ga, 14 (10–17); Nd, 12 (74–128); Li, 11 (2–18). Furthermore, in concentrations less than 10 ppm in descending order: La, Rb, Nb, Pb, Gd, Dy, Sm, Pr, Er, Yb, Th, and Ge; in concentrations less than 1 ppm: Eu, Ho, Hf, Sn, W, Mo, Tb, Be, U, As, Tm, Lu, Ta, Se, Cd, Sb, Cs, Bi, Tl, and Te. The amounts of REEs range from 57 to 160 ppm, with a mean of 111 and a median of 120.

Terrigenous carbonate rocks were characterized by two samples. They had the highest Sr concentrations (average—5532; range 2130–8934 ppm). Accordingly, in descending order: Ba, 240 (28–453); V, 10 (5–15). Then, in concentrations less than 10 ppm in descending order: Zr, Ce, Zn, Y, Cr, La, Pb, Nd, Rb, Ni, Cu, and U; in concentrations less than 1 ppm: Co, Mo, Lo, Pr, Th, Sc, Gd, As, Sm, Dy, Ga, Er, Cd, Yb, Nb, Sn, Hf, W, Eu, Ho, Ge, Tb, Sb, Cs, Be, Tm, Lu, Te, Ta, Tl, Se, Bi, and Ag. The amount of REEs varies from 9 to 30 ppm, with an average content of 20 ppm.

The muddy sediments of the Shara-Nur salt lake are represented by one sample. Sr (1065), Mo (74.28), U (32.24), and Li (18.66) are prominent in its trace element content.

With respect to other trace elements (including REEs), they are generally similar to some varieties of amphibolite schists.

Figure 4 shows REE content profiles normalized to North American shale composite (NASC, according to [32]) in different rock types on Olkhon: from the marl zone of shale rocks at kudur No. 3 and migmatites at kudur No. 1; from amphibolite crystalline schists; from fine-grained sand and diluvium over amphibolite crystalline schists; and from metamorphic rocks of the carbonate series. As can be seen from the graphs presented, the background rocks of the carbonate series on Olkhon Island are characterized by much lower REE contents compared to the American shale. In the amphibolite crystalline schists, a noticeable difference is observed only in the light REE content. This is particularly pronounced in the sample from the deluvium. The highest REE concentrations are characteristic of new mineral formations in the weathering zones of amphibolite crystalline schists and migmatites, along which clayey kudurits are formed.

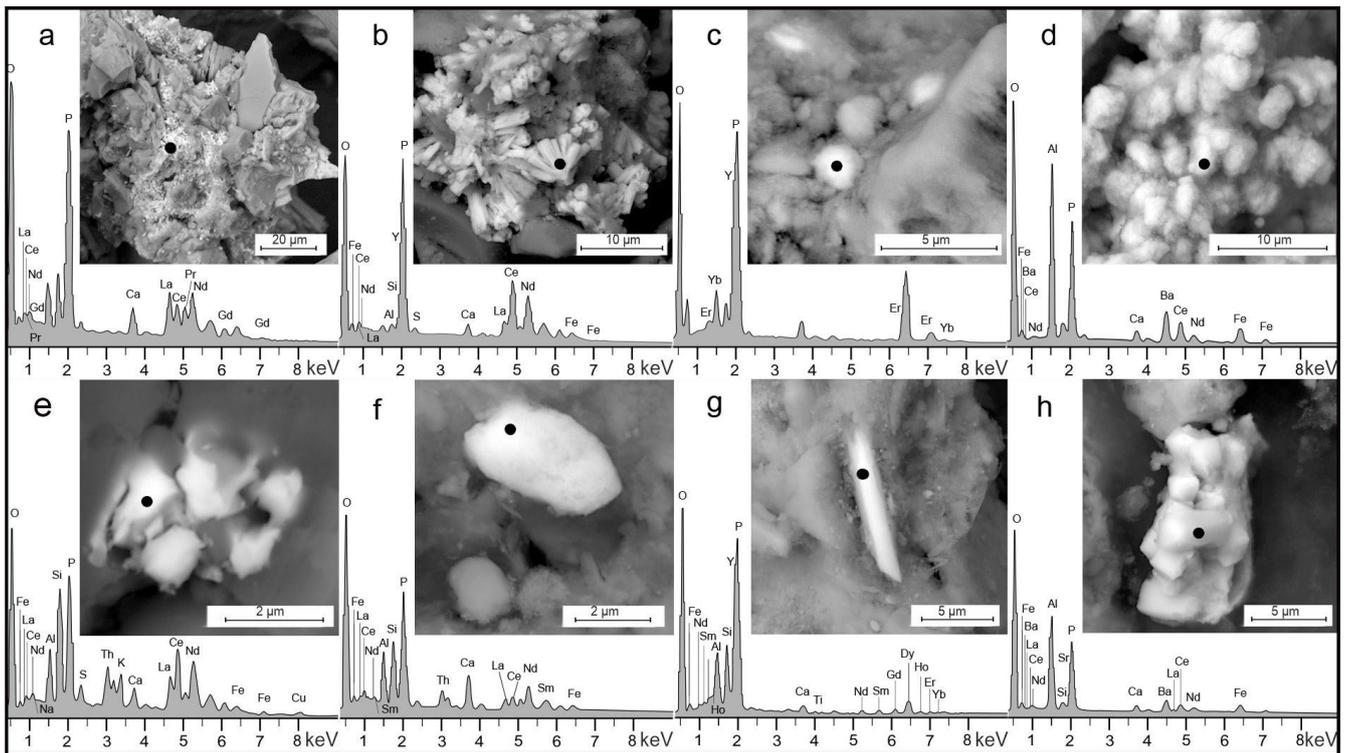


**Figure 4.** Typical NASC normalized REE profiles for different rock types on Olkhon Island. Olkhon: 1—rocks from the weathering zone of migmatites and schists at kudurs No. 1 and 3; 2—amphibolite schists; 3—diluvium on amphibolite schists; 4—marble and terrigenous carbonate schists.

#### 4.4. Scanning Electron Microscopy (SEM) and Energy Dispersive Analysis (EDS)

Mineral REE phases in three kudurit and three coprolite samples were identified as rhabdophane, monazite, xenotime, and REE-crandallite by automated search and determination on an analytical electron microscope (SEM-EDS). The most characteristic of the identified REE mineral phases are shown in Figure 5. In this list, the mineral of interest to us, since it was identified by us in kudurits for the first time, is REE-crandallite (hydrated calcium, barium, and strontium aluminophosphate with iron and rare earth elements). This secondary mineral is characteristic of soils and subsoil horizons formed on REE-rich aluminosilicate rocks in humid tropical climates [33]. In temperate latitudes, it is found in ancient (Mal-Paleogene) weathering crusts of granitoids and other rock types [34].

In four samples of background rocks (amphibolite crystalline schists and terrigenous carbonate rocks), the number of detected REE phases was orders of magnitude lower. Phosphates and fluorocarbonates were found in the REE minerals in the form of very rare thin phenocrysts.



**Figure 5.** Microscopic images in backscattered electron (BSE) and EDS spectra of the composition of rare-earth minerals as single micrograins or mineral phases in accretions from samples of kudurits (a–d) and coprolites (e–h) from Olkhon Island. EDS analysis points marked in the photo: (a)—rhabdophane; (b)—monazite; (c)—xenotime; (d)—REE-crandallite; (e)—monazite; (f)—corroded monazite; (g)—xenotime; (h)—REE-crandallite. Black dots in the figures are EDS imaging locations.

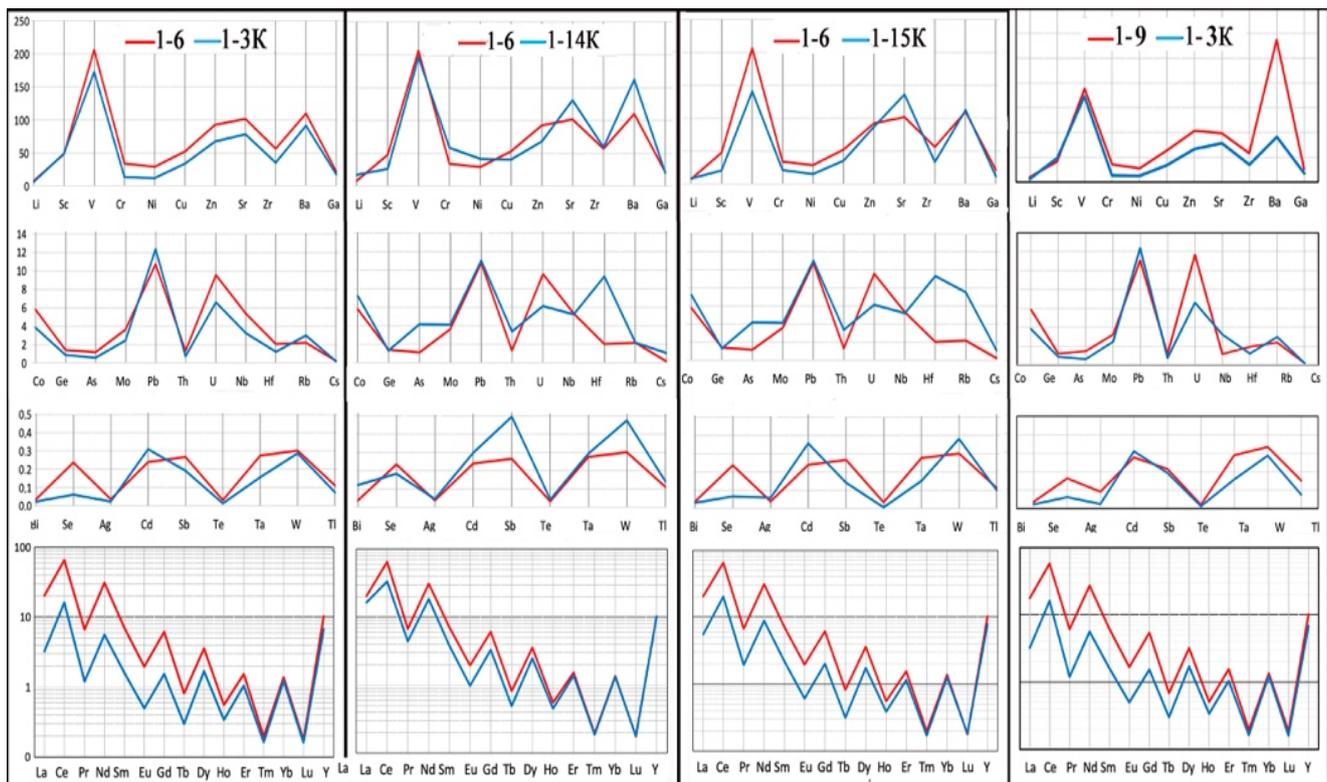
#### 4.5. Comparison of the Elemental Composition of Kudurits and Coprolites

Table 5 lists the compositions of the coprolite–kudurit pairs that showed the closest values of macroelement oxide contents after the proportional distribution of H<sub>2</sub>O and LOI contribution within them. The color indicates the resulting values after the subtraction of coprolite values (leaving the body) from kudurit values (entering the body). Blue color indicates an increase in an element in coprolite, while red indicates a decrease.

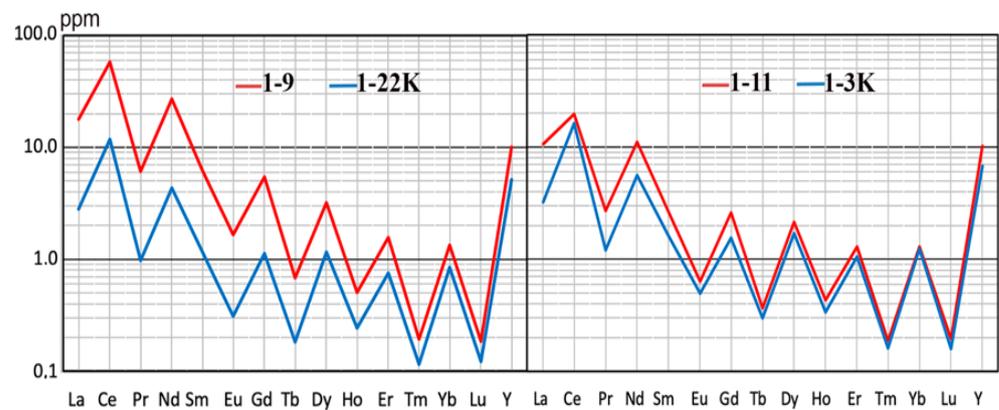
From the data obtained, it is clear that all the major rock-forming macronutrients are somehow involved in metabolic processes with electrolytes in the digestive tract. Ca, K, P, and, apparently, Mg, in this or that amount, are always sorbed by kudurits and removed from the body. Na and Si, on the contrary, are always extracted from kudurits in the digestive tract. The other elements behave differently. Fe and Al tend to be extracted, while Ti and Mn can be both extracted and sorbed by kudurits.

Figure 6 shows the results of the comparison in the first four kudurit–coprolite pairs of concentrations of 47 trace elements, including REEs, in graphical form. In the other two pairs, only REE data are presented (Figure 7). The red profile on the graphs refers to the kudurits, while the blue profile refers to the coprolites. As can be seen from the resulting comparative profiles, the most stable relationships are observed for REEs. And in all cases, there is a clear excess of LREEs in the kudurits compared to the coprolites. For other trace elements, the relationships are not so obvious.

A more detailed analysis of the data obtained is provided in the Discussion section.



**Figure 6.** Bivariate profiles of trace element contents in coprolite–kudurite pairs according to ICP-MS analysis: 1-6-1-3K; 1-6-1-14K; 1-6-1-15K; 1-9-1-3. REE concentrations are normalized to seawater according to [24].



**Figure 7.** Bivariate plots of REE content in coprolite–kudurite pairs: 1-9-1-22K; 1-11-1-3K.

4.6. Acid Extracts

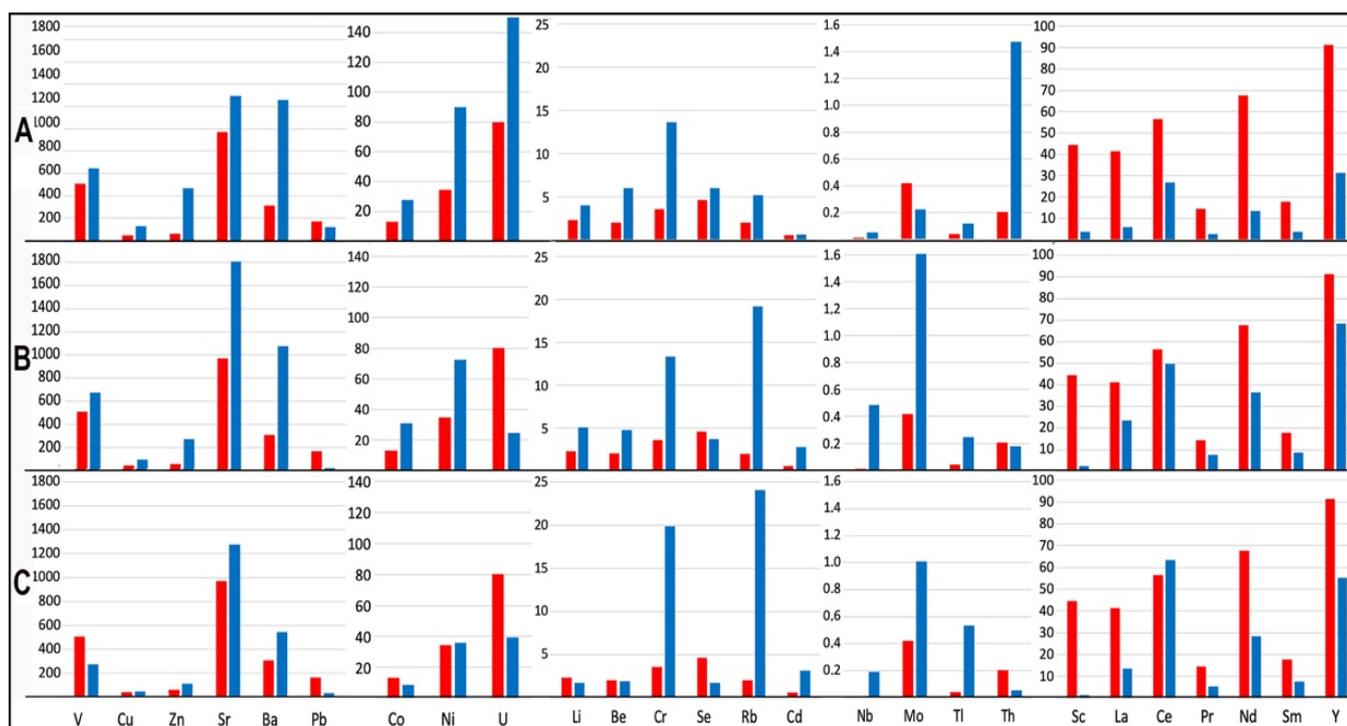
Table 6 shows the yield of major macrocations (Na, K, Ca, Mg, Fe, Mn, P, and Al) from kudurites, coprolites, and bottom sediments of the Shara-Nur salt lake in hydrochloric acid solution. The difference in the concentration of acid-soluble forms of Na in kudurites and coprolites was close to the difference in gross concentrations (see Table 5; when comparing, it should be taken into account that the gross values are given in mg per 100 g and in the oxide form). The highest concentration of acid soluble Na was found in salt lake sediments, which, incidentally, are not of interest to the animals. As for the other elements, the difference between their concentrations in kudurites and coprolites was also comparable with the data in Table 5. Especially noteworthy are the higher concentrations of acid-soluble forms of iron in coprolites compared to kudurites, indicating that iron is not the element the animals are looking for in clays.

**Table 6.** Yield of major macroelements in acid solution (HCl, pH 1.0) from kudurits, coprolites, and bottom sediments of Lake Shara-Nur on Olkhon Island (mg/kg; ppm).

Sample	Na	K	Ca	Mg	Fe	Mn	P	Al
1–6	2180	323	8905	1510	180	16.5	50.0	300
1–10	3805	87.5	2765	1730	228	6.5	89.5	426
1–11	1860	26	7560	1870	232	23.5	66.0	540
3–21	1370	51.5	1100	995	133	4.0	58.5	236
1–3K	51.0	1210	8125	990	1030	61.0	345	359
1–14K	91.5	1380	20485	1635	620	75.0	580	675
3–24K	68.0	2705	11075	1065	550	261	585	439
OZ	54400	13810	21750	15150	0.5	22.5	138	1.5

Note. See the note to Table 4 for sample description.

Figure 8 shows plots of concentrations of acid-soluble forms of trace elements in three kudurit–coprolite pairs (1–6–1–3K; 1–6–1–14K; 1–6–1–15K). From the trace elements determined, only those for which the compared values differed significantly were selected.



**Figure 8.** Diagrams of trace element concentrations in supernatants (in µg/L) after extractions of kudurits and coprolites. Red bar shows concentration in kudurite extract and blue bar in coprolite extract. (A)—samples 1–6 and 1–3K; (B)—samples 1–6 and 1–14K; (C)—samples 1–6 and 1–15K.

As the diagram shows, the trace elements that have a consistent tendency to accumulate in coprolite in an acidic environment in relation to kudurite (in other words, to be sorbed onto kudurite and removed from the body) include Cu, Zn, Sr, Ba, Ni, Be, Cr, Rb, Cd, Nb, and Tl. Micronutrients with a tendency to decrease in concentration in coprolite, relative to kudurite (i.e., to be extracted from kudurite in animal stomachs), include only Pb and REEs (Sc, La, Pr, Nd, Sm, Y) in an acidic environment. The behavior of other trace elements is variable.

#### 4.7. Biogeochemistry

The study of the chemical composition of 14 soil samples showed that, in terms of macro and trace elements, their compositions correspond well to the composition of the parent rocks. Here, it is only necessary to provide data on the content of Cl, Br, I, and Hg (which were not determined in the parent rocks of the island) and Sr, As, Pb, and Cd (since they may be relevant to the problem of geophagy as toxic), as well as on the REEs. The average concentrations of elements in the soils were as follows: Cl, 654 ppm (range 65–1736); Br, 77.1 (8.78–456); I, 8.73 (1.46–36.85); Hg, 0.03 (0.10–0.25); Sr, 74.17 (32.1–272); As, 1.09 (0.25–2.74); Pb, 5.52 (3.24–9.35); and Cd, 0.28 (0.09–0.89).

In eight soil samples collected on background rocks (terrigenous–carbonate and amphibolite schists), the sum of REEs varies from 13.20 to 67.77 ppm (average 43.85). The ranges of average element values in descending order are as follows: Ce, 14.4; Y, 6.50; La, 6.38; Nd, 6.37; Sc, 2.31; Pr, 1.60; Gd, 1.48; Sm, 1.34; Dy, 1.29; Er, 0.70; Yb, 0.67; Eu, 0.34; Ho, 0.26; Tb, 0.22; Tm, 0.10; and Lu, 0.10. In six soil samples collected within kudurs No. 1, 2, and 3, REEs amounts ranged from 73.07 to 285.9 ppm (average, 138.7). The ranges of average element values in descending order are as follows: Ce, 45.13; La, 25.48; Y, 22.18; Nd, 20.20; Pr, 5.31; Gd, 3.84; Sm, 3.74; Sc, 3.26; Dy, 3.15; Er, 2.05; Yb, 1.78; Eu, 0.80; Ho, 0.68; Tb, 0.53; Tm, 0.29; and Lu, 0.28.

The results of determining the concentrations of macroelements in air-dried sedge samples from Olkhon Island are presented in Table 7. They show that most of the island territory is insufficiently supplied with sodium and rather well supplied with other biophilic elements, although there are deviations from the norm in their ratios. For example, the Ca/Mg ratio in sedges varies from 1/1.1 to 1/4, while the norm is 1/3.

**Table 7.** Macroelement content in sedges on Olkhon Island (ppm).

Carex	Na	K	Ca	Mg	P	Mn	Fe	Al	Ti	Si	Cl	SO4
	64.9	9919	2824	1487	1182	52.6	63.6	36.9	5.34	616	3809	2488
	29.3	8800	2918	945	1301	10.1	25.5	17.5	1.98	455	23412	3429
Schist	12.1	8173	3033	1178	1409	113	48.4	20.6	2.33	337	7910	3872
	298	7391	4968	1162	1262	70.9	47.2	11.2	1.74	420	3770	3832
	55.3	4984	2992	735	1410	36.2	136	74.6	7.04	374	7480	3955
	55.8	4301	2462	1872	891	34.8	92.8	57.4	3.70	705	2390	2363
Migmatite	100	27674	4015	2401	2654	53.7	57.6	11.0	3.18	746	9542	6167
	175	28474	5558	1921	2353	49.2	57.6	6.32	2.60	617	8663	3969
	41.4	22358	3241	1229	2297	96.5	50.6	11.3	2.16	521	17437	8338
Shara-Nur	1005	20499	2378	2066	1515	35.5	170	113	9.26	-	-	-

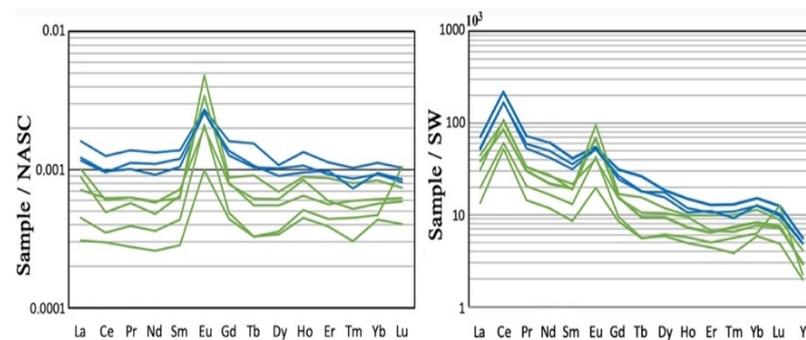
Note. Schist—plants growing on loose sediments (deluvium) on terrigenous–carbonate crystalline schists; Migmatite—plants on deluvium of granitoid migmatites; Shara-Nur—plants near saline lake; “-” —not determined.

The maximum Na content in sedges up to 1 g/kg (which is close to the index in lucerne hay) was determined in the sample from the coastal part of the Shara-Nur salt lake. The average Na content in sedges in the rest of the island is an order of magnitude lower. Such an uneven sodium supply of the island territory has a significant impact on the distribution of ungulates on it. It is worth remembering that about two-thirds of all recorded encounters of deer on the island, both in winter and in summer, were reported in the area of Shara-Nur Lake. This fact indicates that the most attractive site for animals is the forested area in the southwestern sector of the central part of the island (the area in the lower left corner in Figure 1). In this area, there is a natural salt water basin and vegetation enriched with this element.

In the composition of trace elements in sedges, the highest values (ppm) are in Ba (from 9 to 31 with an average of 20). They are followed by Zn (12–36/17); Sr (9–20/14); Cu (3–11/5); Rb (1–20/4); Ni (0.8–8/2); Cr (0.4–2.6/2); and Mo (0.5–1.7/1). The remaining trace elements have concentrations of less than 1 ppm.

In terms of the REE content in vegetation, most of the island’s territory (where terrigenous carbonate rocks and most of the amphibolite schists predominate) is characterized by reduced concentrations of these elements. The amounts of lanthanides with scandium and yttrium in the four sedge samples collected on high carbonate rocks range from 0.054 to 0.127 ppm on dry matter (average—0.093). The REE concentrations in three sedge samples collected on amphibolite crystalline schists range from 0.179 to 0.235 (0.200). The REE concentrations (ppb) in the vegetation are presented in decreasing order as follows: Ce, La, Nd, Y, Sc, Pr, Gd, Sm, Dy, Eu, Er, Yb, Ho, Tb, Lu, and Tm.

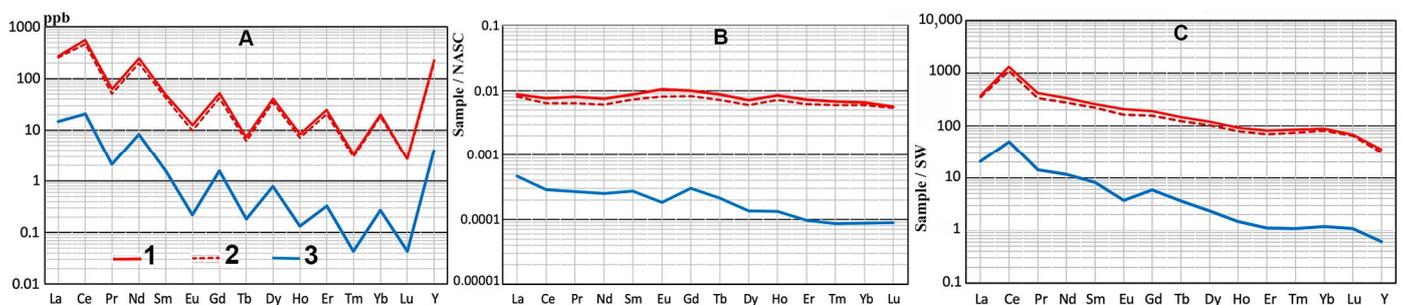
The profiles of NASC-normalized and seawater-normalized REE concentrations in sedge samples collected from background rocks on Olkhon Island are shown in Figure 9.



**Figure 9.** Distribution of REEs in sedges (*Carex*) growing on background rocks in different areas of Olkhon Island. Normalized to NASC and seawater. Blue color indicates profiles on amphibolite crystalline schists; green color indicates profiles on terrigenous-carbonate rocks.

Higher concentrations of REEs (by at least three times) were detected in the sedge sample from Lake Shara-Nur (0.75 ppm), as well as in the sample from the area where granitoid migmatites are distributed (0.64 ppm).

Figure 10A–C shows the profiles of lanthanide and yttrium concentrations in the tail gland of red deer from areas with evidence of mass geophagy in the Altai Mountains (1, 2) and on Olkhon Island (3). The profiles are presented in three variants: in ppb per dry matter (Figure 10A) and normalized to North American shale composite (Figure 10B) and to seawater (Figure 10C). As can be seen, the REE concentrations in the tail gland are a good reflection of the background content of the elements in question in the landscape components of a given region. At the same time, the range of concentration variations by region can be up to two orders of magnitude.



**Figure 10.** (A–C) Profiles of lanthanide and yttrium concentrations in the tail gland of *Cervus elaphus* deer (adult males) from different regions: 1—from the shore of Lake Teletskoye (Altai mountains); 2—repeated analysis; 3—from Olkhon Island. (A)—Yttrium concentrations in ppb per dry matter; (B)—normalized to American shale composite (NASC, by [31]); (C)—normalized to seawater (by [24]).

## 5. Discussion

Taking into account the evidence of geophagy documented all over the world, with a variety of forms of this phenomenon, the authors of this article acknowledge the existence of several reasons that determine the addiction of animals and humans to the consumption of earthy substances. At the same time, the long-term-focused research of the authors on geophagy in regions that differ in geology and landscape geography leads them to the conclusion that there is a “main” cause of geophagy that unites the majority of such cases. This cause may well be an imbalance in the neuroimmunoendocrine system due to disturbances (deviations from the norm) in the REE composition and in the concentration in its structures. In this case, a realistic consideration may be assumed that the nervous, endocrine, and immune systems, i.e., the main control and defense organs of all vertebrates, are largely based on unique physical and chemical properties of f-electron atoms of REEs. The role of such atoms, judging from the already available data [35,36], is largely determined by their effects on ionotropic receptors (membrane channels).

As interesting facts indicating the nature of the corrective effect of REEs on the central nervous system of animals, some experimental data can be cited. In rats, it was shown that the application of Y salts in water-soluble form in the diet [37], as well as La salts as a food additive [38], changed the distribution of a number of microelements (Ca, Zn, Mn, Fe, Ni, Co) in rat brain tissues, which, according to the above researchers, ultimately led to changes in physiological functions in the body.

The experience gained from the use of REEs in medicine and in the practice of animal feeding (reviews by [21] and [20]), as well as the summary of data obtained by the authors of this article on geophagy from the perspective of the REE hypothesis, indicate that only LREEs (La, Ce, Pr, Nd, Sm), as well as Sc and Y, are biologically significant REEs (at least for mammals). In contrast, HREEs, which can also be incorporated into biological tissues to replace their light analogues, are toxic to all vertebrates. It is from the standpoint of these considerations that the results of the studies of the actual materials collected on Olkhon Island will be discussed.

The conducted complex of studies, first of all, revealed that the surface waters of the island contain an order of magnitude fewer dissolved forms of REEs than waters of most rivers of the world and several orders of magnitude fewer than in the Sikhote-Alin areas of mass geophagy. It is important to note that the surface waters of the island are characterized by a reduced concentration of LREEs (see Figure 3) compared to the average values in rivers of the world. Such low concentrations of REEs in surface waters should not be considered unique. Even lower concentrations of REE amounts, from 0.014 to 0.05 ppb, were found in low-alkaline, ultra-fresh (less than 0.3 g/L) surface waters formed among carbonate rocks of the Goloustenskoye series in the Srednye Khomuty gorge area on the western shore of Lake Baikal, where mass cases of geophagy among wild ungulates also occur. According to the data in the literature [39], in the Baikal region, similar quantities of REEs (0.042 to 0.123 ppb) are also found in some mineralized (0.7 to 3.0 g/L) spring waters. Judging by their pH (from 7.0 to 8.8), such waters are formed in carbonate layers at depth.

Low REE concentrations were characteristic of the most widespread rocks on the island. Also, relatively low REE concentrations were found in the herbaceous vegetation over most of the island.

The average value of REEs in the soils on primary rocks is 43.9 ppm. This is 2–3 times lower than the sum of average values in soils of some countries of the world. According to Silva [40], the average value of REEs in the soils of Brazil is 107.5 ppm, and in Japan, it is 98.4; in China, 154.6; in Sweden, 89.3; and in the soils of European countries, 125.3.

The apparent deficiency of REEs in the vegetation and water of Olkhon Island is also indicated by the significantly reduced content of these elements in the deer tail gland in comparison with the glands of deer from areas with excessively high concentrations of REEs.

It was also found that kudurs on the island are formed on clay rocks of weathering crusts enriched in secondary REE minerals in the fault zones of amphibolite schists and granite–gneisses.

Kaolinite dominates in the mineral composition of kudurits, sometimes with the admixture of smectite, hydromica, and calcium carbonates. It should be pointed out that the predominance of kaolinite in the composition of kudurits is rarely found in the zone of temperate latitudes because such composition is typical for the tropics and subtropics. The most common clay minerals in kudurits in hot climates are kaolinite and related halloysite. This is shown by the data of M.J. Wilson [13], who summarized the results of studies on the mineral composition of kudurits carried out by different authors in 14 countries of the equatorial zone. At the same time, in southern Africa, south of the southern tropics, in clays consumed by humans, smectites predominate [18], which are characteristic of kudurits in areas where volcanic rocks are abundant.

### 5.1. On the Topic of Sodium

Judging by the comparison of the chemical composition of kudurits and coprolites from Olkhon Island (Table 5), the sodium yield from clays is about 3 g per 1 kg. This means that animals can obtain 20 g of pure Na (the amount in one tablespoon of common salt, NaCl) by passing about 7 kg of clay through their gastrointestinal tract. When evaluating this fact, the first thought that comes to mind is that the reason for the consumption of clay by animals is sodium. And this assumption is at least incomplete and may be completely wrong.

Noting that the island has a natural saltwater reservoir with sodium-rich vegetation growing around it. Why would the animals consume kilograms of clay when they could always consume water and food rich in the necessary element in an accessible place? The second thing to consider is the long-known ability of animals to subtly sense the presence of Na in water-soluble salts, as demonstrated in an experiment with various salts by D.S. Stokstad et al. [41]. However, as shown by the studies of previous years [24], animals consuming clay sorbents on kudurs, where, according to analyses, there are areas with different concentrations of Na, do not always choose clays with the maximum content of this element. These data are confirmed by other researchers. For example, Klaus and Schmid [5], studying animal geophagy in the Central African Republic, pointed out that almost one-third of the kudurit samples contained lower Na concentrations than the upper layer of widespread forest soils. This suggests that animals are either unable to detect Na ions absorbed by sorbents or at least do not eat clays solely because of the presence of Na in them.

It should be taken into account that the problem of Na deficiency in animals can be solved not only by bringing the sought element into the body but also by reducing its losses from the body. It is well-known that Na loss can occur, for example, in diarrheal diseases, which are widespread among herbivores, especially during periods of seasonal changes in feed [3,4,7]. Mineral sorbents based on a variety of clays (kaolinite, halloysite, smectite, etc.) have long been used effectively in medicine and veterinary science to stop diarrhea. Evaluating these facts, it must be recognized that the desire to stop diarrhea can undoubtedly act as one of the reasons for the consumption of clays by animals. However, it is also impossible to recognize it as the main cause capable of uniting the majority of cases of geophagy in the world. Our studies do not show that the connection between the animal's desire for geophagy and manifestations of diarrhea is the only possible one, although individual facts of such a connection in the spring period have long been noticed by many researchers.

The lack of a direct link between geophagy and sodium in diarrhea is particularly evident in human observations. For example, according to Young et al. [42], the mineral soils consumed by humans sometimes contain no chemically detectable sodium at all. From a literature review [43], the most active consumers of earthy substances in humans are children and pregnant women (as in animals, by the way). In this case, they usually eat

clay without any signs of digestive disorders. For example, the prevalence of geophagy among pregnant women in Tanzania, a country “sandwiched” between the western and eastern branches of the East African Rift Belt, ranges from 28 to 46% in different areas [44].

Following on from the above, it should also be remembered that humans, like animals, can consume earthy substances that contain almost no clay and clay–hydromicaceous minerals, which are generally thought to be effective in alleviating diarrheal syndrome. Human consumption of mineral clays with less than 3% clay content has been described, for example, among the inhabitants of Pemba Island off the southeastern coast of Africa [42]. V.M. Ngole and G.E. Ekosse [45], who studied soil samples consumed by people in South Africa, identified more than 90% sand in a number of samples. Granular mixtures of silty-sandy fractions of siliceous minerals in the mammalian digestive tract are unlikely to act as sorbents, but may serve well as suppliers of some trace elements and/or microorganisms.

The most prominent representatives among animals that consume minerals mainly of the sand fraction are, as is widely known, herbivorous birds. The reasons why birds ingest sand are undoubtedly the same as for mammals that consume polymineral clay sorbents. The mechanism of regulating the elemental balance in herbivorous birds with the help of silica gel sorbents was shown earlier [46]. However, the sorption mechanism of quartz or quartz–feldspar sand is fully realized only in birds and other animals with muscular stomachs.

The final argument that there is no direct cause and effect relationship between diarrhea and clay consumption is based on the fact that we have found animal excrements at many large kudurs that are almost entirely composed of clay (called coprolites). Sometimes clay balls of coprolites literally covered the areas around the licks and the access paths to them. And at the same time, not a single pellet of liquid excrement was found. We have observed such things at kudurs in the Altai Mountains and in the Caucasus in areas with large concentrations of ungulates. Visual field observations at such kudurs show that animals usually consume clayey rocks for several days in a row and defecate during this time without signs of digestive disorders.

### 5.2. On the Topic of Iron

Going back to Table 5, the second element after Na that animals can look for in the clays of Olkhon Island, judging by its relatively stable yield from kudurit in the digestive tract, is Fe. In the acidic environment of the stomach, a proportion of Fe and Al is usually in the hydroxide form, forming positively charged colloids. In this form, these metals actively sorb negatively charged particles, primarily phosphate ions, to form tightly bound compounds. Upon entering the alkaline environment of the intestine, some Fe- and Al-containing colloids naturally decompose into oxides and acquire a negative charge. This may be the reason for their separation from the clay lump and their retention in the electrolyte, which may be expressed in a decrease in their quantity in the coprolites at the end. With some conjecture, it can even be suggested that some of the Fe and Al excreted from the kudurit is assimilated in the body. Several experts who have studied geophagy in humans have shown that Fe, as well as Cu and Zn, are usually removed from the body, resulting in the development of iron deficiency anemia [45,47–49]. Similar results have been obtained in rat experiments [50–53]. Our data on the extracts presented above confirm the conclusions of other researchers for Cu, Zn, and Fe.

To conclude the discussion on the role of iron, the high content of this element in the dominant rocks of the island should be emphasized. Therefore, the suggestion of Fe as an element sought by animals in clays does not deserve attention. The same is true for Ti and Al, since there is no evidence of deficiency of these elements in the animal body.

### 5.3. On the Topic of Ion Exchange

The absorption of K, Ca, P, and, to some extent, Mg and Mn in the digestive tract by clay kudurits has been known for a long time. It is theoretically well founded in classical works on the study of ion exchange substitutions on various types of mineral sorbents and

has been repeatedly described by us in publications comparing the chemical compositions of kudurits and coprolites. A.M. Panichev first pointed out this regularity of ion exchange in kudurits during their passage through the digestive tract in 1987 [54], and later showed it in detail in a monograph [4]. The dietary interest of animals in clayey rocks of weathering crusts, which accumulate the greatest amount of elements in the form of sorbed ions, has also long been noticed by researchers of geophagy in Africa [55].

Summarizing these facts, it should be pointed out that most natural sorbents (clay, clay–hydromicaceous, clay–zeolite, zeolite, and silica gels) will interact with electrolytes in the digestive tract with almost the same result. Only the quantitative parameters of stable association of chemical elements absorbed by sorbents and another similar set of elements removed from the sorbent as a result of equivalent exchange will differ. Evaluating the results of such interaction on the example of kudurits and coprolites from Olkhon Island, the authors of this article were once again convinced that at the macroelement level, there could be no main cause of geophagy, which could unite most cases of this phenomenon all over the world. The fact of ion exchange on natural mineral sorbents, from the point of view of the main cause of geophagy, can be evaluated only as the possibility of the removal from the body or introduction into the body of a single element or a group of geochemically similar chemical elements. And it always occurs with the removal and simultaneous introduction into the body of various types of elements—necessary, unnecessary, and even toxic. In this case, we do not mention sodium because we are convinced that, despite the fact that sodium can be sought by animals in kudurits, nevertheless, the lack of this element in the body cannot be qualified as the main cause of geophagy, which can unite most manifestations of this phenomenon in different groups of animals, as well as humans around the world.

#### 5.4. On the Topic of Trace Elements

Step by step, it was concluded that the main cause of geophagy could be the trace element composition of the ingested soils (some of which the animals need due to a lack of feed) or their sorption properties with respect to some excessive content of trace elements or toxic organic substances. Finally, the clays may contain some microorganisms that the animals need. With regard to microorganisms, it should be noted that the trace elements sought by animals may only be necessary to maintain a certain species composition and the normal functioning of the symbiotic microflora.

To understand the role of trace elements, their concentrations were compared in coprolite–kudurit pairs (see Table 5). The obtained results are presented in the form of bivariate profiles in Figure 6. The presented graphs show that the contents of trace elements in the compared kudurit–coprolite pairs can strongly converge and diverge. As can be seen, only those pairs that are as close as possible in their trace element composition indicate that the kudurits and coprolites are truly coupled. Samples 1–6 and 1–3K can be considered as maximally corresponding pairs. Let us assume that exactly this pair of kudurits and coprolites is truly comparable. In other words, there is a similarity between minerals at the entry into the animal's body and at the exit from it.

Comparing the contents of trace elements in the designated pair, it is quite obvious that the only group of geochemically related elements that can really claim to be released from kudurit in the digestive tract is the LREE group. The yield of these elements from kudurits in the digestive tract, given the data in Figure 7, does indeed confirm all the pairs compared.

A similar pattern of trace elements was demonstrated in the acidic (HCl pH –1) effect on kudurits and their corresponding coprolites in the model of the acidic environment of the rennet stomach of ruminants. Among the trace elements with a stable tendency to be extracted from kudurits, only Pb and a number of elements from the REE group appeared in this model.

In conclusion, based on the comparison of the trace element composition of chemically comparable kudurit–coprolite pairs, it was shown that LREEs and Sc and Y are worthy

candidates for the role of elements sought by the animals in the kudurits of Olkhon Island. Since it is these elements that we have identified as the most probable candidates for the main cause of geophagy according to the results of the above-mentioned studies in Sikhote Alin and in the Altai Mountains, it would be logical to proceed to a discussion of the ability of REEs to be assimilated in the body and also their ability to influence the physiological state of the animal body.

#### *5.5. On the Biological Effects of REEs and Their Ability to Be Absorbed by Mammals*

In the last decades, there has been a growing interest in the use of LREEs in the fattening of various animals. At the same time, a number of researchers [56–60] have shown that only a small amount of orally administered mineral and organomineral forms of REEs are absorbed in the gastrointestinal tract. Nevertheless, due to the obvious ergotropic effects of LREE supplements in the form of a significant increase in body weight gain and improved feed assimilation, as well as the facts of the effect of such supplements on enzyme and hormone activity (including thyroid and epiphysis) and on changes in other blood and intercellular fluid parameters, a number of researchers [57,61] believe that even low doses of LREEs entering the blood can cause significant biological effects. This is supported by earlier studies [62] showing that cerium can be an effective metabolic stimulant in humans following intravenous administration of very low doses of the element. Chinese researchers [63] provide a rather extensive list of already identified biological effects of REEs, which is very revealing in terms of dose dependence. In this list, depending on the dose of REE supplements, the following can be observed: stimulation or inhibition of organism growth, cell proliferation, and apoptosis; antioxidant or pro-oxidant activity; stabilization or destabilization of cytoskeleton; increase in or suppression of cell permeability; positive or negative regulation of cell signaling system; increase or decrease in hemoglobin affinity to oxygen; increase in mineralization or demineralization. These data, in fact, directly support the possibility of health problems in animals living in landscapes with both an excess and a deficiency of the REEs needed in the feed.

It should be noted that the above-mentioned findings of not fully hardened deer antlers on Olkhon Island and in one of the areas on the western shore of Lake Baikal can only be explained by the influence of REEs on mineralization–demineralization processes in the body. There is definitely no calcium and phosphorus deficiency there, and the Ca/P ratio in sedge samples from Olkhon Island does not differ significantly from the optimal ratio for cattle.

To conclude the discussion of ergotropic effects in animals associated with the use of LREE diets, another series of publications should be mentioned [64–66] in which researchers attribute such effects to the effect of LREEs on the development of “necessary” and suppression of undesirable bacterial species in the gastrointestinal tract. They may also be the cause of diarrhea. Here, an idea can be added that it is the symbiotic microorganisms that can transform the mineral forms of LREEs into other forms capable of penetrating the internal environment of the body.

From the above brief review, it is quite obvious that the significance of physiological effects in the body of even negligible doses of LREEs is not questioned by specialists. The question of absorption of REEs in the body is also solved positively.

Thus, we have shown that the main cause of geophagy in ungulates on Olkhon Island may be the lack of light REEs in food and drinking water. Therefore, animals may develop a state of hormonal stress in the neuroimmunoendocrine system as a result of disturbances in the metabolism of such elements. It cannot be excluded that disturbances in the composition and ratio of REEs in the digestive tract may be an important component in the development of disturbances in the symbiont microflora, which may also lead to diarrheal disorders. It is logical to assume that animals in such a situation will seek out and consume clays enriched with some (it is yet unclear which) LREE compounds that the animals need.

To date, it has been reliably demonstrated that profound REE deficiency in landscape components occurs in humid climates on lateritic soils [67]. LREE deficiency in landscapes

should also occur in areas where biogenic carbonate rocks are common, as they accumulate negligible amounts of this group of elements [68]. Animals may also require LREEs if there is a strong bias toward HREE content to the detriment of LREEs in feed and drinking water, or if some toxic element is present in elevated amounts that blocks LREE penetration into the internal environment of the body.

It should be noted that in the equatorial zone of the Earth, where the greatest contrast in the supply of landscapes with rainwater is observed in a hot climate, there are also unusually contrasting conditions for the supply of landscapes with rare earth elements. In other words, it is in the equatorial zone of the Earth that the areas with both hard deficits and hard excesses of such elements in all components of the landscape should be found.

#### 5.6. Searching for Analogies of Landscape Conditions with the Phenomenon of Geophagy on Olkhon Island in Publications by Foreign Authors

Since REE deficiency in soils and vegetation is most common in humid tropical forests, where these elements are actively removed from soils by carbonic-acid-saturated rainwater, the published data of some researchers studying geophagy in such areas will be analyzed below to evaluate them from the point of view of the REE hypothesis regarding the main cause of geophagy, perhaps finding analogies with the situation on Olkhon Island.

First are the articles by W. Mahaney et al. [26,27], in which they attempted to determine the cause of geophagy in mountain gorillas (*Gorilla beringei*) inhabiting the Virunga Volcanic Mountains (the western branch of the East African Rift Belt). Their first article is based on material collected in Volcanoes National Park in northeastern Rwanda, on the border with Uganda and Zaire. The second focuses on Kibale Forest National Park in Uganda, on the border with Zaire. The distance between the study sites is about 40 km. The annual rainfall in Kibale Forest is about 1500 mm, while in Volcanoes Park, it is more than 2000 mm. In the first case, the sum of precipitation approaches the interval of the most characteristic values (1750–2000 mm) for rainforests, and in the second, it falls within this interval.

According to the data published in the above-mentioned articles, the apes spend most of the year in the lower and middle elevations of the Virunga mountain system (Volcano Park) or in the swampy tropical forests of the Virunga foothills (Kibale Forest Park), feeding mainly on celery, nettle, and bamboo shoots (i.e., plants with relatively short root systems that do not penetrate deep into the subsoil horizon). Some groups of mountain gorillas periodically, up to five times a year, leave their main habitats and climb mountains (sometimes to heights of 3000 m) to consume clays from the weathering zone of volcanic rocks dug from the subsoil horizons. Furthermore, the authors [26,27] describe the sites where gorillas consume clays as typical kudurits, which are visited by other herbivores in addition to primates, using our terminology. The clay content (halloysite) of kudurits in both study areas ranges from 15 to 20%, with the remaining fractions being sand and siltstone. The authors note that the chemical composition of soil and kudurits in the subsoil are very similar. A significant difference is noted only in the content of LREEs and some rare elements, which are higher in kudurits. To illustrate, the amount of Ce in kudurits from Volcanoes Park is about 150 ppm, and in kudurits from Kibale Forest Park, it is about 250 ppm. The major macrocations (Na, Ca, and Mg) in kudurits are significantly lower than in uneaten soils. The contents of Fe, Mn, Ba, and Co in kudurits and soils are comparably high.

The main conclusion of said researchers is that animals most likely eat clays from the weathering zone of volcanic rocks because of sodium and iron. Judging from the data presented in the publications, it is quite obvious that the cause of geophagy is directly related to REEs and, most likely, to the lack of REEs in plant food and natural waters in the habitats of certain groups of mountain gorillas due to the active leaching of these elements from soils and subsoil horizons. It is also obvious that the described situations in tropical rainforests have little in common with what we observe on Olkhon Island.

Among the cases of geophagy in tropical forests relevant to the REE hypothesis, very interesting are the observations of monkeys in the Deramakot Forest Reserve on the island

of Borneo [69]. The authors of this article point out that the clays in kudurs are eaten exclusively by herbivorous monkey species, while arboreal species living in the same area, such as the maroon langur (*Presbytis rubicunda*) or Müller's gibbon (*Hylobates muelleri*), which feed mainly on tree leaves and fruits, do not visit kudurs. From the perspective of the REE hypothesis, this phenomenon can be explained by the fact that large trees are better supplied with LREEs because they receive minerals from deeper subsoil horizons, which are much less exposed to intensive leaching by acidic rainwater. The authors of the article also cite interesting data on the geophagy of certain predators at kudurs. These include the leopard cat (*Prionailurus bengalensis*) and the clouded leopard (*Neofelis nebulosa*). The dhole (*Cuon alpinus*) has also been observed eating soil at kudurs in the Jomotsangkha Nature Reserve in the Kingdom of Bhutan [70]. It is quite possible that predators living in areas of mass geophagy may also experience hormonal stress caused by the consumption of meat from victims with low concentrations of rare earth elements.

In evaluating the above data, the following important idea should be noted: it is very possible that birds and mammals (and perhaps all vertebrates) are not only capable of sensing hormonal stress caused by REE imbalances in their neuroimmunoendocrine systems. These animals are also endowed with the ability to "sense" these vital elements in natural substances (including minerals) and replenish their deficiency in the body. When excessive amounts of REEs accumulate in the body, animals are able to instinctively remove them by consuming mineral sorbents. The urge to restore the normal functioning of the main control and protective system in the organism should be strongest in young animals during periods of active growth, in females during pregnancy, and in males after rutting, when a significant part of REEs is lost with sperm. Finally, the above applies to all animals suffering from certain diseases, including those due to disturbances in the composition of the digestive microflora. As one can see, this list covers virtually all known cases of geophagy as described in the extensive scientific literature on the subject.

Finally, another publication should be mentioned. This time, the American authors [71] studied the characteristics of the movements of bighorn sheep (*Ovis canadensis*) in the Big Hatchet Mountains of southwestern New Mexico (USA) by means of radio-collaring. Using radio collars fitted to nine bighorn sheep, it was found that the entire group of these animals inhabiting the limestone massif in the southern part of the Big Hatchet Range (apparently an ancient coral reef) of about 145 km<sup>2</sup> descended from the range 18 times in 21 months, crossing 4 km of Chihuahuan desert and ascending the volcanic Cairn Hills to consume clay substances at two existing kudurs. When crossing the desert, the bighorn sheep usually had predators waiting for them. During the course of the work, it became apparent that the high lamb mortality associated with animal movements to the kudurs in the Cairn Hills was a major limiting factor to population growth. The creation of two large artificial salt licks (with NaCl) in the permanent habitat of bighorn sheep on the limestone massif reduced the number of annual migrations to the volcanic hills by about half, but did not solve the problem completely. At the same time, the authors of the article believed that the reason for the bighorn sheep's desire to eat clay kudurits from the weathered zone of the volcanic rocks was due to the lack of sodium in the feed and drinking water in the animals' permanent habitat. To the authors of this article, however, the situation described in the article appears to be a classic case of LREE deficiency in the landscape due to low concentrations of this group of elements in biogenic carbonate rocks. Sheep inhabiting such a landscape must compensate for the lack of LREE intake by periodic visits to remote kudurs, where they can consume clay weathering products of volcanic rocks (basites) enriched with necessary elements. This situation is undoubtedly very similar to the situation on Olkhon Island, the only difference being that deer on Olkhon, similar to bighorn sheep in arid landscapes on high carbonate rocks with low REE content, obtain the necessary elements from clay weathering crust on granitoids, while bighorn sheep obtain them from clay weathering crust on volcanic rocks.

Unfortunately, it is not yet possible to increase the number of publications analyzing the relationship between geophagy and REEs. Too few researchers of geophagy still pay

attention to the geology of areas and mineralogical and geochemical issues of REEs in the ingested soil.

## 6. Conclusions

Geological and hydrobiogeochemical research carried out on Olkhon Island confirms that the geophagy of wild and domestic herbivores in this area develops in conditions of arid climates in mountain–taiga landscapes with steppe areas, mainly on ancient metamorphic rocks of terrigenous–carbonate formation with low contents of hypogenic REE minerals. These factors cause low concentrations of secondary (hypergenic) REE minerals in the eluvium–deluvium, as well as in their overlying soils and, accordingly, the depletion of LREEs in natural waters and forage vegetation. Such geochemical specificity of the landscape, similarly as it was revealed earlier in Sikhote-Alin and Altai Mountains with excessive content of REEs in natural components, predetermines conditions for disturbances in the neuroimmunoendocrine system, which is a carrier of this group of elements in plant-eating animals, causing a stress reaction of the body. The hormonal stress forces the animals to compensate for the discomfort in the body by consuming mineral sorbents enriched with REEs. The outlined geological–hydrobiogeochemical features of the landscapes and the related phenomenon of geophagy do not seem to be uncommon. A similar treatment of cases of geophagy can be expected in other regions of the world, not only in relation to animals, but also in relation to humans who lead archaic lifestyles and eat mostly plant foods.

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